

JOURNAL OF THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS ON ORGANIC, PHYSIOLOGICAL, AND AGRICULTURAL CHEMISTRY.

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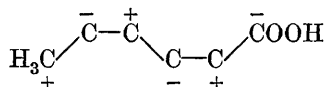
PART I.

Organic Chemistry.

The Oscillation of Physical Constants in Homologous Series. HERMANN PAULY (*Z. anorg. Chem.*, 1921, **119**, 271—291).—The theories put forward by Tammann (A., 1920, ii, 285) and Cuy (A., 1921, ii, 429) to explain the oscillation in the numerical values of different physical properties in homologous series are criticised and an alternative explanation is suggested. A review of the existing data leads to the conclusion that the end groups of the carbon chain and their relationship to each other, especially in the spatial sense, have an important influence on the physical properties. In the fatty acid series, the odd members have proportionately lower molecular volumes and at the same time lower melting points than the even members. It is probable that in the open straight chain compounds the carbon atoms form a zigzag chain, and it follows that when the number of carbon atoms is even the end atoms are relatively farther apart than when the number is odd. The difference is of the “syn” and “anti” type, the odd members having a “syn” structure with low molecular volume and low melting point, the even members the “anti” structure with higher molecular volume and melting point. The odd members, however, have the higher boiling points. Similarly, the solubilities and molecular heats in the fatty acid series oscillate in the opposite direction to the molecular volume.

A special type of oscillation is exhibited by the dissociation
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constants of the fatty acids and by the optical rotations of the acyl-*l*-menthols. When these properties are plotted against the number of carbon atoms in the aliphatic chain, two closely similar curves are obtained showing a kind of double oscillation. When the points corresponding with odd numbers of carbon atoms are joined, a zigzag line is obtained, and the points corresponding with even numbers of carbon atoms lie alternately above and below this line. This type of oscillation appears to be peculiar to the fatty acids and some of their derivatives, and in these series to be confined to dissociation constants and optical rotations. It



is suggested that the phenomenon may be due to the influence of the methyl group on the carboxy-group in, for example, the fatty acid series, when the carbon chain has the form

indicated in the annexed diagram.

E. H. R.

The Structure of Carbon Chains. JOHANNES STARK (*Z. anorg. Chem.*, 1921, **119**, 292—298).—An elaboration of the hypothesis put forward by Pauly (preceding abstract) to account for the difference between the physical properties of the odd and even members of an aliphatic homologous series. Generally, when the numerical value of the physical property is plotted against the number of carbon atoms, the points corresponding with the even members of the series fall on one curve and those of the odd members on another, roughly parallel, curve. The difference must be due to a difference in structure of the carbon chain when the number of carbon atoms is even from the structure when the number is odd. The suggestion is made that the difference lies in the curvature of the zigzag chain. A molecule with a straighter chain would be expected to form a more stable space lattice structure than one with a more curved chain, and hence to have a higher melting point. The compounds of the even series have the higher melting points, and it is concluded that these have the straighter chain and the compounds of the odd series the more curved chain. The molecular volumes and boiling points of the two series are consistent with this conclusion.

E. H. R.

Preparation of Aluminium Carbide and of Marsh Gas. O. OHMANN (*Z. physikal. Chem. Unterr.*, 1921, **34**, 76—77).—A mixture of aluminium filings, potassium chlorate, and iron, when ignited in a stream of carbon dioxide, results in the formation of aluminium carbide, Al_4C_3 . When the powder is finely ground and then gently warmed with water, methane is liberated: $\text{Al}_4\text{C}_3 + 6\text{H}_2\text{O} = 3\text{CH}_4 + 2\text{Al}_2\text{O}_3$. Four grams of aluminium yield 70 c.c. of methane.

CHEMICAL ABSTRACTS.

The Formation of Hexachloroethane from Chloropicrin. OSWALD SILBERRAD (*Chem. News*, 1921, **123**, 271).—When hydrogen chloride is passed through chloropicrin at 100° and the resulting mixed vapours are passed over pumice at 400° , the main products are carbonyl chloride, nitrosyl chloride, and nitric oxide. A small amount of hexachloroethane is also formed, and may be collected

by passing the cooled gases through a tube lightly packed with asbestos. The asbestos is subsequently extracted with a mixture of alcohol and ether and the hexachloroethane allowed to crystallise out.

W. G.

The Elimination of Hydrogen Chloride from Chlorohydrocarbons. W. F. FARAGHER and F. H. GARNER (*J. Amer. Chem. Soc.*, 1921, **43**, 1715—1724).—The chloro- or dichloro-derivatives of hexane, isohexane, heptane, cyclohexane, and benzene were examined, and the results indicate that they can be classified in the following diminishing order of ease with which hydrogen chloride can be split off: hydroaromatic, aliphatic, aromatic compounds. In the aliphatic compounds the stability of the monochloro-compounds at a given temperature decreases with increasing molecular weight at least up to chloroheptane. Of the three catalysts used, namely, alumina, unglazed porcelain, and unglazed porcelain impregnated with barium chloride, the first named is the most efficient, but all three lose their activity rapidly owing to the poisoning produced by the decomposition of the hydrocarbons. This method of removal of hydrogen chloride is quite satisfactory for the preparation of olefine hydrocarbons, but with diolefines secondary decompositions occur and poor yields are obtained.

W. G.

A Reaction between Methyl Alcohol and Water and some Related Reactions. J. A. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1921, **43**, 1670—1672).—When suitable mixtures of methyl alcohol and water are passed over finely-divided reduced copper at 230—250°, carbon dioxide and hydrogen are produced according to the equation $\text{CH}_3\cdot\text{OH} + \text{H}_2\text{O} = \text{CO}_2 + 3\text{H}_2$. Formaldehyde and water behave similarly.

W. G.

Preparation of Ethyl Alcohol. PAUL PASCAL (Swiss Pat., 88188; from *Chem. Zentr.*, iv, 802—803).—Acetaldehyde is submitted to direct reduction by electrolysis in acid solution. The electrolysis takes place in an apparatus with two chambers separated by a porous diaphragm. The cathode consists of mercury or lead, with or without antimony coating. The anode consists of platinum, lead, ferric oxide, graphite, or carbon. Acetaldehyde is gradually added to the cathode chamber and the electrolysis conducted at a temperature not exceeding 40° and a current density not exceeding 2—3 amperes per square metre. The formation of crotonaldehyde is prevented by shortening the period of reduction. Formation of acetic acid is prevented by the use of the diaphragm and the yield is almost theoretical. In the place of acetaldehyde, its polymerides may be used or acetaldehyde may be formed in the apparatus from acetylene by a catalytic process. The electrolysis may be conducted in the presence of sulphuric acid, phosphoric acid, organic sulphonic acids, or sodium hydrogen sulphate.

G. W. R.

Preparation of β -Chlorohydrins. L. SMITH (*Svensk. Kem. Tidskr.*, 1921, **23**, 75—83).—In an attempt to prepare β -chlorohydrin from glycerol by way of $\alpha\gamma$ -dibromohydrin, β -chloro- $\alpha\gamma$ -

dibromopropane, and β -chloro- $\alpha\gamma$ -diacetoxypropane, it was found that the first two reactions proceeded smoothly, but when β -chloro- $\alpha\gamma$ -dibromopropane was treated with potassium acetate in a sealed tube at 170° , and the resulting mixture hydrolysed, the product consisted of 70% of α -chlorohydrin and 30% of β -chlorohydrin, the potassium acetate having caused interchange of a chlorine and a bromine atom before the latter was replaced.

A similar rearrangement was found to occur to a like extent in the attempted preparation of β -chloropropyl alcohol by the action of nitrous acid on β -chloropropylamine. A second method for the preparation of β -chloropropyl alcohol from α -chloro- β -hydroxypropane by way of α -hydroxy- β -benzoyloxypropane, α -bromo- β -benzoyloxypropane, α -phthalimido- β -benzoyloxypropane, and β -chloropropylamine hydrochloride gave a product consisting chiefly of β -chloroisopropyl alcohol.

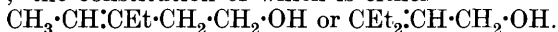
CHEMICAL ABSTRACTS.

New Synthesis of Glycerol and α -Glucoheptol. AMÉ PICTET and ANDRÉ BARBIER (*Helv. Chim. Acta*, 1921, 4, 924—928).—The synthesis is designed to permit the transformation of a sugar of the C_n series to one of C_{n+1} series and is somewhat allied to Kiliani's method except that the hydrocyanic acid of the latter is replaced by nitromethane, reaction occurring in accordance with the scheme: $R \cdot CHO \rightarrow OH \cdot CHR \cdot CH_2 \cdot NO_2 \rightarrow OH \cdot CHR \cdot CH_2 \cdot NH_2 \rightarrow OH \cdot CHR \cdot CH_2 \cdot OH \rightarrow OH \cdot CHR \cdot CHO$. It has been applied successfully to glycollaldehyde and dextrose, but the yields are small; it does not appear to succeed with glycer-aldehyde or *l*-arabinose.

An aqueous solution of glycollaldehyde is heated on a water-bath with the calculated quantity of nitromethane and a little solid potassium hydrogen carbonate. The cooled solution is reduced with aluminium amalgam, the aluminium hydroxide removed, and the base precipitated as the mercurichloride. The latter is decomposed with hydrogen sulphide and the base treated with nitrous acid, whereby glycerol is produced which is isolated in substance and as the tribenzoate. Under similar conditions, arabinose is ultimately converted into a substance, colourless needles, m. p. 152° , which does not appear to be a mixture of mannitol and sorbitol, and could not be investigated completely by reason of the small amount available. Glyceraldehyde appears to give a normal mercurichloride, but the subsequent treatment of the amine with nitrous acid gives a liquid of boiling point much lower than that of erythritol; it could not be caused to crystallise or converted into a benzoyl or an acetyl derivative. Dextrose is transformed into α -glucoheptol, m. p. 134 — 135° . H. W.

The Condensation Products of Ethyl β -Chloropropionate and Ethyl α -Chloropropionate with Magnesium Ethyl Bromide and some Compounds which are Derived from Them. CHARLES MOUREU and GÉRALD BARRETT (*Bull. Soc. chim.*, 1921, [iv], 29, 993—1006).—Magnesium ethyl bromide reacts

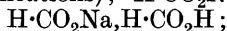
with ethyl β -chloropropionate to give α -chloro- γ -ethylpentan- γ -ol, b. p. $89^\circ/14$ mm.; $d_4^{16.2}$ 1.0164; $d_4^{21.1}$ 1.0108; $n_D^{20.5}$ 1.4579, which is decomposed by potassium hydroxide, giving $\alpha\gamma$ -oxido- γ -ethylpentane, b. p. 129° ; d_4^0 0.8691; $d_4^{18.2}$ 0.8525; n_D^{22} 1.4200 (cf. Maire, A., 1908, i, 247). This oxide, when treated with dry hydrogen chloride, gives γ -chloro- γ -ethylpentan- α -ol, which is very unstable, losing hydrogen chloride on distillation, and gives an unsaturated alcohol, b. p. $79-80^\circ/20$ mm.; d_4^0 0.8822; $d_4^{23.4}$ 0.8658; n_D^{22} 1.4531; the constitution of which is either



Ethyl α -chloropropionate reacts with magnesium ethyl bromide to give β -chloro- γ -ethylpentan- γ -ol, b. p. $76-76.5^\circ/21$ mm.; d_4^{21} 1.0124; $d_4^{25.5}$ 1.0073; n_D^{25} 1.4522, which by the action of potassium hydroxide yields $\beta\gamma$ -oxido- γ -ethylpentane, b. p. $125.4-125.8^\circ/760.4$ mm.; d_4^0 0.8496; $d_4^{24.3}$ 0.8275; $d_4^{27.2}$ 0.8245; $d_4^{27.6}$ 0.8241; $n_D^{27.6}$ 1.4063 (cf. Fournéau and Tiffeneau, A., 1907, i, 817). This oxide unites with hydrogen chloride, giving principally the original chlorohydrin.

W. G.

Compound Formation and Solubility in Systems of the Type, Formic Acid : Metal Formate. JAMES KENDALL and HOWARD ADLER (*J. Amer. Chem. Soc.*, 1921, **43**, 1470—1481; cf. this vol., ii, 33).—The freezing-point curves of the formates of potassium, ammonium, sodium, barium, lithium, calcium, magnesium, zinc, nickel, lead, and copper in formic acid solution, and the acetates of sodium, calcium, zinc, iron (ferric), and silver in acetic acid solution, have been experimentally determined. In the case of the formates, the following compounds have been isolated: $\text{H}\cdot\text{CO}_2\text{K}, 3\text{H}\cdot\text{CO}_2\text{H}$; $\text{H}\cdot\text{CO}_2\text{K}, 2\text{H}\cdot\text{CO}_2\text{H}$; $\text{H}\cdot\text{CO}_2\text{K}, \text{H}\cdot\text{CO}_2\text{H}$ (m. p. 108.6°); $\text{H}\cdot\text{CO}_2\cdot\text{NH}_4, 3\text{H}\cdot\text{CO}_2\text{H}$; $\text{H}\cdot\text{CO}_2\text{NH}_4, \text{H}\cdot\text{CO}_2\text{H}$ (exists in two crystalline modifications); $\text{H}\cdot\text{CO}_2\text{Na}, 2\text{H}\cdot\text{CO}_2\text{H}$;



and $(\text{H}\cdot\text{CO}_2)_2\text{Ba}, \text{H}\cdot\text{CO}_2\text{H}$; whilst in the case of the acetates only two compounds, $\text{CH}_3\cdot\text{CO}_2\text{Na}, 2\text{CH}_3\cdot\text{CO}_2\text{H}$; and $\text{CH}_3\cdot\text{CO}_2\text{Na}, \text{CH}_3\cdot\text{CO}_2\text{H}$ were isolated. The results of the present work closely resemble those obtained with sulphate systems (A., 1921, ii, 45, 453) in following the general rule previously deduced, that compound formation increases in extent with increasing diversity in the character of the components, the significant variable in systems of the general type $\text{HX}\cdot\text{RX}$ being the position of R relative to H in the *E.M.F.* series. An examination of the data for sulphates, formates, acetates, fluorides, and hydroxides shows that the rate of decrease in compound formation, in proceeding from more positive radicles (such as potassium) or less positive radicles (such as silver) towards hydrogen, increases the weaker the acid radicle. Solubility and compound formation are again found to proceed in parallel throughout the series. Salts which show extensive compound formation (such as salts of the alkali metals) are also extremely soluble. In passing down the *E.M.F.* series toward hydrogen, solubility rapidly diminishes and finally becomes inappreciable.

J. F. S.

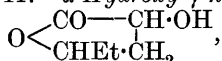
The Action of Mercurous Formate on certain Aliphatic Halogen Compounds. HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Ber. deut. Pharm. Ges.*, 1921, **31**, 344—349).—Mercurous formate was obtained in small, white, glistening, rhombic prisms by dissolving yellow mercuric oxide in formic acid, and rapidly filtering before reduction of the mercuric formate first formed occurs. Mercurous formate reacts with chloral hydrate and halogen hydrocarbons in a similar manner to mercuric acetate (cf. A., 1921, i, 543), the halogen being eliminated, and carbon dioxide and monoxide evolved, according to the equations: (1) $2\text{CCl}_3\cdot\text{CH}(\text{OH})_2 + 10\text{H}\cdot\text{CO}_2\text{Hg} = 3\text{Hg}_2\text{Cl}_2 + 4\text{Hg} + 6\text{H}\cdot\text{CO}_2\text{H} + 2\text{CO}_2 + 6\text{CO} + 2\text{H}_2\text{O}$; (2) $2\text{CHCl}_3 + 10\text{H}\cdot\text{CO}_2\text{Hg} = 3\text{Hg}_2\text{Cl}_2 + 4\text{Hg} + 6\text{H}\cdot\text{CO}_2\text{H} + 2\text{CO}_2 + 4\text{CO}$.
G. F. M.

Catalytic Effect of Ammonia on the Oxidation of Butyric Acid with Hydrogen Peroxide. EDGAR J. WITZEMANN (*J. Biol. Chem.*, 1921, **49**, 123—141).—In his oxidation experiments with hydrogen peroxide, Dakin (A., 1908, i, 74, 119) used the ammonium salts of fatty acids. The author could not repeat Dakin's experiments when using potassium hydroxide (A., 1918, i, 422). He now finds that ammonia acts as a catalyst, up to four equivalents. One equivalent of ammonium or potassium hydroxide is more efficient than two equivalents of either. It is suggested that the ammonia effect may be the agency by which the normal oxidation of fatty acids is brought about by the liver. As in Dakin's experiments, the oxidation took place at the β -carbon atom, acetone being formed.
G. B.

α -Hydroxy-lactones. BURCKHARDT HELFERICH and JOHANN ADOLF SPEIDEL (*Ber.*, 1921, **54**, [B], 2634—2640).—The investigation was undertaken with the object of examining the possibility of the reduction of α -hydroxy-lactones by sodium amalgam in faintly acid solution to $\alpha\gamma$ -dihydroxy-aldehydes. Under these conditions, α -hydroxy- γ -valerolactone and α -hydroxy- γ -hexolactone yield substances with aldehydic properties, but, in each case, the amount of available material was insufficient for an extended examination.

Crystalline chloroparacetaldehyde is obtained conveniently by the distillation of chloroacetal with anhydrous oxalic acid and cautious treatment of the distillate after it has been preserved during three to four days with half its volume of concentrated sulphuric acid at 0° . (Crystalline *bromoparacetaldehyde*, long, colourless needles, is prepared similarly from bromoacetal; when slowly distilled in an atmosphere of carbon dioxide, it gives a colourless liquid of indefinite boiling point which gradually passes into a solid modification distinct from the original compound.) Chloroparacetaldehyde is transformed by an ethereal solution of magnesium ethyl bromide into α -chloro- β -hydroxybutane, a colourless liquid which rapidly darkens when preserved, b. p. $52^\circ/15$ mm., d_4^{18} 1.040, n_D^{18} 1.4353. The latter is converted by a solution of ethyl sodium-malonate in absolute alcohol at the atmospheric temperature into

α -carbethoxy- γ -hexolactone, $\text{O} \begin{array}{c} \text{CO} - \text{CH} \cdot \text{CO}_2\text{Et} \\ \text{CH} \cdot \text{Et} \cdot \text{CH}_2 \end{array}$, a viscous liquid, b. p. $144^\circ/8$ mm., d_4^{25} 1.1119, n_D^{18} 1.4463, which is transformed by bromine in chloroform solution into α -bromo- α -carbethoxy- γ -hexolactone, $\text{O} \begin{array}{c} \text{CO} - \text{CBr} \cdot \text{CO}_2\text{Et} \\ \text{CH} \cdot \text{Et} \cdot \text{CH}_2 \end{array}$, a heavy, yellow liquid, b. p. $148^\circ/5$ mm., d_4^{20} 1.427, n_D^{20} 1.4767. The bromo-derivative is transformed by hydrobromic acid (d 1.49) and subsequent heating of the product at 120 — 150° into (?) bromohexolactone, $\text{C}_6\text{H}_9\text{O}_2\text{Br}$, b. p. $142^\circ/18$ mm., d_4^{20} 1.4826, n_D^{20} 1.4841. α -Hydroxy- γ -hexolactone,



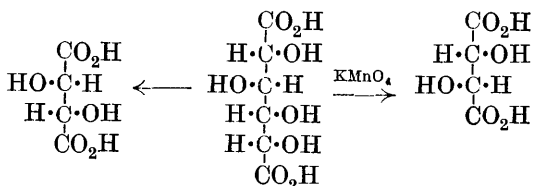
b. p. $127^\circ/5$ mm., d_4^{24} 1.1454, n_D^{24} 1.4517, is prepared by the hydrolysis of the bromo-ester with potassium hydroxide solution and elimination of carbon dioxide from the product by distilling it under diminished pressure. By performing the hydrolysis with barium hydroxide, it is possible to isolate the intermediately-formed β -hydroxybutylhydroxymalonic acid, $\text{OH} \cdot \text{CH} \cdot \text{Et} \cdot \text{CH}_2 \cdot \text{C}(\text{CO}_2\text{H})_2 \cdot \text{OH}$, a viscous, pale red liquid and its barium salt. The hydroxy-lactone is converted by boiling aqueous barium hydroxide solution into barium $\alpha\gamma$ -dihydroxy- n -hexoate, an amorphous, hygroscopic solid.

H. W.

The Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. III. Products Derived from Halogenated Glutaconic Acids. ERNEST HAROLD FARMER and CHRISTOPHER KELK INGOLD (T., 1921, **119**, 2001—2021).

The Reversibility of the Michael Reaction. CHRISTOPHER KELK INGOLD and WALTER JAMES POWELL (T., 1921, **119**, 1976—1982).

Degradation of d -Saccharic Acid to the Dialdehyde of l -Tartaric Acid. MAX BERGMANN (*Ber.*, 1921, **54**, [B], 2651—2658).—The action of bromine and potassium hydroxide on the diamide of saccharic acid leads to the formation of l -tartardialdehyde, which is isolated in the form of its diphenylhydrazone.



Conversion of the latter into the free dialdehyde could not be effected, but the identity of the latter is confirmed by its oxidation to l -tartaric acid. Since

Fischer has shown

that d -tartaric acid is formed by the oxidation of d -saccharic acid with potassium permanganate, an example is given of the production of enantiomorphous forms by the action of different reagents on the same compound owing to removal of different portions of the original molecule as shown by the annexed scheme.

The diamide of *d*-saccharic acid, hexagonal plates, decomp. 170° when rapidly heated, is obtained readily and in excellent yield by the action of concentrated ammonia on free saccharic acid which has been dehydrated at 100° in a vacuum (and hence, presumably, has been converted into the corresponding dilactone). It is oxidised by bromine in the presence of potassium hydroxide to *l*-tartardialdehyde, which is converted by immediate addition of phenylhydrazine into a mixture of *l*-tartardialdehyde- α -diphenylhydrazone, almost colourless, 3- to 6-sided leaflets or microscopic needles, decomp. 177 – 179° after darkening above 160° , $[\alpha]_D^{20} -99.6^{\circ}$ in pyridine solution (the substance is probably not quite homogeneous) and *l*-tartardialdehyde- β -diphenylhydrazone, almost colourless crystals, decomp. 195° after darkening above 170° , $[\alpha]_D -1^{\circ}$ to -2° in pyridine solution. The α -diphenylhydrazone is converted by benzaldehyde in aqueous alcoholic solution into *l*-tartardialdehydemonophenylhydrazone; individual specimens of the latter which appear to be analytically pure show widely-varying melting points, whereas the specific rotation is practically constant ($[\alpha]_D^{18} -182.7^{\circ}$ in alcoholic [50%] solution). The oxidation to *l*-tartaric acid is effected by treatment of the diphenylhydrazone with benzaldehyde as just described, removal of the monophenylhydrazone, and treatment of the filtrates from the latter with bromine at 50° . *l*-Tartardialdehydemonophenylhydrazone is converted by a dilute solution of hydrogen chloride in absolute methyl alcohol at 20° into the base, $C_{10}H_8ON_2$, which is presumably a pyridazine derivative; it crystallises in lustrous, hexagonal plates, decomp. 160 – 170° , according to the rate of heating. The corresponding *hydrochloride*, plates or slender needles, decomp. about 213° , the *nitrate*, plates ($+H_2O$), the *picrate*, canary-yellow prisms, and the unstable *nitrite* are described.

H. W.

A New Preparation of Formaldehyde Hyposulphite and an Economical Generator of Hyposulphurous Acid. PH. MALVEZIN, CH. RIVALLAND, and L. GRANDCHAMP (*Compt. rend.*, 1921, **173**, 1180–1182).—When zinc dust is suspended in a 40% solution of formaldehyde and sulphur dioxide is passed into the solution through the walls of a Chamberland filter, a concentrated solution of zinc-formaldehyde hyposulphite is obtained and the salt crystallises out on cooling. This material is a very powerful reducing agent for dyes such as indigotin, and is much more economical for use in the industry than the 88–90% hyposulphite. W. G.

The Action of Hydrogen Phosphide on Formaldehyde. ALFRED HOFFMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 1684–1688).—When hydrogen phosphide is passed into a warm aqueous solution of formaldehyde acidified with hydrochloric acid, *tetramethylol-phosphonium chloride*, $PCl(CH_2 \cdot OH)_4$, m. p. 151° , is obtained. When acted on by alkali hydroxides or carbonates, it yields a syrupy compound, $C_3H_9O_5P$, which gives a *tribenzoyl* derivative, m. p. 111° . When calcium carbonate is added to an aqueous solution of the phosphonium chloride, carbon dioxide is evolved,

and if the mixture is warmed, hydrogen and formaldehyde pass off and the syrupy compound described above is obtained. When ammonia is passed into a solution of the phosphonium chloride in methyl alcohol, a compound is obtained in the form of a curdy, white precipitate, but its constitution has not been determined.

W. G.

γ -Hydroxyaldehydes. IV. γ -Hydroxyaldehydes with Tertiary Hydroxyl. BURCKHARDT HELFERICH and MAX GEHRKE (*Ber.*, 1921, **54**, [B], 2640—2647; cf. A., 1921, i, 421).—The substances of the types, $\text{CHO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CRMe}\cdot\text{OH}$, or $\text{O} < \begin{array}{c} \text{CH(OH)}\cdot\text{CH}_2 \\ \text{CRMe}-\text{CH}_2 \end{array}$

are prepared by the action of suitable Grignard's reagents on methylheptenol, fission of the primary products with ozone, and reduction of the ozonides. The ethyl, *n*-propyl, phenyl, and benzyl compounds are described. The new aldehydes, like those with the secondary hydroxyl group described previously, appear to be exclusively or mainly cyclic in structure, since they react gradually with magenta-sulphurous acid solution or ammoniacal silver and give methyl semiacetals with methyl alcoholic hydrogen chloride which are hydrolysed by dilute acids, but not by emulsin. They lose water more readily than do the corresponding compounds with a secondary alcoholic group, passing thereby into dihydrofuran derivatives.

*γ -Hydroxy- γ -methyl-*n*-hexaldehyde*, $\text{CHO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMeEt}\cdot\text{OH}$, or 5-hydroxy-2-methyl-2-ethyltetrahydrofuran, $\text{O} < \begin{array}{c} \text{CH(OH)}\cdot\text{CH}_2 \\ \text{CMeEt}-\text{CH}_2 \end{array}$ is a

colourless, mobile liquid, b. p. 77—82°/10 mm., d_4^{18} 0.9742, n_D^{18} 1.4411. The corresponding methyl semiacetal, $\text{O} < \begin{array}{c} \text{CH(OMe)}\cdot\text{CH}_2 \\ \text{CMeEt}-\text{CH}_2 \end{array}$,

a colourless liquid, has b. p. 61.5°/32 mm., d_4^{18} 0.9106, n_D^{18} 1.4218.

β -Propylmethylheptenol, $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CMePr}\cdot\text{OH}$, b. p. 112—113°/10 mm., d_4^{18} 0.8445, n_D^{18} 1.4500, is converted in the usual manner into *γ -hydroxy- γ -methylheptaldehyde* (or 5-hydroxy-2-methyl-2-propyltetrahydrofuran, b. p. 94—95°/12 mm., d_4^{18} 0.9661, n_D^{18} 1.4400, from which 5-methoxy-2-methyl-2-propyltetrahydrofuran, b. p. 58—60°/10 mm., d_4^{18} 0.8990, n_D^{18} 1.4238, is obtained. *β -Phenylmethylheptenol*, b. p. 107—109°/2 mm., d_4^{18} 0.9680, n_D^{18} 1.5205, is transformed into *γ -hydroxy- γ -phenylvaleraldehyde*, b. p. 123—124°/2 mm. (slight loss of water occurs during distillation even at this pressure), d_4^{18} 1.016, n_D^{18} 1.5382, which yields 5-methoxy-2-phenyl-2-methyltetrahydrofuran, a colourless liquid, b. p. 128°/16 mm., d_4^{24} 1.033, n_D^{23} 1.5288. *β -Benzylmethylheptenol*, an almost colourless, viscous liquid, b. p. 127—129°/3 mm., d_4^{23} 0.9550, n_D^{23} 1.5161, is converted into the corresponding aldehyde in a similar manner, but the latter cannot be purified by distillation on account of the readiness with which it loses water and passes into 2-benzyl-2-

methyl-2 : 3-dihydrofuran, $\text{O} < \begin{array}{c} \text{CH}=\text{CH} \\ \text{CMe(CH}_2\text{Ph)}\cdot\text{CH}_2 \end{array}$ a pale yellow liquid, b. p. 118°/2.8 mm., d_4^{22} 1.042, n_D^{22} 1.5329. The undistilled

b*

aldehyde is readily convertible into 5-methoxy-2-benzyl-2-methyltetrahydrofuran, a colourless, viscous liquid, b. p. 133—135°/3·5 mm., d_4^{25} 1·020, n_D^{25} 1·5124. The dihydrofuran derivative unites with bromine in chloroform solution, but removal of the solvent is accompanied by loss of hydrogen bromide and formation of 4(?)-bromo-2-benzyl-2-methyl-2:3(?)-dihydrofuran, $C_{12}H_{13}OBr$, short, colourless prisms, b. p. 140—141°/2·8 mm. H. W.

Synthesis of Sugars from Formaldehyde, Carbon Dioxide, and Water. A. J. EWART (*Proc. Roy. Soc. Victoria*, 1919, **31**, 378—387; cf. *ibid.*, 1918, **30**, 178—209).—The main conditions for the polymerisation of formaldehyde to sugar by alkali hydroxides and carbonates are appropriate dilution and a temperature of 100° to 110°; the most rapid reaction is produced by sodium hydroxide, particularly in the presence of a neutral calcium salt. The by-products are mainly formates and methyl alcohol. The sugar obtained is optically inactive, and contains reducing pentoses and reducing fermentable hexoses. Carbon dioxide and water are readily polymerised to sugar by the aid of magnesium. The production, previously noted, of calcium tartrate during the synthesis of sugar, was not confirmed. CHEMICAL ABSTRACTS.

Starch. J. J. LIJNST ZWIKKER (*Rec. trav. chim.*, 1921, **40**, 605—615).—An investigation of the colloidal condition of grains of four kinds of starch shows that the degree of dispersion is different in each case. Solutions, prepared in the cold from grains which had been mechanically broken up, were submitted to ultra-filtration and the amylose content of the ultra-filtrates was determined. Solutions prepared by heating gave no amylose in the ultra-filtrate. The colloidal condition of amylopectin differs from that of amylose. Amylophosphoric acid derives its character from amylopectin by reason of the nature of the kations which are present; these also have a marked influence on the adsorption power of the starch.

Adsorption experiments are discussed and the conclusion is drawn that starch is more closely allied to cellulose than has hitherto been supposed. H. J. E.

Constitution of Starch Iodide. A. LOTTERMOSER and MAX STEUDE (*Z. Elektrochem.*, 1921, **27**, 496—501; cf. *A.*, 1921, i, 708).—An attempt is made to elucidate the constitution of starch iodide from measurements of *E.M.F.* The potential of the element $PtI_2|I^-|$ has been measured with changing iodine concentration and constant iodide concentration in aqueous solutions. The potassium iodide concentrations used were 0·1*N*, 0·2*N*, and 0·01*N*, and the amount of free iodine added varied from 0·00019 to 0·585 millimols.; all measurements were made at 25°. It is shown that the logarithm of the total iodine concentration varies in an almost linear manner with the potential. Hence knowing the inclination of the curve for a given concentration of potassium iodide, it becomes possible to determine from the curves the total iodine concentration. The curve constants *a* and *b* were determined for each concentration of potassium iodide by the equation $e_h = a + b \log c$, and the

values found were 0.1*N*-potassium iodide $a=0.544$, $b=0.0310$, 0.2*N*-potassium iodide, $a=0.518$, $b=0.0313$, and 0.01*N*-potassium iodide, $a=0.634$, $b=0.0342$. Solutions of potassium iodide in 0.1% soluble starch to which steadily increasing amounts of iodine were added were then measured, and from the potential and the curves the logarithm of the iodine concentration in the water phase was obtained. Thus the quantity of iodine taken up by the starch can be calculated. A number of experiments on the partition of iodine between water and carbon tetrachloride in the presence of starch are described.

J. F. S.

Polysaccharides. XII. Glycogen. P. KARRER (*Helv. Chim. Acta*, 1921, 4, 994—1000).—Glycogen differs from starch mainly in its inability to swell in water and in giving a reddish-brown coloration with iodine. The chemical similarity of the substances is further exemplified by the conversion of glycogen by methyl sulphate and barium or sodium hydroxide into *methyloglycogen*, $[\alpha]_D -206^\circ$ in aqueous solution, the properties of which agree even in detail with those of methylostarch. Similarly, glycogen is transformed by sodium hydroxide into a compound, $(C_{12}H_{20}O_{10}.NaOH)_x$, which therefore has the same composition as the similar substance obtained from starch.

The hypothesis has been advanced previously that glycogen is differentiated from starch chiefly by the degree or mode of polymerisation of the maltose anhydride, although the heats of combustion of the substances show that the difference in the degree of polymerisation cannot be very great. On the other hand, it is possible that starch and glycogen are fundamentally identical, and that their differing behaviour towards iodine and water are caused by the presence of impurities. The formation of coloured adsorption compounds with iodine is characteristic of the colloidal condition and is greatly dependent on the size of the particles and other external factors. The relationship between starch and glycogen is very similar to that between amylose and amylopectin; in the latter case, it is highly probable that the difference is due to the presence of a small amount of a compound of phosphorus.

H. W.

Action of Ferments on Laminarin. (MME) Z. GRUZEWSKA (*Bull. Soc. Chim. Biol.*, 1921, 3, 490—497).—Although laminarin (cf. Kylin, A., 1915, i, 931) can be utilised by the animal organism, experiments in vitro indicate that pancreatic juice, gastric juice, and invertase of animal origin are without action on it. Diastase and invertase from vegetable sources, however, ferment it slowly, whilst hydrochloric acid hydrolyses it completely, the product in each case being dextrose. Of the ferments tested, that obtained from snails (*Helix pomatia*) was found to be most active. E. S.

Comparative Action of Heat on Cellulose, Hydrocellulose, and Oxycellulose and the Characterisation of Hydrocellulose by Dry Heat. ED. JUSTIN-MUELLER (*Bull. Soc. chim.*, 1921, [iv], 29, 987—988).—Hydrocellulose caramellises at a lower temperature than oxycellulose and at a much lower temperature

than cellulose. If the specimen under examination is submitted to dry heat, it will assume a brown colour at 130—150°, at which temperature oxycellulose shows at most only a pale yellow colour and cellulose no change at all. W. G.

Cellulose. V. A New Degradation of Cellulose. Conversion of Cellulose into a Biose Anhydride. KURT HESS (*Ber.*, 1921, 54, [B], 2867—2885).—Previous methods of fission of cellulose have led to the recognition of cellobiose and dextrose as important products, but they do not permit a decision as to whether cellobiose is the fundamental unit in the structure of the cellulose molecule and dextrose is formed therefrom or whether dextrose itself is also an essential factor in the formation of cellulose (cf. A., 1921, i, 710). Various new methods of degrading cellulose have therefore been investigated.

When treated with ethyl alcohol and hydrogen chloride, cellulose yields indefinite, dark-coloured products which do not reduce Fehling's solution and have a small ethoxyl content. A mixture of glacial acetic acid and hydrogen bromide also gives unsatisfactory results. The use of acyl haloids, however, is more promising and the action of acetyl chloride, acetyl bromide, benzoyl bromide, thionyl chloride, and propionyl bromide and absolute hydrogen haloids on cotton cellulose, wood cellulose, acetylcellulose, and ethylcellulose has been investigated. With acetyl chloride, complete solution of the cellulose results within four to five days, whilst with acetyl bromide the process is even more rapid. Benzoyl bromide attacks cellulose without dissolving it. Propionyl bromide causes solution. On the other hand, thionyl chloride appears to have no action on the fibre; a proof is thus afforded that the action observed with other acyl haloids is not entirely due, at any rate, to the liberated halogen acid, but that the acyl haloid must itself play an important rôle.

Cellulose is converted by acetyl bromide into a yellow syrup containing bromine, only part of which can be exchanged for hydroxyl by means of silver carbonate and moist acetone. After acetylation of the crude product with pyridine and acetic anhydride, about one-third of it is obtained in the form of penta-acetyl- β -glucose. The remaining, non-crystalline product contains about 13% of bromine and, as judged from determinations of its molecular weight, contains, in part, a biose derivative. Cellobiose is also converted by acetyl bromide into penta-acetylglucose and sugars containing bromine. Under similar conditions, maltose appears to be transformed into acetyl bromomaltose, which is subsequently decomposed into acetyl bromoglucose and small amounts of an acetyl bromoglucose bromohydrin of doubtful constitution. [This observation throws some doubt on Karrer's claim of the quantitative conversion of amylose into acetyl bromomaltose (cf. A., 1921, i, 311).] Ethylcellulose and acetyl bromide similarly yield a brominated product from which it has been found possible to isolate a crystalline *bromoacetyl ethyl glucose*, m. p. 123°, which is to be more fully described in a subsequent communication.

The action of acetyl chloride proceeds in a totally different manner, an almost colourless solution being obtained which solidifies rapidly when concentrated. The product is separable by solution in glacial acetic acid and precipitation with ether into an insoluble and a soluble portion; the latter, which can be caused to solidify by evaporation of the solution, dissolving the residue in chloroform, and precipitation by ether, has not yet been examined completely. The former consists of a mixture of a hexa-acetylanhydrobiose and a chloropenta-acetylanhydrobiose, the relative proportions of which depend on the duration of the original action. By treatment with acetic anhydride and sodium acetate, this product is converted into an apparently homogeneous *hexa-acetylanhydrobiose*, $C_{24}H_{32}O_{16}$, small, colourless crystals, m. p. $265-270^{\circ}$, $[\alpha]_D^{25} -17.8^{\circ}$, in chloroform solution. The substance has a pronounced tendency to yield colloidal solutions. Dilute solutions of it in glacial acetic acid have a molecular weight corresponding closely with the value calculated from the formula given above, but marked association is observed in more concentrated solutions. In phenol, the substance is bimolecular, whereas in bromoform the association is complete and a depression of the freezing point is not observed. In its general properties, therefore, the new substance exhibits a close analogy with cellulose and its esters. Treatment with alcoholic potassium hydroxide solution at the atmospheric temperature converts the hexa-acetate into the corresponding *anhydrobiose*, $C_{12}H_{20}O_{10} \cdot 2H_2O$, an apparently microcrystalline powder which becomes discoloured at 200° , but is not melted completely at 270° . It is insoluble in water, but soluble in ammoniacal copper hydroxide solution. It is soluble in cold alkali hydroxide and is precipitated unchanged from such solutions by acids; with warm solutions, this is not the case. The solubility in ammoniacal copper hydroxide solution does not depend, however, on the basic character of the latter, since a similar solvent action is exerted by ammoniacal silver oxide, but not by ammoniacal cadmium hydroxide solution. The substance shows distinct adsorptive capacity for substantive cotton dyes.

H. W.

Cellulose Nitrates. G. DE BRUIN (*Rec. trav. chim.*, 1921, **40**, 632—664).—A résumé is given of the more generally accepted views as to the constitution of cellulose from the point of view of its nitration products and also of the various methods of determining its stability and the ratio of nitrogen content to stability. For the work described, a large quantity of material was used and details are given with regard to the cellulose, acids, nitration, stabilisation, and method of sampling and of carrying out estimations of nitrogen content. The relation between stability and nitrogen content at 95° and 132° is expressed both numerically and graphically, the author's method of investigation being described in detail. This is followed by a review of work carried out on the solubility of cellulose nitrates in mixtures of alcohol and ether, together with methods of experiment hitherto in use. The author's results as regards solubility, expressed as the mean of a series

of determinations of the ratio of solubility to nitrogen content vary considerably with methods of preparation of the cellulose nitrate. The author infers from his experimental work on stability and solubility that there are simple cellulose nitrates the nitrogen content of which is about 12% and 12.5% respectively; it is shown that the substance containing 12.75% of nitrogen is present as a mixture of two isomerides one of which is soluble in a mixture of alcohol and ether, the other being insoluble. These results are in accordance with the theory put forward by Vieille. H. J. E.

Lignosulphonic Acid. PETER KLASON (*Zellstoff u. Papier*, 1921, **1**, 56).—The author criticises the formula proposed for the barium salt of lignosulphonic acid by Hönig and Fuchs (A., 1920, i, 753) and proposes $C_{19}H_{18}O_{11}SBa$ in place of the formula $C_{18}H_{30}O_{10}SBa$.
CHEMICAL ABSTRACTS.

Action of Ozone on Aliphatic and Aromatic Substitution Products of Ammonia. WILHELM STRECKER and MAX BALTES (*Ber.*, 1921, **54**, [B], 2693—2708; cf. Strecker and Thienemann, A., 1921, ii, 44).—The action of ozone on substitution products of ammonia only leads to oxidation with addition of oxygen when the radicles attached to the nitrogen atom are similar to one another and of not too great molecular weight; thus, the tertiary aliphatic amines give the corresponding amine-oxides, whereas triphenylamine gives at the most a highly unstable product. If the substituents differ from one another, as is the case with the primary and secondary aliphatic amines and the *N*-alkylanilines, ozonisation causes the degradation of the molecule. With aromatic derivatives, ozonisation does not cause an extensive change in the molecule when the oxidation product is a particularly stable substance.

Undiluted trimethylamine reacts explosively with ozone. In chloroform solution at -80° , the base is converted into a mixture of trimethylamine *N*-oxide and its hydrochloride (cf. Dunstan and Goulding, T., 1899, **75**, 792, 1005), the requisite hydrogen chloride being derived from a partial oxidation of the solvent. A precisely similar reaction is observed in carbon tetrachloride solution at -30° . In aqueous solution, trimethylamine oxide is likewise produced in small amount, but, in this instance, its formation is accompanied by the production of formaldehyde. Ozonisation in the presence of much hexane gives formaldehyde and a viscous, white mass which melts to a yellow oil, insoluble in hexane, when removed from the cooling bath. The oil soon decomposes with evolution of nitrogen, hydrogen, and formaldehyde; on distillation, it yields carbon dioxide, formaldehyde, and monomethylamine. When treated with hydrogen chloride either before or after the spontaneous evolution of gas, it gives small amounts of trimethylamine oxide hydrochloride. Formaldehyde and dimethylamine are obtained when its aqueous solution is evaporated with hydrochloric acid. It appears probable that an aldim or a substance such as trimethyltrimethyleneamine is intermediately formed.

Ozonisation in ethyl chloride solution proceeds in much the same manner as in hexane, except in so far as small amounts of trimethylamine oxide hydrochloride are formed.

Triethylamine is less vigorously attacked than trimethylamine by ozone, but the processes are otherwise similar. In chloroform solution, triethylamine oxide hydrochloride together with small amounts of diethylamine hydrochloride are produced. In hexane, a pale yellow oil is formed which contains diethylamine and acetaldehyde, from which gas is not evolved. A similar effect is observed in ethyl chloride, but, in this case, triethylamine oxide hydrochloride is also produced in small quantity.

Tri-*n*-propylamine when dissolved in chloroform gives tripropylamine oxide hydrochloride (identified as the picrate, m. p. 129.5°). In the absence of solvent, the amine oxide is also formed, but the oxidation proceeds farther with production of aldehyde and nitrate.

Dimethylaniline could not be converted into its oxide by means of ozone, the main products being formaldehyde and more or less resinous substances. Diphenylamine and tetraphenylhydrazine did not give characteristic products when ozonised. Triphenylamine yielded a flocculent precipitate which decomposed with evolution of gas when filtered; possibly an unstable amine oxide is formed. In substance or in solution, phenylhydrazine is decomposed extensively by ozone, with the production of a black mass resembling pitch. Phenylhydroxylamine, on the other hand, is transformed into nitrobenzene in fairly good yield, whilst hydrazobenzene is converted smoothly into azobenzene. Tribenzylamine is oxidised to benzoic acid, small amounts of benzaldehyde being also produced.

H. W.

Ammonium Radicles. II. Tetraethylammonium. II.

HANS HEINRICH SCHLUBACH and FRITZ BALLAUF (*Ber.*, 1921, **54**, [B], 2811—2825).—An extension of previous work (Schlubach, A., 1920, i, 822).

A solution of tetraethylammonium iodide in liquid ammonia at -70° is subjected to electrolysis in a specially designed cell which is fully described and figured in the original. The phenomena are very similar to those observed with tetraethylammonium chloride, blue streaks appearing immediately at the cathode and a dark blue solution being formed. The latter is decolorised immediately by iodine, with formation of tetraethylammonium iodide and reacts with sulphur with apparent formation of *tetraethylammonium sulphide*, $(\text{NEt}_4)_2\text{S}$. When a slow current of dry oxygen is passed over the cathode, the blue solution becomes slowly decolorised, but the phenomenon is not caused by union of the radicle with the gas (see later), and a substance analogous to potassium peroxide does not appear to be formed. With 2 : 6-dimethyl- γ -pyrone, an immediate change in colour from blue to yellow is observed, and the solution, when evaporated, leaves a red *substance* analogous to Schlenk and Thal's potassium-dimethylpyrone (A., 1913, i, 1205); the product is stable in an atmosphere of nitrogen at the atmospheric temperature, but rapidly

becomes smeary when exposed to air. Similarly, benzophenone gives a pale violet compound. Attempts to prepare triphenylmethyltetraethylammonium, either from its components in liquid ammonia or by the simultaneous electrolysis of tetraethylammonium chloride and triphenylmethyl chloride, did not lead to the desired result.

The observation that the amount of tetraethylammonium iodide produced does not vary greatly with the intensity of the blue colour of the solution of the radicle has led to the discovery that the solutions gradually become colourless when preserved at a low temperature, but retain their ability to react with iodine, sulphur, and 2 : 6-dimethyl- γ -pyrone in the same manner as do the blue solutions. The blue radicle, therefore, becomes transformed into a colourless variety. The same modification is produced when a slight excess of tetraethylammonium chloride is allowed to remain for twenty to twenty-four hours in contact with a solution of potassium in liquid ammonia at -70° . The latter method of preparing the radicle is preferable to the electrolytic process, since it permits the use of larger quantities of material and also avoids the decomposition of the product by the heat liberated by the current. The colourless form of tetraethylammonium is unstable at the temperature of boiling ammonia, since it is decomposed completely when its solutions are evaporated. The change does not appear to occur in the same manner as with the blue variety, since the volume of gas evolved is greatly in excess of that required by the equation $2\text{NEt}_4 \rightarrow 2\text{NEt}_3 + \text{C}_4\text{H}_{10}$ (cf. Schlubach, *loc. cit.*).

The relationship between the blue and colourless varieties has not been elucidated completely, but it is suggested that a case of association is presented, 2NEt_4 (blue) \rightleftharpoons $\text{NEt}_4 \cdot \text{NEt}_4$ (colourless); the phenomena are thus comparable with those observed with triarylmethyls and hexa-arylethanes and with diarylnitrogens and tetra-arylhydrazines.

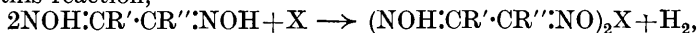
H. W.

Bromo-salts of Ruthenium [Ruthenibromides]. A. GUTBIER and F. KRAUSS (*Ber.*, 1921, **54**, [B], 2835—2838).—In continuation of previous work on ruthenichlorides (A., 1915, i, 120), a series of the corresponding bromo-salts is described.

The following pentabromo-compounds were prepared by mixing suitably concentrated solutions of their components. They are readily decomposed in aqueous or aqueous-alcoholic solution, particularly when warmed. They can be crystallised from moderately dilute hydrobromic acid, from which they separate in lustrous, dark-coloured crystals which are stable towards air. *Methylammonium ruthenipentabromide*, $(\text{NH}_3\text{Me})_2\text{RuBr}_5$, needles; *dimethylammonium*, $(\text{NH}_2\text{Me}_2)_2\text{RuBr}_5$; *trimethylammonium*; *tetramethylammonium*, leaflets; *ethylammonium*, needles; *diethylammonium*, needles; *triethylammonium*, thick plates; *tetraethylammonium*, leaflets; *n-propylammonium*, needles; *isopropylammonium*, needles; *dipropylammonium*; *n-butylammonium*, small needles; *isobutylammonium*; *isoamylammonium*, needles; *pyridinium*, scales; β -*picolinium*, $(\text{C}_5\text{H}_4\text{Me}\cdot\text{NH})_2\text{RuBr}_5$; *quinolinium*, needles.

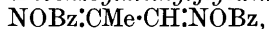
The solutions of the pentabromides in hydrobromic acid instantly react with bromine vapour at the atmospheric temperature, giving the hexabromides, which separate in sparingly soluble, dark coloured crystals. The following new compounds are described; *dipropylammonium ruthenihexabromide*, $(\text{NH}_2\text{Pr}_2)_2\text{RuBr}_6$, long needles; *isoamylammonium*; β -*picolinium*, needles; *quinolinium*. H. W.

Dioximes. GIACOMO PONZIO (*Gazzetta*, 1921, **51**, ii, 213—228; *Atti Accad. Sci. Torino*, 1921, **56**, 90—106).—In hot aqueous solution, the *syn*-modifications of dioximes of α -keto-aldehydes and α -diketones react directly with iron, copper, nickel, and cobalt in compact strips, giving the corresponding internal complex salts. In this reaction,



which possibly occurs also with other elements of Group VIII in the periodic system, the *syn*-glyoximes resemble strong acids, although they are not electrolytes and attack neither magnesium nor zinc. In this way, cobalt, copper, and iron mostly yield either deep brown colloidal solutions or amorphous precipitates, but cupric dimethylglyoxime has been obtained crystalline.

Methylglyoxime, prepared by way of oximinacetone, exhibits normal cryoscopic behaviour in water, has the molecular electrical conductivity Λ_{32} 0.062, and dissolves in water to the extent of approximately 2.08% at 8°, 4.58% at 26°, and 7.56% at 40°. Nickel methylglyoxime (Tschugaev, A., 1911, i, 261) crystallises in bright red prisms, begins to turn brown at about 200° without melting, dissolves in water to the extent of 0.0131% at 16° and 0.0396% at 100°, yields a scarlet precipitate of nickel dimethylglyoxime when treated in aqueous solution with dimethylglyoxime and a drop of ammonia solution, and dissolves in sodium hydroxide solution, giving an orange-yellow liquid which gradually deposits nickelous hydroxide. *Dibenzoylmethylglyoxime*,



crystallises in white needles, m. p. 164—165°.

Two methods are given for the preparation of dimethylglyoxime, both making use of oximinomethyl ethyl ketone, which is prepared in the one case from methyl acetoacetate and in the other from methyl ethyl ketone. When crystallised from toluene, dimethylglyoxime has m. p. 240° (partial sublimation), and its solubility in water varies from 0.32 gram per litre at 0° to 5.66 grams at 100° and is represented by the expression, $\log S = \bar{1}.50515 + 0.015251t - 0.000027725t^2$. Its copper compound, contrary to Tschugaev's statement (A., 1905, i, 743), is insoluble in the ordinary organic solvents with the exception of alcohol. The *cobaltous* salt, $(\text{C}_2\text{H}_5\text{O}_2\text{N}_2)\text{Co}$, obtained by heating either the aqueous solution of the glyoxime with a strip of copper or the alcoholic solution with aqueous cobalt acetate, forms a coffee-coloured powder with violet reflexion and commences to undergo change at about 200°. The dibenzoyl derivative has m. p. 225° (cf. Diels and Stern, A., 1907, i, 480).

Methylethylglyoxime, $\text{NOH}:\text{CMe}\cdot\text{CEt}:\text{NOH}$, crystallises in white

needles or laminæ, m. p. 172—173°, and its solubility in water is expressed by the equation $\log S = \bar{1} \cdot 81837 + 0 \cdot 02317t - 0 \cdot 00009015t^2$. The compound described in Richter's Lexikon (I, 290) as $\alpha\beta$ -dioxydiminopentane, $\text{NOH}:\text{CH}:\text{CPr}:\text{NOH}$, m. p. 168°, does not exist. *Dibenzoylmethylethylglyoxime*, $\text{C}_{19}\text{H}_{18}\text{O}_4\text{N}_2$, crystallises in long, white, lustrous plates, m. p. 173°.

Methyl-*n*-propylglyoxime crystallises in large, lustrous plates or long, flattened needles, m. p. 175°, and its solubility in water is given by the expression,

$$\log S = \bar{1} \cdot 23045 + 0 \cdot 00478637t + 0 \cdot 0001350812t^2.$$

The nickel salt forms orange needles, m. p. 159—160°, and the same melting point is found for the compound prepared by Tschugaev's method (*loc. cit.*), although this author gave m. p. 144°. The *dibenzoyl* derivative, $\text{C}_{20}\text{H}_{20}\text{O}_4\text{N}_2$, crystallises in white needles, m. p. 128°.

Methylisopropylglyoxime, $\text{C}_6\text{H}_{12}\text{O}_2\text{N}_2$, crystallises in lustrous laminæ or long, slender needles, m. p. 157—158°, and its solubility in water is expressed by

$$\log S = 0 \cdot 23044 - 0 \cdot 00075979t + 0 \cdot 00015876t^2.$$

The *nickel* compound, $(\text{C}_6\text{H}_{11}\text{O}_2\text{N}_2)_2\text{Ni}$, crystallises in lustrous, orange-yellow laminæ, m. p. 229°, and the *dibenzoyl* derivative, white prisms, m. p. 112—113°.

Chloromethylglyoxime has m. p. 188—189°. Its *nickel* compound, $\text{C}_6\text{H}_8\text{O}_4\text{N}_4\text{Cl}_2\text{Ni}$, forms lustrous, wine-red plates, and begins to blacken at about 200°.

Nickel acetylhexoyldioxime, $(\text{C}_8\text{H}_{15}\text{O}_2\text{N}_2)_2\text{Ni}$, crystallises in brick-red prisms, m. p. 157—158°. *Nickel acetyl-n-nonoyldioxime*, $(\text{C}_{11}\text{H}_{21}\text{O}_2\text{N}_2)_2\text{Ni}$, crystallises in yellowish-brown plates, m. p. 125°. *Nickel acetylpalmityldioxime*, $(\text{C}_{18}\text{H}_{35}\text{O}_2\text{N}_2)_2\text{Ni}$, forms yellow plates, m. p. 88—89°. *Nickel acetylstearyldioxime*, $(\text{C}_{20}\text{H}_{39}\text{O}_2\text{N}_2)_2\text{Ni}$, crystallises in orange plates, m. p. 89°. *Nickel phenylmethylglyoxime*, $\text{C}_{18}\text{H}_{18}\text{O}_4\text{N}_4\text{Ni}$, forms scarlet needles, m. p. 239—240. *Nickel methylbenzylglyoxime*, $(\text{C}_{10}\text{H}_{11}\text{O}_2\text{N}_2)_2\text{Ni}$, crystallises in orange laminæ, m. p. 180°.

T. H. P.

Chromithiocyanates. I. NIELS BJERRUM (*Z. anorg. Chem.*, 1921, **118**, 131—164).—A detailed study has been made of the formation of complex thiocyanatochromi-compounds from chromium thiocyanate, of their properties, methods of analysis, and of their equilibria in solution. The existence of six different complexes has been established, of which four have been isolated.

Experiments with mixed solutions of chromic nitrate and potassium thiocyanate, in which the formation of chromi-complexes was followed by observing the gradual diminution of the conductivity of the solution, showed that a condition of equilibrium is eventually reached, very slowly in the cold in dilute solution, much more quickly at higher temperatures or at greater concentrations. At the point of equilibrium, the number of (CNS) groups associated with each chromium atom in the complex depends on the ratio of thiocyanate to chromium salt originally present. A mixture of compounds is formed, which can be separated by taking advantage of their

different solubilities in ether. After acidification and extraction with ether, the aqueous solution contains a mixture of monochromipentaquothiocyanate and chromitetraquodithiocyanate salts. The existence of these salts was inferred from analysis of the solution. Their colour in solution is reddish-violet. They are quite stable in acid, but unstable in alkaline solution. The velocity constant in the formation of the mono-complex compound from chromium nitrate and potassium thiocyanate is 0.13 at 50°, the equilibrium constant 328, and the decomposition constant 0.0004.

Complex chromithiocyanates are also obtained by drying slowly a solution of a hexaquochromithiocyanate. During drying, the colour deepens, the solution becomes syrupy, and eventually indistinct, red crystals of a chromitriaquotrithiocyanate appear. The mixture contains, however, both higher and lower complex thiocyanato-compounds. The trithiocyanato-complex can be extracted with ether, in which the higher tetra-, penta-, and hexa-compounds are not soluble in absence of free acid. It was not found possible to obtain the trithiocyanato-compound perfectly pure, but the analytical figures for the compound approximated to $[\text{Cr}(\text{CNS})_3(\text{H}_2\text{O})_3]$. The aqueous solution is red, but it gives a green solution in ether, with which it forms a compound, probably containing 3 mols. of the solvent. It is quite stable in ether and in acid aqueous solution, but is rapidly decomposed by alkalis, and even by sodium acetate. Determinations of the partition coefficient between water and ether gave results varying from 3.3 to 4.7, and it is supposed from this circumstance that the substance may be a mixture of two stereoisomerides.

The rate of decomposition of potassium chromihexathiocyanate was studied in aqueous, acid, alkaline, and alcoholic solution in the dark and in daylight. In the dark there is not much difference in the rate of decomposition in any of these media; the fact that the hexathiocyanato-compound is not sensitive to alkali confirms the opinion that in the other compounds of the series decomposition by alkali is due to replacement of water in the inner complex by hydroxyl. In daylight, the rate of decomposition is about ten times as fast as in the dark. When an acid solution of the above potassium salt is shaken with ether, three layers are formed, the inner layer being a concentrated solution of chromihexathiocyanato-acid in ether. The acid, however, rapidly decomposes in ether. The following well-characterised, insoluble salts were prepared. *Pyridine* salt, $(\text{C}_5\text{H}_5\text{N})_3\text{Cr}(\text{CNS})_6 \cdot \text{H}_2\text{O}$, reddish-violet, small, flat needles. *Quinoline* salt, $(\text{C}_9\text{H}_7\text{N})_3\text{Cr}(\text{CNS})_6 \cdot \text{H}_2\text{O}$, very small crystals, similar to those of the pyridine salt, with a very small solubility product.

E. H. R.

Chromithiocyanates. II. NIELS BJERRUM (*Z. anorg. Chem.*, 1921, **119**, 39—53; cf. preceding abstract).—After many unsuccessful attempts to isolate a chromiaquopentathiocyanate derivative, this was accomplished by means of the quinoline salt. A solution containing potassium chromihexathiocyanate and

potassium thiocyanate in the mol. ratio 1 : 3 was heated for two days at 50°, and after acidification first the unchanged chromi-hexathiocyanate and then the chromipentathiocyanate were separately precipitated with quinoline sulphate. Quinoline chromiaquopentathiocyanate, $[\text{Cr}(\text{CNS})_5\text{H}_2\text{O}](\text{C}_9\text{H}_8\text{N})_3\text{H}_2\text{O}$ forms bluish-violet, small, well developed crystals, readily decomposed by ammonia. An aqueous solution of the sodium salt was obtained by shaking the quinoline salt with ether and aqueous sodium acetate-acetic acid solution. Its colour is reddish-violet; the free acid in ether is greenish-violet, changing to green as it decomposes into the tetrathiocyanato-acid. The rate of decomposition of the chromipentathiocyanato-ion was determined in aqueous acid solutions varying from $p_{\text{H}}=1$ to $p_{\text{H}}=8$. The stability increases with the acid strength; in alkaline solution decomposition is rapid. A solution of chromitetrathiocyanato-acid was prepared from the mixture obtained from the slow drying of a solution of hexaquo-chromic thiocyanate (*loc. cit.*), taking advantage of the fact that the neutral trithiocyanate is extracted by ether from neutral solution, the tetrathiocyanate only after acidification. It is stable in ether, unlike the pentathiocyanate, and forms a green ethereal solution. In water, it forms a reddish-violet solution and is quite stable in presence of acid. No well-defined crystallised salt of the chromitetrathiocyanato-acid was discovered; the quinoline salt is readily soluble and the quinine and strychnine salts form blue, flocculent precipitates of varying composition. E. H. R.

Chromithiocyanates. III. NIELS BJERRUM (*Z. anorg. Chem.*, 1921, **119**, 54—68).—This paper gives an account of the methods used for the analysis of complex mixtures of chromithiocyanato-compounds (preceding abstracts). Chromium was always estimated by titration with thiosulphate after oxidation to chromate with hydrogen peroxide. Titration of a solution of complex chromithiocyanate with silver nitrate by the Volhard method gives the total of ionic thiocyanate plus that present as chromi-tetra-, penta-, and hexa-thiocyanato-ions. The titrated solution is then boiled with sodium hydroxide to decompose chromithiocyanato-complex compounds and after acidification is again titrated by the Volhard process. The second titration gives all the thiocyanate present in the form of chromi-mono-, di-, and tri-thiocyanate compounds plus three thiocyanate groups for each molecule of the chromi-tetra-, penta-, and hexa-thiocyanate compounds. This method is useful only for determining the proportion of ionic and of total complex combined thiocyanate present. The ionic thiocyanate can also be determined colorimetrically with an accuracy of 5—10% by comparing the colour given with ferric nitrate with standard thiocyanate solutions. When a large proportion of complex thiocyanato-chromium compounds is present their colour makes it impossible to use this method. The different complex compounds are estimated as follows. Chromi-hexa- and penta-thiocyanato-compounds are precipitated as quinoline salts, and from an estimation of chromium and thiocyanate in the mixture

the proportion of each can be estimated. The remaining solution is then acidified with sulphuric acid and extracted with ether, after which the ether is again extracted with an aqueous sodium acetate-acetic acid solution. In this way, the trithiocyanate is obtained in the ether and the tetrathiocyanate in the aqueous acetate solution and both can be estimated. The original aqueous solution now contains chromium thiocyanate with chromi-mono- and dithiocyanato-compounds. It is analysed for total chromium and complex combined thiocyanate. An estimation of chromium thiocyanate is made on the original solution by adding potassium sulphate and alcohol, filtering, and analysing the precipitated chrome alum. A small proportion of chromium present as "concealed basic chromium" cannot be estimated in presence of chromi-thiocyanato-compounds. From the data obtained it is possible to estimate approximately the proportions of chromi-mono- and dithiocyanato-compounds present.

E. H. R.

Chromithiocyanates. IV. NIELS BJERRUM (*Z. anorg. Chem.*, 1921, 119, 179—201; cf. preceding abstracts).—Experiments were made to study the equilibrium between different complex chromi-thiocyanato-compounds at 50°. At the ordinary temperature, the velocity of formation of the complex compounds is extremely slow, but at 50° it proceeds at a speed convenient for measurement. The reaction was followed in solutions of chromic nitrate (0.01*N*) and potassium thiocyanate containing varying proportions of the latter, by means of conductivity measurements, and the solutions were analysed when equilibrium had been reached (cf. Pt. III). Six equilibrium constants are involved, corresponding with the series of six reactions, of which the first is $\text{Cr}(\text{H}_2\text{O})_6^{+++} + \text{CNS}^- = \text{Cr}(\text{H}_2\text{O})_5\text{CNS}^{++} + \text{H}_2\text{O}$, and the last $\text{Cr}(\text{H}_2\text{O})(\text{CNS})_5^{--} + \text{CNS}^- = \text{Cr}(\text{CNS})_6^{---} + \text{H}_2\text{O}$. These constants may be designated $K_{\text{Cr}(\text{CNS})_1}$, $K_{\text{Cr}(\text{CNS})_2}$, ..., $K_{\text{Cr}(\text{CNS})_6}$, and the values found are 328, 17.5, 4.56, 1.93, 0.81 and 0.41. From these constants can be calculated the affinities of each successive thiocyanate group for the chromium atom. These, calculated from the equation $A = RT \log K$ and expressed in gram-calories are 3710, 1840, 970, 420, -130 and -570. From the equilibrium constants were calculated the proportions of each of the complex chromi-thiocyanato-compounds which will be present in solution in chemical equilibrium for concentrations of ionic thiocyanate from 10^{-3} to 10 molar, and these results are embodied in a diagram by means of which the concentration of each complex compound can be found when the thiocyanate-ion concentration is known. A curve is given showing the relation between the concentration of ionic thiocyanate and the number of combined thiocyanate groups per atom of chromium. At 100°, equilibrium is reached in about half an hour, but apparently a rather smaller proportion of complex compounds is present at equilibrium. On the other hand, a solution which had stood for several years at room temperature showed a greater proportion of higher complex compounds than a solution of the same total concentration in equilibrium at 50°.

E. H. R.

Preparation of Organic Compounds of Boron with the Aid of Boron Fluoride. I. Boron Alkyls and Alkylboric Acids. ERICH KRAUSE and RUDOLF NITSCHKE (*Ber.*, 1921, **54**, [B], 2784—2791).—Boron trialkyls are prepared readily by passing gaseous boron trifluoride (prepared from potassium borofluoride, boric anhydride, and concentrated sulphuric acid and purified by condensation by liquid air and subsequent fractionation of the liquefied gas) into an ethereal solution of the requisite Grignard's reagents. They are isolated by distillation of the crude product of the reaction (under diminished pressure, if necessary) in an atmosphere of nitrogen. They are colourless, mobile liquids with a not unpleasant odour. They are readily oxidised on exposure to air, frequently becoming spontaneously ignited. They can be preserved indefinitely, even if exposed to light, in an atmosphere of nitrogen in sealed tubes. In spite of their relatively high boiling points, they are readily volatile at the atmospheric temperature. They are very slowly decomposed by water. The alkylboric acids, $\text{Alk}\cdot\text{B}(\text{OH})_2$, are most conveniently prepared by preserving the boron trialkyls in a loosely-stoppered flask originally filled with nitrogen; in consequence of the inward diffusion of air, they then become oxidised gradually to the boronalkyl oxides, $\text{Alk}\cdot\text{B}\cdot\text{O}$, which are converted by crystallisation from a small quantity of hot water into the alkylboric acids. The latter are crystalline compounds which are very soluble in the usual media. They reduce alcoholic silver nitrate solution when warm, but not in the cold. Their volatility is remarkable.

Boron triisoamyl, $\text{B}(\text{C}_5\text{H}_{11})_3$, has b. p. $119^\circ/14\text{ mm.}$, $d_4^{25.4}(\text{vac.})$ 0.7600, $d_4^{25.6}(\text{vac.})$ 0.7607, $n_{\text{H}_a}^{22.6}$ 1.42983, $n_{\text{B}}^{22.6}$ 1.43207, $n_{\text{H}_\beta}^{22.6}$ 1.43782, $n_{\text{H}_\gamma}^{22.6}$ 1.44254. *Boron triisobutyl* has b. p. $86^\circ/20\text{ mm.}$, $188^\circ/760\text{ mm.}$, $d_4^{25.0}(\text{vac.})$ 0.7380, whence $d_4^{22.3}(\text{vac.})$ 0.7400, $n_{\text{H}_a}^{22.6}$ 1.41652, $n_{\text{D}}^{22.8}$ 1.41882, $n_{\text{H}_\beta}^{22.3}$ 1.42445, $n_{\text{H}_\gamma}^{22.8}$ 1.42882. *Boron tri-n-propyl*, b. p. $60^\circ/20\text{ mm.}$, $156^\circ/760\text{ mm.}$, has $d_4^{24.7}(\text{vac.})$ 0.7024, whence $d_4^{22.5}(\text{vac.})$ 0.7225, $n_{\text{H}_a}^{22.5}$ 1.41129, $n_{\text{D}}^{22.5}$ 1.41352, $n_{\text{H}_\beta}^{22.5}$ 1.41895, $n_{\text{H}_\gamma}^{22.5}$ 1.42354.

isoAmylboric acid, $\text{C}_5\text{H}_{11}\cdot\text{B}(\text{OH})_2$, colourless, rectangular plates, m. p. 169° , *isobutylboric acid*, long, colourless, pointed plates, m. p. 112° , and *n-propylboric acid*, thick, rectangular plates, m. p. 107° , are described.

H. W.

Constitution of Grignard's Compounds. JULIUS VON BRAUN (*Ber.*, 1921, **54**, [B], 2687).—The idea that the primary product of the interaction of a Grignard reagent with a carbonyl compound is a molecular additive product (Meisenheimer and Caspar, A., 1921, i, 654) has been advanced previously by the author (A., 1918, i, 107; 1920, i, 30). He, however, has regarded the addition as occurring at the oxygen atom, whereas Meisenheimer and Caspar consider it to take place at the magnesium atom.

H. W.

Lignite Producer Tar. S. RUHEMANN (*Ber.*, 1921, **54**, [B]-2565—2568).—A preliminary account. The crude tar is dehydrated, freed from mechanical impurities, distilled under diminished

pressure (about 20 mm.), and finally treated with steam at 100°. The investigation of the neutral oils and phenols is confined for the present to the steam distillate, whereas the total vacuum distillate is used for the examination of the acids. The neutral oil is collected in a number of fractions between 83 and 166°/12 mm. The separate portions are characterised by a pleasant odour and deep blue fluorescence which gives place after a time to a dark brown coloration. They all contain sulphur (3·4—1·8%) which is removed only to a small extent by distillation over sodium, but can be considerably eliminated by treatment with sodium in boiling alcoholic solution; oxygen is also present. Further purification is conveniently effected by agitating them with methyl alcohol, which dissolves the greater proportion of the sulphur and the whole of the oxygen compounds and gives a residue containing essentially paraffins and naphthenes. The latter are readily destroyed by treatment with fuming nitric acid. A neutral fraction, b. p. 140—145°/12 mm. when treated in this manner, yielded a product, b. p. 144—147°/12 mm., which appears to be hexadecane or the next higher homologue.

The portion of the tar soluble in sodium carbonate solution appears to contain acids of the series $C_nH_{2n-2}O_2$ and $C_nH_{2n-4}O_2$, the investigation of which is not complete.

The sodium hydroxide extract of the tar consists essentially of phenols which distil at 88—178°/12 mm., with considerable formation of pitch. They can be most readily separated from one another by conversion into the arylurethanes, $NH_2 \cdot CO \cdot O \cdot Ar$, and crystallisation of the latter from a mixture of benzene and light petroleum. Regeneration is effected by heating the esters when they are decomposed into the phenols and cyanic acid. The presence of cresol and its three next higher homologues has been established. Phenol appears to be absent.

H. W.

Sulphuryl Chloride. I. Influence of Catalysts: a Convenient Method of Chlorinating Benzene. OSWALD SILBERRAD (T., 1921, 119, 2029—2036).

The *o*- and *p*-Nitrobenzyl Bromides. CHARLES MOUREU and RALPH L. BROWN (*Bull. Soc. chim.*, 1921, [iv], 29, 1006—1008).—*o*-Nitrobenzyl bromide may readily be obtained by the action of either hydrogen bromide or phosphorus pentabromide on *o*-nitrobenzyl alcohol in chloroform solution (cf. Norris, Watt, and Thomas, A., 1916, i, 461). *p*-Nitrobenzyl bromide is obtained with a 30% yield by the direct nitration of benzyl bromide (cf. Lyons and Reid, A., 1917, i, 559).

W. G.

The Action of Cupric Chloride on Organometallic Derivatives of Magnesium. EUSTACE EBENEZER TURNER (*J. Roy. Soc. New South Wales*, 1920, 54, 37—39).—The method of preparing diphenyl by the interaction of magnesium phenyl bromide in ethereal solution and anhydrous cupric chloride (cf. T., 1919, 115, 559) was found to be successful for the preparation of 1:1'-ditolyl, but could not be used for coupling two dissimilar groups.

Cupric chloride did not react with the magnesium derivatives of halogenated fatty acids to give succinic acids, but ethyl α -bromobutyrate reacted in ethereal solution with magnesium and cupric chloride, giving ethyl *s*-diethylsuccinate. W. G.

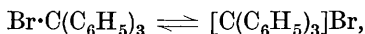
The Behaviour of Azo-compounds and their Salts with Aromatic Hydrocarbons and Aluminium Chloride. RUDOLPH PUMMERER and JOSEPH BINAPFL (*Ber.*, 1921, **54**, [B], 2768—2784).—An attempt has been made to extend Scholl's condensations with aluminium chloride in the anthracene and naphthalene series to the benzene series by carrying out the reactions in presence of a substance, such as azobenzene, capable of undergoing hydrogenation. It is uncertain whether diphenyl is formed, for the greater part of the benzene is converted into viscous, high molecular condensation products, thus benzene and aluminium chloride begin to react at 40°, but no gaseous hydrogen can be detected. Bisdiphenylene-ethylene, however, when dissolved in dry xylene, b. p. 135—138°, and treated with five equivalents of aluminium chloride for twelve hours at 35—40°, is converted into bisdiphenylene-ethane (67% yield), long, glistening needles from benzene and alcohol, m. p. 238·5—239°. The hydrogenating action of dry benzene, free from thiophen, and aluminium chloride on azobenzene for three-quarters of an hour at 60° results in the formation of hydrazobenzene in 18% yield. In presence of hydrogen chloride, phenylation occurs with the formation of aminodiphenyl, m. p. 53°, in a yield of 70—80%, together with 10% of benzidine, some aniline, and 7—10% of an oxidisable substance which is possibly a semidine base. The course of the reaction in the formation of the aminodiphenyl is probably as follows: $\text{NPh:NPh} + \text{C}_6\text{H}_6 \rightarrow \text{NHPH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Ph}$; $\text{NHPH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Ph} \rightarrow \text{NPh:N}\cdot\text{C}_6\text{H}_4\text{Ph}$; $\text{NPh:N}\cdot\text{C}_6\text{H}_4\text{Ph} + \text{C}_6\text{H}_6 \rightarrow \text{C}_6\text{H}_4\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Ph}$; $\text{C}_6\text{H}_4\text{Ph}\cdot\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Ph} + 2\text{H} \rightarrow 2\text{C}_6\text{H}_4\text{Ph}\cdot\text{NH}_2$; which is equivalent to: $\text{NPh:NPh} + 2\text{C}_6\text{H}_6 = 2\text{C}_6\text{H}_4\text{Ph}\cdot\text{NH}_2$. This reaction is not limited to the use of azobenzene and benzene, for a similar reaction proceeds even more readily when the latter is replaced by toluene or xylene. F. M. R.

The Alleged Hexavalency of Carbon in Carbonium and Dyestuff Salts. A. HANTZSCH (*Ber.*, 1921, **54**, [B], 2569—2572).—Kehrmann's theory of the hexavalency of carbon in carbonium salts (*A.*, 1918, i, 311) is refuted, and is shown to be entirely lacking in experimental support. The extension of Kehrmann's theory to the yellow salts obtained from fuchsonimonium chloride and to the salts of aminoazo-colouring matters (*A.*, 1917, i, 593) is equally unsound. F. M. R.

The Constitution of Carbonium Salts. A. HANTZSCH (*Ber.*, 1921, **54**, [B], 2573—2613).—Determination of the absorption spectra, conductivity measurements, and chemical investigation show the existence of only two sharply-defined groups of triphenylmethane derivatives, which are interconvertible, and which give rise to equilibrium mixtures. In addition to the normally-con-

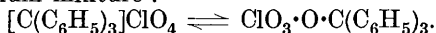
stituted, colourless, non-conducting triphenylmethane compounds there exist only the well-characterised, anomalous, yellow conducting triphenylcarbonium salts, which may be recognised by their absorption spectra. The latter compounds are not to be regarded as compounds which possess "ionisable" carbon valencies, or individual unsaturated carbon atoms, or quinonoid or quinolide rings, as has been the case hitherto, but are to be regarded as carbonium salts similarly constituted to the azonium, phosphonium, oxonium, and thionium salts. As is usually the case with -onium haloids, two series of isomeric halogen derivatives exist in the case of the carbonium compounds, viz., pseudo-salts with a direct non-ionising linking of the halogen atom, such as $X \cdot C(C_6H_5)_3$, and true salts with an indirect ionising linking of the halogen atom, such as $[C(C_6H_5)_3]X$.

Under suitable conditions the compounds are partly isomerised when dissolved in inert solvents with the formation of an equilibrium mixture, thus :



the tendency being towards the formation of the pseudo-salt. The more readily and completely the halogen atom forms complex anions with chemically active substances, the greater the tendency of the equilibrium towards the formation of the carbonium salt containing the complex kation $[C(C_6H_5)_3]$.

Even the carbonium perchlorate in an inert solvent such as chloroform is converted into the pseudo-salt with the formation of the equilibrium mixture :



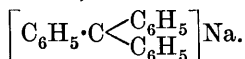
Ether, in suitable concentrations, converts all the equilibrium mixtures into colourless solutions of the pseudo-salts, but, in the case of the pseudo-perchlorate, when the ether is removed, isomerisation occurs and the true salt is formed. The chemical behaviour of carbonium salts also can only be explained by the complex formula $[C(C_6H_5)_3]X$. As is the case with all groups attached directly to the central atom of a complex kation, the benzene nucleus in carbonium salts cannot be detected by its usual reactions, such as bromination, sulphonation, or nitration. The carbonium salts are structurally related to the diazonium salts, as is shown by the common possession of several characteristic reactions; for example, alcohol converts triphenylcarbonium salts into triphenylmethane in a similar manner to the conversion of benzenediazonium salts into benzene.

The yellow salts of rosaniline dyes formed in strongly acid solution are also carbonium salts, thus pararosaniline forms tri-anilino-sulphato-carbonium sulphate, $[C(C_6H_4 \cdot NH_3 \cdot SO_4H)_3]SO_4H$.

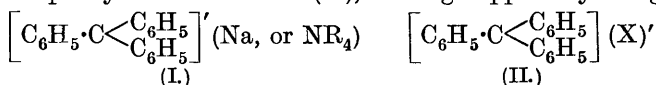
F. M. R.

The Coloured Alkali Salts of Triphenylmethane, and Triphenylmethyl as an Amphoteric Ion. A. HANTZSCH *Ber.*, 1921, 54, [B], 2613—2620).—The proof that the coloured salts of triphenylcarbinol are true -onium salts (cf. preceding abstract) in which the triphenylmethyl residue functions as a

kation leads to the conclusion that the coloured alkali salts, such as triphenylmethyl-sodium, are neither true triphenylmethane derivatives with an ionisable carbon valency nor quinonoid compounds, but are also complex salts in which the triphenylmethyl residues function as an anion, thus :



In the same manner that the neutral triphenylmethyl residue in the colourless, non-conducting triphenylmethyl compounds, $\text{R} \cdot \text{C}(\text{C}_6\text{H}_5)_3$, acts as kation in combination with strongly negative acidic residues or anions, it acts as anion when combined with strongly positive metals or kations. Consequently, alkali and tetra-alkylammonium salts (I) are chemically similarly constituted to the triphenylcarbonium salts (II), although oppositely charged :



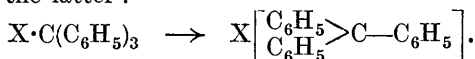
Just as the triphenylcarbonium salts are derived from the similarly coloured true base, $[\text{C}(\text{C}_6\text{H}_5)_3]\text{OH}$, which is spontaneously isomerised to the colourless pseudo-base, $\text{HO} \cdot \text{C}(\text{C}_6\text{H}_5)_3$, so the coloured alkali salts are derived from the true colour acid, $[\text{C}(\text{C}_6\text{H}_5)_3]\text{H}$, which is spontaneously isomerised to the colourless pseudo-acid, $\text{H} \cdot \text{C}(\text{C}_6\text{H}_5)_3$.

There is, therefore, an analogy with the *aci*-trinitromethane salts, and consequently the coloured metallic salts of triphenylmethane are *aci*-triphenylmethane salts. Colourless pseudo-metallic salts, such as $\text{MgCl} \cdot \text{C}(\text{C}_6\text{H}_5)_3$, or $\text{Zn}(\text{CH}_2 \cdot \text{C}_6\text{H}_5)_3$, also exist and correspond with the colourless pseudo-haloid salts, $\text{X} \cdot \text{C}(\text{C}_6\text{H}_5)_3$.
F. M. R.

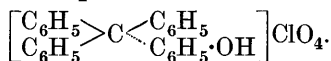
The So-called Halochromism of Triphenylmethane Derivatives. A. HANTZSCH (*Ber.*, 1921, 54, [B], 2620—2627).—A. von Baeyer's conception of halochromism rests on a purely empirical basis and merely expresses the fact that certain colourless substances are converted into coloured salts by means of colourless acids or bases, without explaining the phenomenon. In the author's opinion, halochromism is produced by a discontinuous chemical reaction resulting in an alteration in structure, such as the alternate transition between an ionogenic and non-ionogenic linking, that is, isomerism between electrolytes and non-electrolytes. As it has been shown by optical measurements that normal salt formation from true acids, which occurs without any structural alteration, is an optically indifferent process, it follows that halochromism does not occur without structural alteration. Kauffmann's recent work on the derivation of valency laws (A., 1920, i, 50) is discussed and his deductions are refuted.
F. M. R.

The Co-ordination Number of Carbon. A. HANTZSCH (*Ber.*, 1921, 54, [B], 2627—2633).—As the haloid pseudo-salts of triphenylmethyl are isomerised under suitable conditions to the true triphenylcarbonium haloids, it follows that the normally

quadrivalent carbon atom in the former possesses the co-ordination number 3 in the latter :



Carbon retains this co-ordination number also in all other electrolytes in which it is the central atom of kations or anions, for example, in the yellow carbonium salts which contain more than two equivalents of acid to one of base, such as $[C(C_6H_5)_4 \cdot NH_3 \cdot SO_4H]_3[SO_4H]$, and in the red anions of the alkali salts, such as $[CH_2 \cdot C_6H_5]Na$, $[CH(C_6H_5)_2]Na$, $[C(C_6H_5)_3]Na$, etc. Under suitable conditions, the co-ordination number of carbon in the kation of the carbonium salts can be raised from 3 to 4, particularly in media which dissolve these salts without decomposition, thus :



F. M. R.

Catalytic Oxidation of Naphthalene. C. R. DOWNS (U.S. Pat. 1374722).—Naphthalene vapour is partly oxidised to form phthalic anhydride by subjecting it to the action of an oxidising gas such as air at a temperature of about 450° in the presence of aluminium oxide as a catalyst.

CHEMICAL ABSTRACTS.

Catalytic Oxidation of Fluorene. J. M. WEISS and C. R. DOWNS (U.S. Pat. 1374695).—Fluorenone is produced by oxidising fluorene vapour with air at a temperature of 300—700° in the presence of a catalytic metal oxide.

CHEMICAL ABSTRACTS.

Determination of the Melting- and Boiling-points of Anthracene, Phenanthrene, and Carbazole. W. KIRBY (*J. Soc. Chem. Ind.*, 1921, **40**, 274T).—Determinations of the melting- and boiling-points of anthracene, phenanthrene, and carbazole, using specially purified materials, gave the following results: anthracene, m. p. 218°, b. p. 340°; phenanthrene, m. p. 101°, b. p. 332°; carbazole, m. p. 247°, b. p. 351.5°. Earlier recorded values were generally lower in the case of the melting-points and higher in the case of the boiling-points.

G. W. R.

o-Quinones and 1:2-Diketones. IV. Synthesis of Acenaphthene. A. SCHÖNBERG (*Ber.*, 1921, **54**, [B], 2838—2839).—A preliminary note. A suitable synthesis of acenaphthene and its derivatives has not been described previously. It is now shown that acenaphthenedisemicarbazone gives a 50% yield of acenaphthene when heated at 200° with a solution of sodium in alcohol (cf. Wolff, A., 1912, i, 988). The application of the synthesis to derivatives of acenaphthene is being investigated.

H. W.

New Derivatives of Diphenylamine. A. V. BLOM (*Helv. Chim. Acta*, 1921, **4**, 1036—1039).—The following new derivatives of diphenylamine are described: 4'-Chloro-2:4-dinitrodiphenylamine, orange-red needles, m. p. 166°, which on reduction with

sodium sulphide and alcohol yields 4'-chloro-4-nitro-2-amino-diphenylamine, brownish-violet needles, m. p. 177°; 2:4-dinitro-4'-ethoxydiphenylamine, glistening, red plates, m. p. 119—120°, which on reduction yields 4-nitro-2-amino-4'-ethoxydiphenylamine, brown plates, m. p. 153°; 2:4-dinitro-4'-methoxydiphenylamine, dark red, glistening needles, m. p. 140°; 4:4'-dichloro-2-nitro-diphenylamine, reddish-brown, glistening needles, m. p. 149—150°.

In an attempt to prepare carbazole derivatives, the above nitro-aminodiphenylamine derivatives were converted into the azimines, but nitrogen could not be removed from the latter; 4'-chloro-4-nitrophenylaziminobenzene, forms brown needles, m. p. 212—213°, and on reduction and acetylation yields 4'-chloro-4-acetylaminophenylaziminobenzene, silvery needles, m. p. above 300°; 4-nitro-4'-ethoxyphenylaziminobenzene, crystallised in pale brown needles, m. p. 145—146°.

F. M. R.

The History of the Blue Oxidation Product from Diphenylamine. F. KEHRMANN and ST. MICEWICZ (*Helv. Chim. Acta*, 1921, 4, 949).—Blom's view (A., 1921, ii, 664) that the cause of the colour reaction between diphenylamine, nitric acid, and sulphuric acid is still undecided is corrected (cf. Wieland and Müller, A., 1913, i, 1386; Kehrmann and Micewicz, A., 1912, i, 1020). The authors, in their former publication (*loc. cit.*), attributed the discovery of this reaction to Merz and Weith (*Ber.*, 1872, 5, 283), whereas it was actually due to A. W. Hofmann (*Annalen*, 1864, 132, 165).

F. M. R.

Ketens. XXXVII. Ketenimine Derivatives. H. STAUDINGER and E. HAUSER (*Helv. Chim. Acta*, 1921, 4, 887—896).—It has been shown previously (Staudinger and Meyer, A., 1920, i, 228) that a ketenimine derivative is prepared by the action of triphenylphosphinephenylimine with diphenylketen thus: $\text{PPh}_3\text{:NPh} + \text{CPh}_2\text{:C:O} \rightarrow \text{PPh}_3\text{:O} + \text{CPh}_2\text{:C:NPh}$. The same substance can also be obtained from triphenylphosphinediphenylmethylen and phenylcarbimide: $\text{PPh}_3\text{:CPh}_2 + \text{NPh.CO} \rightarrow \text{PPh}_3\text{:O} + \text{CPh}_2\text{:C:NPh}$. The former reaction occurs with greater readiness and smoothness, however, and has now been subjected to an extended examination. Differently substituted ketens, which in other reactions exhibit such unusual diversity, react with about equal ease with phosphineimine derivatives. On the other hand, diphenylketen reacts much more readily with alkylated than with arylated phosphineimines (cf. Staudinger and Hauser, this vol., i, 68). When the act is considered that the replacement of the carbonyl by the C:N·R group usually causes enhanced activity, it is remarkable to find that the ketenimine compounds are highly stable. They do not suffer autoxidation and do not unite with unsaturated compounds. They are generally stable towards water and alcohol, but are hydrolysed by acids to the corresponding acid amides. They react fairly readily with aniline and phenylhydrazine, but much less vigorously than do the ketens. On the other hand, the ease with which the simple ketenimines undergo polymerisation is surprising in such stable substances.

Diphenylketenphenylimine, $\text{CPh}_2\text{:C:NPh}$ (*loc. cit.*), is converted by aniline into diphenylacetodiphenylamidine, m. p. 114° , and by phenylhydrazine into the compound, $\text{CHPh}_2\text{:C}(\text{N:NHPh})\text{:NHPh}$, m. p. 117° . It undergoes autoxidation at 150° , partly in accordance with the scheme: $\text{CPh}_2\text{:C:NPh} + \text{O}_2 \rightarrow \text{COPh}_2 + \text{O:C:NPh}$. Triphenylphosphinemethylimine and diphenylketen give triphenylphosphine oxide and *diphenylketenmethylimine*, $\text{CPh}_2\text{:C:NMe}$, a yellow liquid, b. p. $120^\circ/0.2$ mm., which could not be obtained quite pure. It is a very stable substance which shows little tendency towards polymerisation; it is converted by concentrated hydrochloric acid into *diphenylacetomethylamide*, colourless crystals, m. p. 164.5° . In contrast with diphenylketenaphthenylimine, the methyl compound unites with methyl iodide, but the methiodide has not been examined further. *Dimethylketenphenylimine*, $\text{CMe}_2\text{:C:NPh}$, is a pale yellow liquid, b. p. $98-100^\circ/12$ mm.; it is transformed by concentrated hydrochloric acid into *isobutyranilide*, m. p. 104° . *Ketenphenylimine*, $\text{CH}_2\text{:C:NPh}$, a colourless, mobile liquid, b. p. $35^\circ/0.1$ mm., which solidifies to a colourless, crystalline mass at about -40° , is prepared from triphenylphosphinephenylimine and keten in light petroleum solution at -20° . It readily becomes polymerised to a black, amorphous solid when preserved, but is otherwise surprisingly stable; it does not appear to react with water, alcohol, benzaldehyde, dimethylaminobenzaldehyde, benzylideneaniline, thiobenzophenone, azidocarboxylic ester, or quinoline and carbon disulphide. Concentrated hydrochloric acid transforms it immediately into acetanilide. *Ketenethylimine*, $\text{CH}_2\text{:CH:NEt}$, could not be isolated with certainty by reason of the readiness with which it polymerises even at -20° . *Ethyl phenylimineketendicarboxylate*, $\text{NPh:C:C}(\text{CO}_2\text{Et})_2$, forms colourless crystals, m. p. $80-83^\circ$; it is much more sensitive to moisture than the products described above.

H. W.

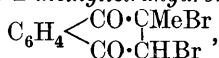
The 2-Methylnaphthalene Series. K. FRIES and W. LOHMANN (*Ber.*, 1921, **54**, [B], 2912—2924).—Previous experiments have shown that 1-methyl- β -naphthol is very readily converted into derivatives of 1:2-dihydronaphthalene under the influence of mild oxidising agents (A., 1906, i, 190). Under similar conditions, 4-chloro-2-methyl- α -naphthol is transformed into 2-methyl-1:4-naphthaquinone.

2-Methyl- α -naphthylamine is prepared conveniently by reducing 1-nitro-2-methylnaphthalene with tin and hydrochloric acid and is converted by chlorine in the presence of glacial acetic and fuming hydrochloric acids into 1-*keto*-2-methyl-2:3:4:4-tetrachlorotetrahydronaphthalene, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO} - \text{CMeCl} \\ | \\ \text{CCl}_2 - \text{CHCl} \end{smallmatrix}$, colourless, prismatic crystals,

m. p. 118° . The latter is attacked but slowly by reducing agents, and does not liberate iodine from potassium iodide. It is converted by stannous chloride in glacial acetic acid solution into 4-chloro-2-methyl- α -naphthol, colourless needles, m. p. 104.5° (*acetate*, needles, m. p. 87°), which is oxidised by an excess of aqueous ferric chloride (less readily by hydrogen peroxide, nitrous or nitric acids)

to 2-methyl-1 : 4-naphthaquinone, long, yellow needles, m. p. 104°; the quinone is prepared more easily by the oxidation of a solution of 2-methyl- α -naphthylamine sulphate in boiling glacial acetic acid with hydrogen peroxide. It is reduced by stannous chloride in the presence of glacial acetic acid to 1 : 4-dihydroxy-2-methylnaphthalene, colourless needles, m. p. (indefinite) 160°, after incipient darkening at about 120° (diacetate, prisms, m. p. 113°). Chlorine converts the quinone or quinol into 2 : 3-dichloro-1 : 4-diketo-2-methyltetrahydronaphthalene, $C_6H_4 \begin{smallmatrix} \diagup CO \cdot CMeCl \\ \diagdown CO \cdot CHCl \end{smallmatrix}$, small, pale yellow

crystals, m. p. 45.5°, which is transformed, slowly by stannous chloride and boiling glacial acetic acid but more rapidly by hot concentrated sulphuric acid, into 3-chloro-2-methyl-1 : 4-naphthaquinone, dark yellow needles, m. p. 153°. It is remarkably stable towards aniline. Reduction with stannous chloride transforms it into 3-chloro-1 : 4-dihydroxy-2-methylnaphthalene, long needles, m. p. (indefinite) 160°, after darkening at 130° (diacetate, slender, colourless needles, m. p. 194°). The action of bromine on 2-methyl-1 : 4-naphthaquinone gives a mixture of 3-bromo-2-methyl-1 : 4-naphthaquinone, yellowish-brown needles, m. p. 151°, and 2 : 3-dibromo-1 : 4-diketo-2-methyltetrahydronaphthalene,



coarse, pale yellow prisms, m. p. 107°. 3-Bromo-1 : 4-dihydroxy-2-methylnaphthalene crystallises in colourless prisms or needles, which darken above 95°, but do not appear to melt (diacetate, colourless needles, m. p. 209°).

If hydrogen peroxide is added cautiously to a solution of 2-methyl- α -naphthylamine sulphate in boiling glacial acetic acid, the separation of 4 : 4'-diamino-3 : 3'-dimethyldinaphthyl sulphate is observed. The free base forms colourless, prismatic crystals, m. p. 213° (diacetyl derivative, m. p. above 300°). The presence of two free amino-groups in the molecule is proved by its conversion into the di-p-nitrobenzylidene compound, $C_{36}H_{26}O_4N_4$, small red crystals.

H. W.

Chromo-isomeric Silver Salts of Pentabromophenol, and a Theory of Chromo-isomerism of Solid Compounds.

HOWARD J. LUCAS and ARCHIE R. KEMP (*J. Amer. Chem. Soc.*, 1921, **43**, 1654—1665).—The silver salt of pentabromophenol exists in two forms, one pink and the other colourless, and in both forms silver is linked to oxygen. The moist pink salt is converted into the more stable, colourless form on heating or in the presence of a small amount of alcohol or of ammonia. If treated with stronger aqueous ammonia, it is converted into a white ammoniate, $C_6Br_5 \cdot O \cdot NH_4 \cdot C_6Br_5 \cdot OAg \cdot 2NH_3 \cdot H_2O$, which changes into a yellow ammoniate, $C_6Br_5 \cdot OAg \cdot 2NH_3$, when warmed with stronger ammonia solutions. The pink salt is more reactive than the white salt. Thus with ethyl iodide it more readily gives the ethyl ether, and it more rapidly absorbs ammonia from an atmosphere containing it.

To explain these facts, a new theory of chromo-isomerism is

proposed, on the basis of which the wave-length of the light absorbed by a substance will change as the electrostatic environment of the absorbing atoms or ions changes, and will be longest when the electrostatic fields are the strongest. This theory offers a satisfactory explanation of the yellow colour of aqueous solutions of the colourless sodium pentabromophenoxide, of the colour of the two forms of the silver salt, and of the yellow colour of the ammoniate of the latter. Absorption of light in these cases is attributed to the isorropesis of the benzene ring, which is undoubtedly a factor in colour production in other benzene derivatives.

The theory offers a satisfactory explanation of the different colours of polymorphic forms of inorganic compounds such as mercuric iodide, thallous iodide, etc. The more symmetrical form is the darker coloured because the electrostatic fields about the atoms are stronger in the more symmetrical forms. W. G.

Production of Picric Acid from the Sulphonic Acids of Phenol. RUTH KING (T., 1921, **119**, 2105—2119).

Preparation of *p*-Methylaminophenol. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Swiss Pat., 88561; from *Chem. Zentr.*, 1921, iv, 803—804).—*p*-Arylsulphonamidophenyl esters of the formula $\text{Acyl}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{SO}_2\cdot\text{Aryl}$ are methylated on the *N*-hydrogen atom and the monomethyl derivatives thus obtained are hydrolysed to form *p*-methylaminophenol by the usual methods. By treatment of 4-toluenesulphonamidophenyl toluenesulphonate, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, with sodium hydroxide solutions, the sodium salt is obtained as leaf-like, white crystals. This is heated with methyl alcohol and methyl chloride under pressure for a few hours at 100—120°, whereby 4-toluenesulphonmethylamidophenyl toluenesulphonate is obtained; it forms needles, m. p. 162°. This is heated with 70% sulphuric acid, and by cautious addition of water to the brown product a clear solution is obtained, which is heated with dilute sodium carbonate solution, *p*-methylaminophenol is extracted from the weak alkaline solution with ether.

G. W. R.

Metallic Derivatives of Nitrophenolic Compounds. II. Some Nitrotolyloxides of Metals of Group II. DOROTHY GODDARD and ARCHIBALD EDWIN GODDARD (T., 1921, **119**, 2044—2048).

Thymol from Nitrocymene. R. M. COLE (U.S. Pat., 1378939).—Thymol is prepared by electrolytic reduction of nitrocymene and diazotisation and reduction of the resulting 2-amino-5-hydroxy-1-methyl-4-isopropylbenzene. CHEMICAL ABSTRACTS.

Preparation of Thymol, Menthone, and Menthol from Eucalyptus Oils. HENRY G. SMITH and A. R. PENFOLD (*J. Roy. Soc. New South Wales*, 1920, **54**, 40—47; cf. T., 1921, **119**, 779).—Piperitone, a natural constituent of certain eucalyptus oils (*loc. cit.*), when oxidised with ferric chloride and acetic acid, gives a 25% yield of thymol. When reduced by hydrogen in the presence

of nickel at 175—180°, piperitone gives an almost quantitative yield of menthone, which on further treatment with sodium in aqueous ether gives menthol.

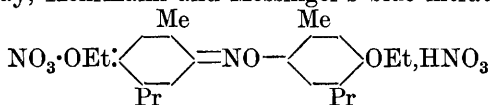
W. G.

Oxonium Salts from Phenol Ethers and Phenols. I. Nitrosophenol Dyes. IV. F. KEHRMANN, H. DECKER, and B. SOLONINA (*Ber.*, 1921, **54**, [B], 2427—2435).—With reference to Decker and Solonina's quinonoid oxonium formula for Kehrman and Messinger's colour salt from thymol ethyl ether (*A.*, 1902, i, 767), Meyer and Billroth (*A.*, 1920, i, 37) state that the compound was not purified by crystallisation, and that the constitution of the diphenylamine derivative obtained by reduction was not definitely proved. These assertions are controverted by the authors, who apply the oxonium theory to explain the constitution of other similar compounds.

T. H. P.

Oxonium Salts from Phenol Ethers and Phenols. II. Decomposition of Oxonium Salts from Thymol Ethyl Ether and from Anisole by Water or Substances of Alkaline Reaction. F. KEHRMANN, H. DECKER, and CH. SCHMAJEWSKI (*Ber.*, 1921, **54**, [B], 2435—2440).—The authors have investigated further the red compounds obtained from oxonium salts by the action of basic compounds or water (Decker and Solonina, *A.*, 1902, i, 767).

In this way, Kehrman and Messinger's blue nitrate,



(cf. Meyer and Billroth, *A.*, 1920, i, 37), yields a mixture, from which the following two compounds have been isolated: (1) Thymoinodiphenol ethyl ether (Decker and Solonina, *loc. cit.*), and (2) a small proportion of a compound, crystallising in pale orange-yellow needles, m. p. 125—126°, and of unknown constitution; the expected diethyl ether of dithymylnitric oxide was not detected.

When dianisylnitric oxide is prepared by the action of pyridine on the perchlorate of the blue compound formed by nitration of anisole (Meyer and Billroth, *loc. cit.*), it is accompanied by *indophenol oxide monomethyl ether*, $\text{O} : \begin{array}{c} \diagup \quad \diagdown \\ \text{C} = \text{C} \\ \diagdown \quad \diagup \end{array} = \text{NO} - \begin{array}{c} \diagup \quad \diagdown \\ \text{C} = \text{C} \\ \diagdown \quad \diagup \end{array} \text{OMe}$, which crystallises in lustrous, pale orange-yellow needles, m. p. 125—126°, forms a violet solution in concentrated sulphuric acid, and is reduced by stannous chloride to *p*-hydroxy-*p'*-methoxydiphenylamine. By ferric chloride, the latter is oxidised to *indophenol monomethyl ether*, which crystallises in lustrous, yellowish-red, unstable crystals, and may be prepared from the potassium derivative of indophenol, by way of the corresponding silver compound.

T. H. P.

Studies in the Dihydronaphthalene Series. II. The *ar*-Dihydro-*a*-naphthols and their Derivatives. FREDERICK MAURICE ROWE and ESTHER LEVIN (*T.*, 1921, **119**, 2021—2029).

Nitro-Derivatives of Quinol. F. KEHRMANN, M. SANDOZ, and R. MONNIER (*Helv. Chim. Acta*, 1921, **4**, 941—948).—The observation that quinol monobenzoate is nitrated when dissolved in amyl nitrite led to this investigation of the quinol benzoates. The nitration of quinol monobenzoate, m. p. 163—164°, in acetic acid solution with one molecular proportion of nitric acid yields 2-nitro-quinol 4-monobenzoate, golden-yellow needles, m. p. 95—96°, identical with that obtained by the action of amyl nitrite. Hydrolysis converts it into *o*-nitroquinol, m. p. 133—134° (Elbs, A., 1893, i, 640), and benzylation yields *o*-nitroquinol dibenzoate, white, silky needles, m. p. 139—140°. Further nitration yields 2:6-dinitro-quinol 4-benzoate, citron-yellow needles, m. p. 150—151°, which on hydrolysis is converted into 2:6-dinitroquinol, long, yellow needles containing water of crystallisation, m. p. 134—135° (Nietzki, A., 1883, 465); 2:6-dinitroquinol 4-nitrobenzoate, straw-yellow needles, m. p. 161—162°; *o*-nitroquinol dinitrobenzoate, small, white crystals, m. p. 214—215°.

The nitration of quinol dibenzoate, m. p. 180—181°, yields 2:6-dinitroquinol dinitrobenzoate, yellow needles, m. p. 158—159°. It is interesting to note that two nitro-groups enter the quinol nucleus in this case, whereas a second nitro-group cannot be introduced into the quinol nucleus by the nitration of 2-nitroquinol dibenzoate. The nitration of quinol dibenzoate never results in the formation of a mononitro-derivative, which is in agreement with Nietzki's observations (*loc. cit.*) with quinol diacetate. F. M. R.

Nuclear Condensations of Ethers of Phenylmercaptan. I.

A. BISTRZYCKI and FRANZ KUBA (*Helv. Chim. Acta*, 1921, **4**, 969—981).—*p*-Methylthioltriphenylacetic acid, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, colourless needles or microscopic prisms, m. p. 208—210° after softening at 204°, is prepared in almost quantitative yield by the gradual addition of anhydrous stannic chloride to a gently boiling solution of benzilic acid and anisyl mercaptan in benzene. The silver salt and methyl ester, colourless prisms, m. p. 141—142·5°, are described. Attempts to demethylate the acid by hydriodic acid or aluminium chloride alone or in the presence of benzene or carbon disulphide did not lead to the desired result. The acid is converted by sulphuric acid (95%) at the atmospheric temperature into *p*-methylthioltriphenylcarbinol, $\text{SMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{OH}$, pale yellow prisms, m. p. 65—68° after slight previous softening, which is reduced by zinc dust in glacial acetic acid solution to *p*-methylthioltriphenylmethane, colourless needles, m. p. 68—69°. The carbinol is converted by hydrogen chloride in ethereal solution into *p*-methylthioltriphenylchloromethane, rhombic platelets, m. p. 88·5—89·5°, which undergoes a complicated decomposition when heated. The acid is converted by nascent bromine into *p*-methylsulphoxidetriphenylacetic acid, $\text{SOMe} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, colourless, microscopic prisms, decomp. 130° (after four years the decomp. temperature had risen to 219—220°; the reason for this is unknown), and by potassium permanganate into *p*-methylsulphonetriphenylacetic acid, $\text{SO}_2\text{Me} \cdot \text{C}_6\text{H}_4 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, microscopic prisms, decomp. 140°. The

latter is transformed by concentrated sulphuric acid into *p*-methylsulphonetriphenylcarbinol, which appears to exist in two forms, m. p. 178—179° and 132° respectively; the former is produced when the latter is preserved, whilst the reverse change can occasionally be induced by crystallisation from a mixture of acetone and water.

Diphenyl- α -methylthiolnaphthylacetic acid, $\text{SMe} \cdot \text{C}_{10}\text{H}_6 \cdot \text{CPh}_2 \cdot \text{CO}_2\text{H}$, rhombic leaflets, m. p. about 204° (decomp.) after previous darkening and softening, is prepared from benzilic acid and α -naphthyl methyl sulphide. (The sodium salt, needles, and methyl ester, colourless needles, m. p. 185—186°, are described.) It does not appear to be converted into the corresponding carbinol by treatment with sulphuric acid, although evolution of carbon dioxide occurs. When heated at 200—225°, it passes into *diphenyl- α -methylthiolnaphthylmethane*, $\text{CHPh}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{SMe}$, prisms, m. p. 157—158°.

Diphenyl sulphide can be condensed with benzilic acid, but the product has not been obtained in the crystalline condition.

The condensation of diphenyleneglycollic acid and anisyl mercaptan in boiling benzene solution in the presence of stannic chloride leads to the production of 9-*p*-methylthiolphenylfluorene, $\text{C}_6\text{H}_4 > \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{SMe}$, long needles, m. p. 126—128°. 9-*p*-Methyl-

thiolphenylfluorene-9-carboxylic acid, $\text{C}_6\text{H}_4 > \text{C} < \begin{matrix} \text{C}_6\text{H}_4 \cdot \text{SMe} \\ \text{CO}_2\text{H} \end{matrix}$, large,

almost colourless leaflets, m. p. about 170° (decomp.), can, however, be obtained when diphenyleneglycollic acid and thioanisole react in glacial acetic acid solution in the presence of concentrated sulphuric acid at a temperature not exceeding 40—45°. Under the latter conditions, benzilic acid can be condensed with thiophenol, but investigation of the product is not complete. H. W.

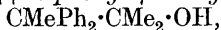
Derivatives of Cinnamyl Alcohol and Phenylallyl Alcohol.

α -Phenylglycerol. CHARLES MOUREU and PATRICK GALLAGHER (*Bull. Soc. chim.*, 1921, [iv], **29**, 1009—1017).—Phenylallyl alcohol or cinnamyl alcohol, when acted on by phosphorus tribromide or hydrogen bromide, gives in all cases the compound $\text{C}_6\text{H}_5 \cdot \text{C}_3\text{H}_4\text{Br}$, which has, in all probability, the constitution $\text{CHPh} \cdot \text{CH} \cdot \text{CH}_2\text{Br}$ (cf. Klages and Klenk, A., 1906, i, 638). This monobromo-derivative on bromination gives $\alpha\beta\gamma$ -tribromo- α -phenylpropane, which, when heated with silver acetate and acetic acid at 120—125° for thirty-five hours, gives *phenylglyceryl triacetate*, b. p. 175°/5—6 mm.; d_4^{20} 1.1871; n_D^{20} 1.4972. This triacetate, when boiled with dilute hydrochloric acid, yields *α -phenylglycerol*, b. p. 181°/4 mm.; d_4^{35} 1.2213; n_D^{35} 1.5605; n_D^{15} 1.5600; $n_D^{18.5}$ 1.5593. W. G.

The Molecular Transposition accompanying the Dehydration of $\alpha\alpha$ -Diphenyl- $\beta\beta$ -dimethylpropan- α -ol. (MME) RAMART (*Compt. rend.*, 1921, **173**, 1182—1184).—It has previously been shown that, when $\alpha\alpha$ -diphenyl- $\beta\beta$ -dimethylpropan- α -ol is dehydrated by means of a mixture of acetic anhydride and acetyl

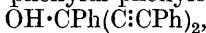
chloride, a hydrocarbon and a chloro-compound, $C_{17}H_{19}Cl$, m. p. 109—110°, are obtained (cf. A., 1913, i, 1325). This chloro-compound yields with silver acetate a *hydrocarbon*, $C_{17}H_{18}$, and its constitution is now established as being $CH_3 \cdot CPh_2 \cdot CMe_2Cl$.

$\alpha\alpha$ -Diphenylpropaldehyde reacts with magnesium ethyl bromide to give $\beta\beta$ -*diphenylpentan- γ -ol*, b. p. 210—212°/40 mm., which by the action of thionyl chloride is converted into γ -*chloro- $\beta\beta$ -diphenylpentane*. Ethyl $\alpha\alpha$ -diphenylpropionate reacts with magnesium methyl iodide to give $\beta\beta$ -*diphenyl- γ -methylbutan- γ -ol*,

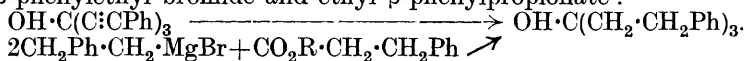


b. p. 186—187°/14 mm., which with thionyl chloride yields γ -*chloro- $\beta\beta$ -diphenyl- γ -methylbutane*, m. p. 108—109°, identical with the chloro-compound mentioned above. W. G.

Triphenylethynylcarbinol and its Analogues. KURT HESS and WILHELM WELTZIEN (*Ber.*, 1921, 54, [B], 2511—2521).—The authors have prepared and investigated triphenylethynylcarbinol, $OH \cdot C(C: CPh)_3$, phenyldi-phenylethynylcarbinol,



and diphenylphenylethynylcarbinol, $OH \cdot CPh_2 \cdot C: CPh$, in order to ascertain if, as regards halochromy, these compounds resemble the carbinols including radicles of the triphenylmethyl type containing so-called tervalent carbon. The third of the above compounds is Nef's benzophenonephenylacetylene (A., 1900, i, 21) obtained by the action of sodium phenylacetylde on benzophenone, and the authors have prepared all three compounds by this method which gives, however, poor yields. Better results were obtained by the use of magnesium phenylethynyl bromide. That the reactions really proceed in the direction supposed and that, for instance (Kohler and Reimer, A., 1905, i, 347), in the action of magnesium phenylethylene bromide on phenylpropionic chloride the acetylene linking of the phenylpropionic acid does not participate, is shown by the fact that the action of hydrogen and platinum black in alcoholic solution converts the triphenylethynylcarbinol into a compound obtainable also from magnesium β -phenylethyl bromide and ethyl β -phenylpropionate:



The action of magnesium phenylethynyl bromide on distyryl ketone yields a *compound*, $C_{25}H_{20}O$, which forms a yellow syrup solidifying to a deep brown, vitreous mass, gives a red solution with concentrated sulphuric acid, and has probably the constitution $CPh: C \cdot C(OH)(CH: CPh)_2$, although here also combination of phenylacetylene at an ethylene gap of the ketone is not excluded.

The three carbinols exhibit typical halochromy, and give respectively: (1) with concentrated sulphuric acid, bluish-violet, magenta, and orange-red solutions, (2) with perchloric acid, deep bluish-violet, Bordeaux, and orange-red precipitates, and (3) with stannic chloride, bright blue, Bordeaux, and reddish-violet precipitates. The colorations and precipitates are, however, so sensitive that no double compounds have yet been isolated. With

phenylacetylene or toluene, no sign of halochromy is revealed by the above reagents. The conclusion is drawn that the triphenylmethane configuration with its typical effects on the carbinol need not be attributed to the aromatic character of the benzene nucleus, since halochromy is observed when the benzene nuclei are replaced by "gap-linkings." Owing to the instability of these acetylene compounds, it was not found possible to replace the hydroxyl of the carbinols by halogens, so that the question of radical-dissociation remains open.

Oxalyl chloride and magnesium phenylethynyl bromide react, giving a compound agreeing in composition with the formula $\text{OH}\cdot\text{C}(\text{C}:\text{CPh})_2\cdot\text{C}(\text{C}:\text{CPh})_2\cdot\text{OH}$, and an attempt is to be made to obtain by pinacolone rearrangement a compound which, with magnesium phenylethynyl bromide, will yield an ethane derivative which contains only one hydroxyl group and may be examined for dissociation.

For the purpose of testing Gomberg's quinocarbonium theory, Schlenk and Ochs (A., 1915, i, 579) prepared tri-2-thionylcarbinol and regarded the halochromy of this compound as explainable by quinonoid rearrangement (cf. Pfeiffer and Böttler, A., 1919, i, 62). For triphenylethynylcarbinol, however, quinonoid rearrangement is excluded, unless a highly improbable allenic structure is assumed.

Tri-phenylethynyl-carbinol, $\text{C}_{25}\text{H}_{16}\text{O}$, prepared from magnesium phenylethynyl bromide and phenylpropionic chloride, crystallises in long, colourless needles, softening at 122° , m. p. $126\text{--}128^\circ$ (browning).

Phenylidiphenylethynylcarbinol, $\text{C}_{23}\text{H}_{16}\text{O}$, prepared from magnesium phenylethynyl bromide, ethyl bromide, magnesium, and phenylacetylene, forms a yellow oil.

Tri- β -phenylethylcarbinol, $\text{OH}\cdot\text{C}(\text{CH}_2\cdot\text{CH}_2\text{Ph})_3$, crystallises in bundles of long, colourless needles, softening at 66° , m. p. $68\text{--}69^\circ$.

The compound $\text{C}_{34}\text{H}_{22}\text{O}_2$ (see above), obtained from magnesium phenylethynyl bromide and oxalyl chloride, forms pale yellow crystals, softening at 128° , m. p. $130\text{--}131^\circ$ (decomp.). T. H. P.

Action of Nitrogen Iodide and of Cyanogen Iodide on Benzamidine. PAUL ROBIN (*Compt. rend.*, 1921, **173**, 1085—1086).—Nitrogen iodide readily reacts with benzamidine to give iodobenzamidine (A., 1920, i, 568), but cyanogen iodide gives a very unstable, additive compound, $\text{C}_7\text{H}_8\text{N}_2\cdot\text{CNI}$, m. p. 72° (decomp.). W. G.

Electrolytic Reduction of some Carboxylic Acids. HARUSHIGE INOUE (*J. Chem. Ind. Japan*, 1921, **24**, 906—918).—By the electrolytic reduction of (a) phenylacetic acid, (b) cinnamic acid, and (c) benzoic acid, the following substances were isolated in each case: (a) Phenylethyl alcohol and *r*- $\beta\gamma$ -dihydroxy- $\alpha\delta$ -diphenylbutane, m. p. 114.5° . (b) γ -Phenylpropyl alcohol and *r*- $\gamma\delta$ -dihydroxy- $\alpha\zeta$ -diphenylhexane. (c) Benzyl alcohol. $\beta\gamma$ -Dihydroxy- α -phenyl- γ -methylbutane, m. p. 145° , was prepared by the same reducing method (cf. *J. Soc. Chem. Ind.*, 1922, Jan.). K. K.

The Electrochemical Oxidation of Aromatic Nitriles.

FR. FICHTER and GUSTAV GRISARD (*Helv. Chim. Acta*, 1921, 4, 928—941).—The behaviour of benzonitrile, the three toluonitriles, phenylacetoneitrile, and allied substances has been examined.

Benzonitrile is extensively degraded by electrochemical oxidation, in addition, hydroxylation of the nucleus takes place with the formation of catechol and 2:5-dihydroxybenzonitrile, colourless needles, m. p. 151°.

p-Toluenitrile is electrochemically oxidised at lead peroxide anodes with exceptional smoothness to *p*-cyanobenzoic acid; in the most favourable circumstances, the total yield of this substance and terephthalic acid amounts to 44.6%. *p*-Toluic acid, when dissolved in a mixture of acetone and sulphuric acid, is converted at a lead peroxide anode into terephthalic acid, the yield being 14%. In warm solution and with an excess of current, *p*-xylene is oxidised at a lead peroxide anode mainly to *p*-tolualdehyde, small quantities of *p*-toluic acid being also formed. From these results it is apparent that the electrochemical oxidation of the methyl to the carboxyl group is greatly facilitated by the presence of the cyano-radicle.

In a well-cooled solution, *o*-toluenitrile is converted at a lead peroxide anode into *o*-cyanobenzoic acid, the yield being 6.25%; in addition, very considerable degradation occurs. If the cooling is not efficient the nitrile becomes hydrolysed to *o*-toluic acid, which becomes oxidised to *o*-phthalic acid. *o*-Toluic acid is very extensively degraded in acetone-sulphuric acid solution at lead peroxide anodes; phthalic acid is formed to the extent of 5%.

m-Cyanobenzoic acid is produced in 28% yield from *m*-toluenitrile dissolved in a mixture of acetone and sulphuric acid at lead peroxide anodes; the formation of dark, resinous products is more marked in this case than with the other isomerides.

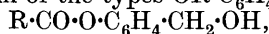
Under all conditions of electrochemical oxidation, phenylacetoneitrile is attacked and suffers fission at the methylene group; the sole products are benzaldehyde and benzoic acid, which are also produced from phenylacetic acid. H. W.

Nitration, Chlorination, and Bromination of *m*-Hydroxybenzoic Acid. P. H. BEYER (*Rec. trav. chim.*, 1921, 40, 621—631).—On nitration *m*-hydroxybenzoic acid yields the 2-nitro-, 4-nitro-, and 6-nitro-derivatives together with a small quantity of a dinitro-acid (cf. Griess, A., 1887, 485). Chlorination yields the 2-chloro- and 6-chloro-acids (cf. Zincke and Walbaum, A., 1891, i, 708, and Mazzara, A., 1900, i, 596). Bromination, in acetic acid solution, yields the 4-bromo-derivative only (cf. Coppadoro, A., 1903, i, 257). For purposes of comparison with acids which other workers had stated to be obtainable by the methods used, but which were not so obtained, the following were prepared: 5-nitro-*m*-hydroxybenzoic acid, pale yellow crystals, m. p. 194—195°, was obtained by hydrolysis of the methyl ester prepared as described by Cohen and McCandlish from methyl 3:5-dinitrobenzoate (T.,

1905, **87**, 1266). Griess's 5-nitro-acid (A., 1887, 485) is in reality 6-nitro-*m*-hydroxybenzoic acid; 4-chloro-*m*-hydroxybenzoic acid, m. p. 219·5—220·5°, was obtained from 4-nitro-*m*-hydroxybenzoic acid by reduction, diazotisation, etc.; and 6-bromo-*m*-hydroxybenzoic acid, m. p. 185° (decomp.), was prepared similarly from 6-nitro-*m*-hydroxybenzoic acid.

H. J. E.

Some Derivatives of Saligenin. MERRILL C. HART and ARTHUR D. HIRSCHFELDER (*J. Amer. Chem. Soc.*, 1921, **43**, 1688—1693).—With a view to study their pharmacological properties derivatives of saligenin of the types $\text{OR}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{OH}$,



and $\text{R}\cdot\text{CO}\cdot\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{O}\cdot\text{COR}$ were prepared. The ethers were prepared by heating potassium saligenate with the alkyl or aryl haloid on a water-bath under a reflux condenser. In this way, the authors obtained the ethyl ether, b. p. 264° (cf. Bötsch, A., 1882, 174), the *propyl* ether, b. p. 155—157°/24 mm.; the *n-butyl* ether, b. p. 160—162°/25 mm.; the *isoamyl* ether, b. p. 176°/27 mm., and the *benzyl* ether, b. p. 221—222°/25 mm., m. p. 37°.

The mono-esters were prepared by the action of acid chlorides or anhydrides on potassium saligenate in ether or alcoholic solutions. The *monoacetate* has b. p. 167—168°/29 mm.; the *monobenzoate* was a colourless oil; the *dibenzoate* obtained by benzylation in pyridine solution had m. p. 51°.

Potassium saligenate is best obtained by the action of alcoholic potassium hydroxide on saligenin in acetone solution. A good yield of 5-bromo-2-hydroxybenzyl alcohol was obtained by the method of Auwers and Büttner (A., 1899, i, 36). For the preparation of 5-iodo-2-hydroxybenzyl alcohol, Seidel's method (cf. A., 1899, i, 597) is not satisfactory. A good yield is obtained by treating saligenin in aqueous solution with a solution of iodine in aqueous potassium iodide.

W. G.

Complex Metallic Ammines. VI. *cis*-Phthalato-, *cis*-Homophthalato-, and other Diethylenediaminecobaltic Salts. JAMES COOPER DUFF (T., 1921, **119**, 1982—1988).

The Optically Active Forms of the Keto-dilactone of Benzophenone-2 : 4 : 2' : 4'-tetracarboxylic Acid. WILLIAM HOBSON MILLS and CHARLES REYNOLDS NODDER (T., 1921, **119**, 2094—2104).

Preparation of Vanillin from Acetylisoegenol. W. C. SIEVERS and L. GIVAUDAN AND CO. (Swiss Pat., 89053; from *Chem. Zentr.*, 1921, iv, 911).—Acetylisoegenol is oxidised in the presence of aromatic aminocarboxylic acids. For example, acetylisoegenol, as such, or dissolved in an appropriate solvent, is added to an aqueous solution of sodium dichromate. The mixture is mechanically shaken at 80° while a solution of *p*-aminobenzoic acid in 50% sulphuric acid is added. *Acetylvanillin* is extracted from the

products of reaction. The bisulphite compound is obtained and treated successively with acid and sodium hydroxide. G. W. R.

The Preparation of Aldehydes from Acid Chlorides. IV. Dialdehydes. I. KARL W. ROSENMUND, FRITZ ZETZSCHE, and CHR. FLÜTSCH (*Ber.*, 1921, **54**, [B], 2888—2893).—An examination of the possibility of preparing di- and poly-aldehydes by the catalytic reduction of the corresponding acid chlorides (cf. A., 1918, i, 300; 1921, ii, 320).

The action is carried out by means of hydrogen in the presence of palladised kieselguhr in hot xylene solution, "sulphured" quinoline being used as regulator. Suberyl, isophthalyl, and terephthalyl chlorides are thus converted into the corresponding dialdehydes in 75—85% yield. *s-o*-Phthalyl chloride, on the other hand, gives mainly phthalide under these conditions; presumably the symmetrical is transformed into the unsymmetrical acid chloride by the palladium chloride formed during the reaction in the same manner as by aluminium chloride.

The following substances are described. Suberdialdehyde (disemicarbazone, m. p. 183—185°, dioxime, m. p. 152°; *diphenylhydrazone*, colourless needles, m. p. 84—86°); *isophthaldialdehyde*, m. p. 88—89°; *terephthaldialdehyde*, m. p. 116°; *terephthalylidinedi- α -naphthylamine*, $C_{28}H_{20}N_2$, yellow crystals, m. p. 223—225° after softening at 210°; *terephthaldialdehydedi-p-nitrophenylhydrazone*, crystalline powder, m. p. 281° (decomp.) after softening at 272°; *terephthaldialdehydediphenylhydrazone*, yellow leaflets, m. p. 278° (decomp.) after softening at 265°.

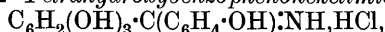
Terephthalyl chloride is converted by aniline in xylene solution into the *dianilide*, long, colourless needles, m. p. 334—337°, by α -naphthylamine into the *di- α -naphthalide*, needles, m. p. 334—335° (slight decomp.) after softening at 325°, and by diphenylamine into the *bisdiphenylamide*, colourless needles, m. p. 272—273° (decomp.) after softening at 268°. H. W.

The supposed True Dibenzoylmethane of Wislicenus; New Experiments. CHARLES DUFRAISSE and PIERRE GÉRALD (*Compt. rend.*, 1921, **173**, 985—987).—It has been shown previously (A., 1921, i, 114) that the compound obtained by Wislicenus by the saponification of phenyl bromostyryl ketone with alcoholic sodium hydroxide is not dibenzoylmethane, $CH_2(COPh)_2$, and evidence is now produced to show that the compound is really α -benzoyl- β -ethoxy- β -phenylethylene, $COPh\cdot CH\cdot CPh\cdot OEt$.

Benzoylphenylacetylene readily condenses with ethyl alcohol (cf. Moureu and Brachin, A., 1904, i, 811) to give a compound which is identical with Wislicenus's compound. Wislicenus's reaction really takes place in two stages. In the first stage, a molecule of ethyl alcohol is added at the double linking, giving α -bromo- α -benzoyl- β -ethoxy- β -phenylethane, $COPh\cdot CHBr\cdot CPh\cdot OEt$, m. p. 60—61°; b. p. 182—183°/3—4 mm., which then loses a molecule of hydrogen bromide, giving Wislicenus's compound.

W. G.

Hydroxycarbonyl Compounds. 2:4:6:2'-Tetrahydroxybenzophenone. P. KARRER (*Helv. Chim. Acta*, 1921, 4, 992—993).—2:4:6:2'-*Tetrahydroxybenzophenoneketimide hydrochloride*,



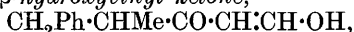
colourless needles, separates gradually when a solution of salicylonitrile and phloroglucinol in anhydrous ether is saturated with hydrogen chloride in the presence of anhydrous zinc chloride and preserved at the atmospheric temperature during several days; it is a relatively stable substance which may be crystallised from fuming hydrochloric acid. It is hydrolysed by hot water to 2:4:6:2'-*tetrahydroxybenzophenone*, $\text{C}_6\text{H}_2(\text{OH})_3\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, yellow leaflets which gradually decompose and blacken when heated; the latter has marked anti-diarrhœic action. H. W.

The Products of the Reduction of Hydroxymethyleneacetophenone [Phenyl β -Hydroxyvinyl Ketone] and of α -Hydroxymethylene- α -benzylacetone [β -Phenyl- α -hydroxymethylene-ethyl Methyl Ketone]. HANS RUPE and HANS MÜLLER (*Helv. Chim. Acta*, 1921, 4, 841—860).—The successful reduction of hydroxymethylenecamphor to camphylcarbinol by hydrogen in the presence of nickel has led the authors to investigate the behaviour of phenyl β -hydroxyvinyl ketone and β -phenyl- α -hydroxymethylene-ethyl methyl ketone under similar conditions; the reactions in these cases are found to follow a complex course.

Phenyl β -hydroxyvinyl ketone, $\text{COPh}\cdot\text{CH}:\text{CH}\cdot\text{OH}$, is not smoothly reduced by hydrogen in the presence of nickel in aqueous-alcoholic solution. Its reduction by aluminium amalgam in moist ethereal solution, and the action of nickel and hydrogen, sodium amalgam, and zinc dust and ammonium chloride respectively on its sodio-compound, are described fully. Apart from the formation of very considerable amounts of resinous by-products, hydrogenation proceeds in such a manner that the double bond and the ketonic group are affected simultaneously, giving the corresponding glycol, which passes by loss of water into the unsaturated secondary alcohol, thus: $\text{COPh}\cdot\text{CH}:\text{CH}\cdot\text{OH} + 2\text{H}_2 = \text{OH}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH} \xrightarrow{-\text{H}_2\text{O}} \text{OH}\cdot\text{CHPh}\cdot\text{CH}:\text{CH}_2$. $\alpha\gamma$ -*Dihydroxy- α -phenylpropane* is a colourless, odourless liquid, b. p. 175°/11 mm. (slight decomp.). It is smoothly transformed by benzoyl chloride in the presence of pyridine into the corresponding *dibenzoate*, colourless needles, m. p. 51°, which loses benzoic acid when heated and passes into *cinnamyl benzoate*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OBz}$, a highly refractive liquid, b. p. 209°/13 mm. α -*Phenylallyl alcohol*, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}:\text{CH}_2$, is a colourless liquid, b. p. 92°/11 mm., 214°/760 mm., the constitution of which is proved by its conversion, by means of ozone, into mandelic acid. The corresponding *benzoate*, a colourless, mobile liquid, has b. p. 182°/12 mm.

The reduction of styryl methyl ketone to β -phenylethyl methyl ketone, b. p. 112—113°/12 mm., is effected with unusual ease and in 98—100% yield by means of hydrogen and nickel. The condensation of the saturated ketone with ethyl formate in the presence of sodium, sodamide, or sodium ethoxide is described

fully, the latter agent being preferentially used, since it leads to the production of the α -compound (yield 80%) and γ -compound (yield 10—15%) which are separated by taking advantage of the solubility of the copper salt of the latter in cold benzene in which the copper compound of the former does not dissolve. β -Phenyl- α -hydroxymethylene-ethyl methyl ketone, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{CH}\cdot\text{OH})\cdot\text{COMe}$, is an extremely unstable substance characterised by the readiness with which it passes into β -acetylundene (see later) when heated or, more particularly, when treated with a trace of acid; the corresponding *sodium* salt, a pale yellow, amorphous powder, *copper* salt, steel-blue leaflets, m. p. 184° , and amorphous *nickel* salt are described. The sodium salt is readily converted in aqueous solution by the addition of the hydrochloride of the requisite base into the *anilide*, $\text{CH}_2\text{Ph}\cdot\text{CAc}\cdot\text{CH}\cdot\text{NHPh}$, lemon-yellow needles, m. p. 130 — 134° (indefinite), and *p-toluidide*, pale yellow needles, m. p. 103° . The corresponding *amide* crystallises in long, almost colourless needles, m. p. 95° . The *benzoate*, triclinic crystals, m. p. 73° , is most conveniently prepared from benzoyl chloride and the copper salt in well-cooled pyridine solution. By reason of its instability, the reduction of β -phenyl- α -hydroxymethylene-ethyl methyl ketone appears to be impossible, but the benzoate is readily hydrogenated in accordance with the scheme: $\text{CH}_2\text{Ph}\cdot\text{CAc}\cdot\text{CH}\cdot\text{OBz} + \text{H}_2 \rightarrow \text{CH}_2\text{Ph}\cdot\text{CHAc}\cdot\text{CH}_2\cdot\text{OBz} \rightarrow \text{CH}_2\text{Ph}\cdot\text{CAc}\cdot\text{CH}_2 + \text{Ph}\cdot\text{CO}_2\text{H} \xrightarrow{+\text{H}_2} \text{CH}_2\text{Ph}\cdot\text{CHMe}\cdot\text{COMe}$. α -Phenylisopropylethyl methyl ketone, b. p. 118 — $120^\circ/14$ mm., gives a *semicarbazone*, colourless needles, m. p. 112° ; it is converted by ethyl formate and sodium ethoxide into α -phenylisopropyl β -hydroxyvinyl ketone,



slender, colourless needles, m. p. 62° (the *sodium*, *nickel*, and *copper* salts are described).

β -Acetylundene, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH} \end{smallmatrix}\rangle\text{CAc}$, asbestos-like needles, m. p. 122° (*phenylhydrazone*, colourless needles, m. p. 225°) is most conveniently prepared from β -phenyl- α -hydroxymethylene-ethyl methyl ketone by the action of hydrochloric or formic acid. It is converted by concentrated nitric acid or ozone into phthalic acid; the isolation of an intermediate compound could not be effected.

β -Phenylethyl β -hydroxyvinyl ketone, $\text{CH}_2\text{Ph}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}\cdot\text{CH}\cdot\text{OH}$ (see above), crystallises in colourless needles, m. p. 99° , b. p. 139 — $140^\circ/12$ mm. It is moderately stable when pure and dry, but is rapidly and quantitatively decomposed by traces of mineral acids into formic acid and β -phenylethyl methyl ketone. The *sodium* and *copper* salts and the *benzoate*, colourless needles, m. p. 99 — 100° , are described.

H. W.

Additive Reactions of the Carbonyl Group involving the Increase in Valency of a Single Atom. JAMES B. CONANT (*J. Amer. Chem. Soc.*, 1921, **43**, 1705—1714, 2125; cf. preceding abstracts).—The additive reactions of the phosphorus haloids with carbonyl compounds are of a different type from the reactions of

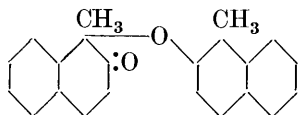
most reagents with these compounds in that they involve the formation of a cyclic compound and the increase in valency of a single phosphorus atom. The reaction is reversible and is analogous to reactions such as the addition of halogen acids to ammonia. The author has applied Lewis's theory of the cubical atom (cf. A., 1916, ii, 310) to this problem. He considers that the positive nucleus of the carbon atom of the carbonyl group is exposed by the drawing away of the electrons of the double bond, and that the exposed nucleus behaves, in additive reactions, like a positively charged atom and unites with atoms having unshared electrons. Such an atom is the phosphorus atom in phosphorus trichloride and the nitrogen atom in ammonia. The resulting additive compounds may undergo various irreversible intramolecular changes or react irreversibly with other reagents giving stable products.

Phosphorus tribromide combines with phenyl styryl ketone in the 1:4-position, the reaction being parallel to that with the trichloride and the equilibrium has been determined in each case. It is more in favour of the additive product in the case of the tribromide than with the trichloride.

W. G.

1:2-Naphthaquinols. K. FRIES (*Ber.*, 1921, **54**, [B], 2925—2930).—The compound described by Fries and Hübner (A., 1906, i, 190) as 1:2-naphthamethylenequinone, $C_6H_4 \begin{smallmatrix} C(CH_2) \cdot CO \\ CH=CH \end{smallmatrix}$,

has been shown by Pummerer and Cherbuliez (A., 1915, i, 418; 1919, i, 440) to have the constitution indicated by the annexed formula and to be dissociable in solution into 1:2-naphthamethylenequinone and 1-methyl- β -naphthol.



They have therefore considered that the dehydro-compound obtained from 6-bromo-1-methyl- β -naphthol (Fries and Hübner, *loc. cit.*) must yield 6-bromo-1-methyl- β -naphthyl acetate (in addition to the compound, $C_{13}H_{10}O_2ClBr$, previously isolated) when acted on by acetyl chloride; this is now shown to be the case.

It is also shown that the constitution, $C_6H_3Br \begin{smallmatrix} C(CH_2Cl) \cdot C \cdot OAc \\ CH=CH \end{smallmatrix}$, assigned previously to the compound $C_{13}H_{10}O_2ClBr$, is incorrect, since it is hydrolysed to 4-chloro-6-bromo-1-methyl- β -naphthol, needles, m. p. 179°, and hence must be 4-chloro-6-bromo-1-methyl- β -naphthyl acetate. The course of the reaction is explained by the fission of dehydro-6-bromo-1-methyl- β -naphthol into the quinol chloride, $C_6H_3Br \begin{smallmatrix} CMeCl \cdot CO \\ CH=CH \end{smallmatrix}$, which is converted into the acetate of 4-chloro-6-bromo-1-methyl- β -naphthol and 6-bromo-1-methyl- β -naphthol which becomes acetylated.

The following new compounds are described. 4-Chloro-1-methyl- β -naphthol, colourless needles, m. p. 101°, and its acetate, lustrous prisms, m. p. 78°; the compound, $C_6H_3Br \begin{smallmatrix} CMe(NO_2) \cdot CO \\ CCl=CH \end{smallmatrix}$, small

prisms, m. p. 127° (decomp.); 1 : 3 : 4 : 4-tetrachloro-2-keto-1-methyl-tetrahydronaphthalene, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CMeCl} \cdot \text{CO} \\ \text{CCl}_2 - \text{CHCl} \end{smallmatrix}$, prisms, m. p. 82° .

H. W.

Oxidation and Reduction of Quinol and Quinone from the Point of View of Electromotive Force Measurements.

F. S. GRANGER and J. M. NELSON (*J. Amer. Chem. Soc.*, 1921, **43**, 1401—1415).—The reaction $\text{C}_6\text{H}_6\text{O}_2 \rightleftharpoons \text{C}_6\text{H}_4\text{O}_2 + 2\text{H} + 2\ominus$ has been investigated by measurement of the *E.M.F.* of solutions of quinone, quinol, and quinhydrone in water and hydrochloric acid by means of combinations of the type $\text{Hg} | \text{HgCl (sat.)} | \text{KCl} | \text{KCl (sat.)} | \text{Solution of } \text{C}_6\text{H}_6\text{O}_2 \text{ and } \text{C}_6\text{H}_4\text{O}_2 \text{ in HCl} | \text{Pt}$. In addition to the *E.M.F.* data, values for the solubility of the constituents in water and hydrochloric acid are required and were obtained. The solubility of quinol at 25° is found to be (a) in water 0.645 mol. per litre, (b) in 0.01*N*-hydrochloric acid, 0.645 mol. per litre, (c) in 0.1*N*-hydrochloric acid, 0.633 mol. per litre, and (d) in *N*-hydrochloric acid, 0.494 mol. per litre. The solubility of quinone at 25° in water is 0.1266 mol. per litre, in 0.1*N*-hydrochloric acid 0.1275 mol. per litre, and in *N*-hydrochloric acid 0.1332 mol. per litre. The solubility of quinol, quinone, and quinhydrone in the presence of one another has been determined and the dissociation constant (*K*) of quinhydrone calculated. The value of *K* in water is 0.289, in 0.1*N*-hydrochloric acid 0.263, and in *N*-hydrochloric acid 0.267. Several tables of potential measurements are given, and these values are compared with calculated values and found to be in fair agreement. The equilibrium constant (*k*) for the reaction $\text{quinol} \rightleftharpoons \text{quinone}$ is calculated by means of the equation $\pi = 0.0298 \log (q/h) + 0.0596 \log (\text{H}') - 0.0298 \log k$, and the value 1.6×10^{-23} obtained.

J. F. S.

The Dibromoanthraquinones. MARTIN BATTEGAY and J. CLAUDIN (*Bull. Soc. chim.*, 1921, [iv], **29**, 1017—1027; cf. Grandmougin, A., 1921, i, 871).—A more detailed account of work already published (A., 1921, i, 349). 1 : 6-Dibromoanthraquinone, m. p. 204° , is obtained by heating 1-nitro-6-sulphoanthraquinone with bromine in a sealed tube for eight hours at 210° . 1 : 7-Dibromoanthraquinone, m. p. 220° , is obtained in the same manner from 1-nitro-7-sulphoanthraquinone, or from 1 : 7-diaminoanthraquinone by the Sandmeyer reaction.

W. G.

The Homonuclear Dibromoanthraquinones. E. GRANDMOUGIN (*Compt. rend.*, 1921, **173**, 839—840; cf. A., 1921, i, 871).—Very scanty details are given for the preparation of the four homonuclear dibromoanthraquinones, namely, the 1 : 2-, 1 : 3-, 1 : 4-, and 2 : 3-derivatives.

W. G.

The Dibenzoyldiaminoanthraquinones. MARTIN BATTEGAY and J. CLAUDIN (*Bull. Soc. chim.*, 1921, [iv], **29**, 1027—1036).—In part a more detailed account of work already published (cf. A., 1921, i, 513). 1 : 2- and 2 : 3-Diaminoanthraquinones when

benzoylated in neutral or acid media give the corresponding 2-phenyl-anthraquinoneiminazole, but in alkaline solution the benzoylation yields the dibenzoyl derivative. 2-Phenyl- α -anthraquinoneiminazole, m. p. 235° (Schaarschmidt, A., 1915, i, 177 gives m. p. 271°), in an alkaline vat dyes cotton an orange-yellow, which passes by oxidation to a very fast, intense bright yellow. 1:2-Dibenzoyldiaminoanthraquinone has m. p. 355°. 2-Phenyl- β -anthraquinoneiminazole has m. p. >360° (Schaarschmidt, *loc. cit.*, gives >385°), and 2:3-dibenzoyldiaminoanthraquinone has m. p. 315°. 2:6-Dibenzoyldiaminoanthraquinone has m. p. 300°, and 2:7-dibenzoyldiaminoanthraquinone has m. p. 300°. Of these dibenzoyl derivatives only the 1:4-, 1:5-, and 1:8-derivatives are powerful dyes.

W. G.

The Intermediate Products in the Synthesis of Alizarin.

EUGÈNE GRANDMOUGIN (*Compt. rend.*, 1921, **173**, 1176—1178; cf. A., 1921, i, 871).—The author considers that the stages in the synthesis of alizarin from anthracene are: anthracene \rightarrow 9:10-dibromoanthracene \rightarrow its tetrabromide \rightarrow 2:3:9:10-tetrabromoanthracene \rightarrow 2:3-dibromoanthraquinone \rightarrow alizarin.

W. G.

Derivatives of *l*-Menthol. E. A. LÜCK (*Apoth.-Zeit.*, 1921, **36**, 279; from *Chem. Zentr.*, 1921, iii, 721).—The following derivatives of *l*-menthol are described: *cyanomenthane*, $C_{11}H_{19}N$, yellowish-white needles; *potassium menthancarboxylate*, $C_{11}H_{19}O_2K$, long, yellow needles; *menthancarboxylic acid*, $C_{11}H_{20}O_2$, white needles; *menthanealdehyde* corresponding with the latter acid, $C_{11}H_{20}O$, silky needles; the secondary *alcohol* from the aldehyde, $C_{22}H_{40}O_2$, slender, white needles; the *ketone*, $C_{22}H_{38}O_2$, white needles; *sesquiterpene* from menthone, $C_{15}H_{24}$ or $C_{30}H_{48}$, brownish-black, thick mass, not solidifying after two months; *nitrosos sesquiterpene*, $C_{30}H_{47}NO$, a light yellow syrup; the *compound*, $CSSK \cdot C_{30}H_{45}NO \cdot OK$, yellow needles, detonating on heating.

G. W. R.

Essential Oil of *Nepeta japonica*, Maxim.

I. YOSHIHARU MURAYAMA and TAKEYOSHI ITAGAKI (*J. Pharm. Soc. Japan*, 1921, 869—880).—An essential oil (1.8%) was obtained by steam distillation of *Nepeta japonica*, Maxim, from China. It boils at about 205° or 63—83°/10 mm. and contains *d*-limonene and a small quantity of free acids, esters, and alcohols, but consists mainly of a ketone, $C_{10}H_{18}O$, which seems to be *d*-menthone, the optical antipode of the common *l*-menthone.

K. K.

The Essential Oils of *Leptospermum flavescens* var. *grandiflorum* and *Leptospermum odoratum*.

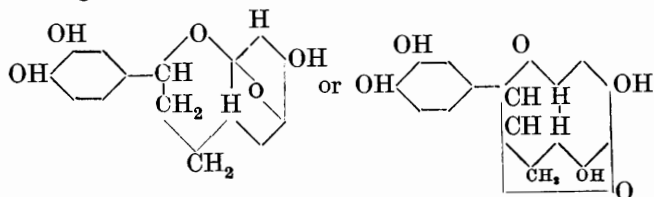
A. R. PENFOLD (*J. Roy. Soc. New South Wales*, 1920, **54**, 197—207; cf. A., 1921, i, 859).—The chief constituents of the essential oil of *Leptospermum flavescens* var. *grandiflorum* are the two sesquiterpenes aromadendrene and eudesmene, together with a sesquiterpene alcohol not identified. The oil has d_{15}^{20} 0.9324; $[\alpha]_D^{20}$ -2.42° ; n_D^{20} 1.5048 and is

distinct from the oil of *Leptospermum flavescens*. The principal constituents of the essential oil of *Leptospermum odoratum*, Cheel, are eudesmol, aromadendrene, and eudesmene, β -pinene, α -pinene, the butyric and acetic esters of an unknown alcohol, together with a small amount of an alcohol having an odour of citronellol, but not being either geraniol or citronellol, and small amounts of a solid and liquid phenol. The yield of oil was much higher from leaves cut in August or October than from those cut in May, and the eudesmol was present in minimum amount in the latter oil.

W. G.

The Structural Formula of Caoutchouc according to Harries. S. C. J. OLIVIER (*Rec. trav. chim.*, 1921, **40**, 665—676; cf. Harries, A., 1904, i, 757, and 1905, i, 364).—The author has repeated some of Harries's work and has obtained, in some cases, different results. He concludes that the assumption of homogeneity for the ozonide of caoutchouc is not valid and that the molecular weight cannot serve as a basis for estimating that of caoutchouc itself; further, that it is impossible in the present state of our knowledge to choose between the ring formula suggested by Harries and the Weber open-chain formula. H. J. E.

Catechu and Catechin. ÅSTRID CLEVE VON EULER (*Svensk. Kem. Tidskr.*, 1921, **33**, 88—98; from *Chem. Zentr.*, 1921, iii, 731).—A theoretical discussion of the chemistry of catechu and catechin. From a consideration of existing experimental work, the following alternative formulæ for catechin are suggested:



G. W. R.

The Course of the Reaction in the Synthesis of Oxindigo (2:2'-Diketo- $\Delta^{1:1'}$ -dicoumaran). K. FRIES and H. HASENJÄGER (*Ber.*, 1921, **54**, [B], 2931—2934; cf. Fries and Hasselbach, A., 1911, i, 150).—When 6-methyl-3-coumaranone reacts with 3-keto-2-*p*-dimethylaminoanilicoumaran in xylene solution, 2'-*p*-dimethylaminoanilino-6-methyl-2 : 2'-dicoumaranone, brownish-red, glistening needles, m. p. 232° (decomp.), after sintering at 229°, is obtained. It is hydrolysed by strong acids to *p*-aminodimethylaniline and "6-methyloxindigo." 3-Keto-2-*p*-dimethylaminoanil-6-methylcoumaran and 3-coumaranone, on the other hand, yield the isomeride 2-*p*-dimethylaminoanilino-6-methyl-2 : 2'-dicoumaranone, pale brownish-red needles, m. p. 211° (decomp.), after sintering at 208°. It is hydrolysed by strong acids to *p*-aminodimethylaniline and "6-methyloxindigo."

2 : 2'-Diketo-6-methyl- $\Delta^{1:1'}$ -dicoumaran ("6-methyloxindigo," "6-methyl-2 : 2'-dicoumaranone-indigo"), crystallises from glacial acetic acid in small, yellow, prismatic crystals, m. p. 265° (decomp.), after darkening at 220° and sintering at 240°.

It follows, therefore, that the isomeric 2- or 2'-*p*-dimethylamino-anilino-6-methyl-2 : 2'-dicoumaranones are the primary reaction products and not "6-methyloxindigo." F. M. R.

Syntheses in the Thianthren Series. I. JÑANENDRA NATH RÂY (T., 1921, 119, 1959—1967).

Preparation of Nitrosulphonic Acids of Hydrogenated Cinchona Alkaloids. C. F. BOEHRINGER & SÖHNE (D.R.-P. 338738; from *Chem. Zentr.*, 1921, iv, 709—710).—Nitrosulphonic acids are prepared by dissolving hydrogenated cinchona alkaloids or their salts in a mixture of sulphuric and nitric acids, or nitric acid or an alkali nitrate is added to a solution of them in sulphuric acid, or their nitro-compounds are dissolved in strong sulphuric acid. *Nitrohydrocinchonidinesulphonic acid*, $C_{19}H_{23}O_6N_3S$, forms yellow, microscopic crystals; hexagonal plates are obtained from methyl alcohol; it is decomposed by heating with hydrochloric acid, giving *nitrohydrocinchonidine* and sulphuric acid. It chars without melting. *Nitrohydroquininesulphonic acid*, $C_{20}H_{25}O_7N_3S$, forms yellow needles; it chars without melting on heating above 250° and darkens on exposure to light. By heating with hydrochloric acid, sulphuric acid and *nitrohydroquinine* are obtained. The latter forms thin, yellow leaflets, m. p. 212° (decomp.). *Nitroethylhydrocupreinesulphonic acid*, $C_{21}H_{27}O_7N_3S$, forms yellow crystals which darken at about 260° and char at about 280° without melting. It is decomposed on heating with hydrochloric acid into sulphuric acid and *nitroethylhydrocupreine*. G. W. R.

Preparation of Aminosulphonic Acids of Hydrogenated Cinchona Alkaloids. C. F. BOEHRINGER & SÖHNE (D.R.-P. 339947; from *Chem. Zentr.*, 1921, iv, 912).—Nitrosulphonic acids, derived from hydrogenated cinchona alkaloids, are reduced by means of ferrous sulphate and alkali hydroxide. For example, nitrohydroquininesulphonic acid is reduced by ferrous sulphate in the presence of an aqueous or methyl-alcoholic solution of barium hydroxide to *aminohydroquininesulphonic acid*; it forms yellow needles, m. p. 222—224°. The red crystalline sulphate gives *aminohydroquinine*, m. p. 216—218°, by hydrolysis with strong hydrochloric acid. G. W. R.

Preparation of Acetylsalicylyl Compounds of Quinine and its Derivatives. E. MERCK, CLAUS DIEHL, and HANS MAYEN (D.R.-P. 338853; from *Chem. Zentr.*, 1921, iv, 709).—*o*-Acetoxycarbonyl chloride is allowed to react with molecular proportions of quinine or its derivatives in a suitable solvent. By the action of *o*-acetoxycarbonyl chloride on dry quinine in dry alcohol, *o*-acetoxycarbonylquinine hydrochloride is obtained in white needles or plates, m. p. 242° (decomp.). From a solution of ethylhydrocupreine in dry

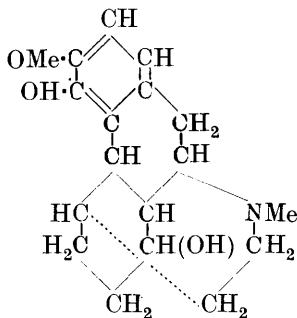
toluene, *o*-acetoxymethylhydrocupreine hydrochloride is similarly prepared; it forms white needles, m. p. 252° (decomp.).

G. W. R.

The Active Constituent of Ergot. K. SPIRO and A. STOLL (*Verh. Schweiz. Nat. Ges.*, 1920, reprint; from *Chem. Zentr.*, 1921, iii, 889—890).—Ergotamine, obtained in crystallisable form from ergot, on treatment with methyl alcohol gives a new, less active, alkaloid, *ergotaminine*. Ergotamine acts paralytically on the sympathetic system, causes contraction of plain muscular tissue, and a slight decrease in blood pressure. It acts on the uterus even at great dilutions. Ergotaminine exerts a similar effect. Histamine takes no part in the typical ergot effect. Ergotamine, however, acts similarly to ergot and may be used in the same way.

G. W. R.

Hydrogenation of isoCodeine and ψ -Codeine. EDMUND SPEYER and HERMANN WIETERS (*Ber.*, 1921, 54, [B], 2647—2650).—Catalytic hydrogenation in the presence of palladium proceeds differently in the cases of *isocodeine* and ψ -codeine, since the former is transformed into a dihydro-derivative, whereas the latter gives tetrahydro- ψ -codeine to which, on the basis of Knorr's formula for ψ -codeine, the annexed configuration is assigned.



Dihydroisocodeine, $C_{18}H_{23}O_3N$, crystallises in small, rhombic prisms, m. p. $199-200^{\circ}$; the corresponding *picrate*, m. p. $235-237^{\circ}$, after previous softening, the *hydrochloride* and *hydroiodide* are described. The *methiodide* forms leaflets, m. p. 272° . *Tetrahydro- ψ -codeine*, $C_{18}H_{25}O_3N \cdot 0.5H_2O$, crystallises in rhombic prisms, m. p. $114-115^{\circ}$ after softening at 110° ; it dissolves in solutions of alkali hydroxides from which it is precipitated by ammonium chloride.

The *hydrochloride*, microscopic prisms, m. p. $238-240^{\circ}$ (decomp.), and *methiodide*, prisms, m. p. $249-250^{\circ}$ (decomp.), are described.

H. W.

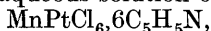
Constitution of Rutaecarpine. YASUHIKO ASAHINA and ATSUSHI FUJITA (*J. Pharm. Soc. Japan*, 1921, 863—869).—Asahina and Mayeda (cf. A., 1916, i, 238, 621; A., 1921, i, 48) proposed constitutional formulæ for evodiamine and rutaecarpine, alkaloids isolated from the fruits of *Evodia rutaecarpa*, Benth. and Hook. The authors attempted to reduce rutaecarpine with alcohol and sodium, with hydriodic acid, with zinc amalgam and hydrochloric acid, and with acetic acid and sodium amalgam in methyl-alcoholic solution without obtaining any definite compound except rutaecarpine hydriodide, m. p. 270° . When rutaecarpine was heated with amyl alcohol and potassium hydroxide for two hours, anthranilic acid and 2- β -aminoethylindole-3-carboxylic acid, $C_{11}H_{12}O_2N_2$, were isolated in almost quantitative amount. The acid forms

white, silky crystals, m. p. 257° , is almost insoluble in common organic solvents, but soluble in acetic acid and hot dilute alcohol; yields a *picrate*, orange-yellow scales, m. p. 247° (decomp.), and when boiled with dilute hydrochloric acid for two to three hours, is resolved into 2- β -aminoethylindole and carbon dioxide. This confirms the constitution previously suggested for rutaecarpine.

K. K.

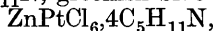
The Addition of Organic Bases to Metallic Salts. WALTER PETERS (*Z. anorg. Chem.*, 1921, **118**, 172—176).—It was shown in previous papers (A., 1913, ii, 42; 1915, i, 504) that by the addition of ammonia or amines to complex salts, compounds of much higher co-ordination number were obtained than by the addition of ammonia to simple salts. The work has now been extended by the preparation of a number of pyridine, piperidine, and ethylenediamine additive compounds of double platino- and platini-chlorides. No relation was found between the number of molecules of each base combined with a salt and the affinity or dissociation constant of the base. The following compounds were prepared.

Pyridine compounds: $\text{CuPtCl}_6 \cdot 6\text{C}_5\text{H}_5\text{N}$, long, thick, cornflower-blue needles; $\text{CdPtCl}_6 \cdot 6\text{C}_5\text{H}_5\text{N}$, a white, curdy precipitate by adding pyridine to the aqueous solution of the salt;



a brick-red precipitate changing to brown; $\text{NiPtCl}_6 \cdot 6\text{C}_5\text{H}_5\text{N}$, yellowish-green; $\text{CoPtCl}_6 \cdot 6\text{C}_5\text{H}_5\text{N}$, yellowish-brown.

Piperidine compounds: $\text{Na}_2\text{PtCl}_4 \cdot 2\text{C}_5\text{H}_{11}\text{N}$, reddish-brown precipitate; $\text{BaPtCl}_4 \cdot 4\text{C}_5\text{H}_{11}\text{N}$; $\text{Na}_2\text{PtCl}_6 \cdot 4\text{C}_5\text{H}_{11}\text{N}$, pale yellow crystals; $\text{CuPtCl}_6 \cdot 2\text{C}_5\text{H}_{11}\text{N}$, greenish-blue precipitate;

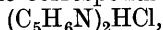


white; $\text{CdPtCl}_6 \cdot 2\text{C}_5\text{H}_{11}\text{N}$, olive; $\text{NiPtCl}_6 \cdot 6\text{C}_5\text{H}_{11}\text{N}$, dirty green.

Ethylenediamine compounds: $\text{ZnPtCl}_6 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$, white; $\text{CdPtCl}_6 \cdot 6\text{C}_2\text{H}_4(\text{NH}_2)_2$, small crystals with a yellow tinge; $\text{NiPtCl}_6 \cdot 2\text{C}_2\text{H}_4(\text{NH}_2)_2$, bright red.

E. H. R.

Action of Sodammonium on Pyridine. Preparation of the Hydrate of Tetrahydrodipyridyl. P. LEBEAU and M. PICON (*Compt. rend.*, 1921, **173**, 1178—1180).—When pyridine, cooled to -60° , is allowed to drop slowly on to sodammonium, a compound, $(\text{C}_5\text{H}_5\text{NNa})_2\text{NH}_3$, is obtained which retains its ammonia even in a vacuum. This compound is spontaneously inflammable in air and detonates. It reacts with methyl and propyl iodides, *tert.*-amyl chloride, and ethylene dichloride giving in all cases unstable substances. By the controlled action of alcohol and water in the presence of ether, *tetrahydrodipyridyl hydrate*, $(\text{C}_5\text{H}_6\text{N})_2 \cdot \text{H}_2\text{O}$, is obtained from which the corresponding *hydrochloride*,



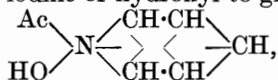
and *mercurichloride*, $(\text{C}_5\text{H}_6\text{N})_2\text{HCl} \cdot \text{HgCl}_2$, were prepared. W. G.

Reduction of Pyridine with Zinc Dust and Acetic Anhydride. OTTO DIMROTH and RICHARD HEENE (*Ber.*, 1921, **54**, [B], 2934—2942).—Pyridine is readily reduced by zinc dust in the presence of acetic anhydride to 1:1'-*diacetyltetrahydro-4:4'-dipyridyl*,

$\text{AcN} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{CH-CH} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{NAc}$, long, yellow needles, m. p. 124—125°, which on exposure to moist air is converted gradually into 4:4'-dipyridyl and acetic acid. De-acetylation and oxidation to 4:4'-dipyridyl is also observed by the action of manganese dioxide or lead dioxide on the substance dissolved in acetic acid or by the action of air or nitrous fumes on the alcoholic solution. It is transformed by iodine in benzene solution to 4:4'-dipyridyl, but pyridine is the main product of the action of iodine dissolved in potassium iodide on a solution of the acetyl compound in acetic acid. Conversely, 4:4'-dipyridyl is reduced by zinc dust and acetic anhydride to 1:1'-diacetyltetrahydro-4:4'-dipyridyl. The relationships are thus similar to those observed by Emmert between pyridine and tetrahydrodipyridyl (A., 1919, i, 415; 1920, i, 331). Like the dialkyl compound, 1:1'-diacetyltetrahydro-4:4'-dipyridyl undergoes dissociation into radicles; the solution of the substance in glacial acetic acid becomes intensely blue when gently warmed, but is decolorised by air and the alternate coloration and decolorisation can be repeated until the substance is completely oxidised. It appears that the radicle can react in two forms, $\text{NAc} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{C} \begin{array}{c} \text{H} \\ \text{H} \end{array}$

and $\text{Ac} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{CH}$. The first form gives a peroxide,

$\text{NAc} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{CH} \cdot \text{O} \cdot \text{O} \cdot \text{CH} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{NAc}$, with air which, possibly after transformation into $\text{NAc} \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} \text{C} \begin{array}{c} \text{OH} \\ \text{OH} \end{array}$, loses acetic acid, whereupon two residues unite to form 4:4'-dipyridyl. The second form adds iodine or hydroxyl to give



which loses acetic acid and yields pyridine.

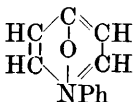
Diacetyltetrahydrodipyridyl can also be obtained in a colourless *modification* when the yellow variety is warmed with alcoholic potassium hydroxide solution (the acetyl groups are remarkably stable towards this reagent). Since the yellow and colourless forms are chemically indistinguishable and have the same melting point, it would appear at first sight that the coloured crystals are contaminated by some persistent, coloured impurity. Against this view, however, it is observed that the solution of the colourless compound in acetic anhydride becomes yellow when warmed and deposits yellow crystals when subsequently cooled. The yellow compound deposits a small quantity of orange-red *needles*, m. p. (indefinite) 248°, when warmed with a small quantity of acetic acid or acetic anhydride; the substance has not yet been investigated completely.

Quinoline, also, is readily reduced by zinc dust and acetic anhydride, giving an amorphous powder, m. p. (very indefinite)

190°, the analyses of which give results agreeing approximately with those required for 1 : 1'-*diacetyltetrahydroquinolyl*. H. W.

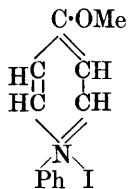
Fission of γ -Pyrone by Aniline and *N*-Phenyl-4-pyridone.

W. BORSCHÉ and IRIS BONACKER (*Ber.*, 1921, **54**, [B], 2678—2686).— γ -Pyrone is readily converted by aniline into di-anilino-vinyl ketone, $\text{CO}(\text{CH}:\text{CH}\cdot\text{NHPh})_2$, which easily loses aniline and passes into 1-phenyl-4-pyridone. The latter may be regarded, not only as a γ -pyridone derivative, but also as an *N*-disubstituted aromatic amine of the type of dimethylaniline. It exhibits, however, few of the reactions typical of this type of substance. Its indifference towards ketonic reagents, alkyl haloids, and nitrous acid has led Smernov (*A.*, 1921, i, 594) to regard it as an internal ammonium oxide (annexed formula). This view is not shared by the authors, since the quinquevalency of the nitrogen atom is opposed to its ability to add Grignard's reagents. They consider



that its stability is due to the unsaturated nature of the two carbon atoms attached to the nitrogen atom and the consequent greater demand on its valency whereby its power of influencing reactions in the aromatic portion of the molecule is correspondingly diminished. If this is the case, 1-phenyl-4-piperidone should exhibit the reactivity of an *N*-dialkylaniline. Since the ketone could not be prepared in sufficient quantity, this point has not been tested experimentally, but it is shown that the corresponding saturated secondary alcohol is a highly reactive substance.

Bishydroxymethyleneacetonedianilide [*di-anilino*vinyl ketone], yellow, silky needles, m. p. 150°, is prepared by the action of aniline on γ -pyrone in dilute acetic acid solution at the atmospheric temperature (a substance, $\text{C}_{17}\text{H}_{16}\text{ON}_2$, m. p. 167°, is obtained as by-product in quantity too small for extended investigation). Fission of the γ -pyrone ring can also be effected by substituted anilines and its homologues if the latter possess pronounced basic properties; the corresponding *p*-toluidino-, pale yellow leaflets, m. p. 167°, and *m*-nitranilino-compounds, m. p. 223°, are described in detail. ($\alpha\alpha'$ -Dimethyl- γ -pyrone, on the other hand, appears to be stable towards aniline.) The dianilino-ketone is converted by hydrochloric acid, by sodium ethoxide, or by distillation in a vacuum into 1-phenyl-4-pyridone, long, colourless needles, m. p. (+2H₂O) 104—105°. Anhydrous 1-phenyl-4-pyridone, m. p. 116° (Smernov, *loc. cit.*, gives 125°), is conveniently prepared by distillation of aniline chelidonate under diminished pressure.



The corresponding *picrate*, yellow leaflets, m. p. 190°, and *methiodide*, colourless rhombohedra, m. p. 146°, are described; the latter, however, appears to be a *pseudomethiodide* (annexed formula), since the corresponding hydroxide passes into 1-phenyl-4-pyridone and methyl alcohol when its aqueous solution is evaporated. 1-Phenyl-4-pyridone forms an additive compound with magnesium methyl iodide, from which

the parent substance is regenerated by dilute acid.

4-Hydroxy-1-phenylpiperidine, m. p. 69—70°, is prepared by the reduction of 1-phenyl-4-pyridone by sodium in boiling alcoholic solution. The *picrate*, dark yellow needles, m. p. 145—147°, *methiodide*, m. p. 153—155°, *benzoate*, coarse, colourless prisms, m. p. 102—103°, and *p-nitrobenzoate*, yellow leaflets, m. p. 156°, are described. 4-Hydroxy-1-phenylpiperidine does not react simply with nitrous acid, since the secondary alcoholic group is liable to be attacked, but the formation of a *p-nitroso*-derivative is established by the isolation of the corresponding gallocyanin *dye*, $C_{25}H_{21}O_7N_2Cl$, bluish-green needles, m. p. 140°. With a diazotised solution of aniline, 4-hydroxy-1-phenylpiperidine gives 4-hydroxy-1-*p*-benzene-azophenylpiperidine, small, brown crystals, m. p. 127° (*benzoyl* derivative, m. p. 125°), whilst with diazotised sulphanilic acid it gives the corresponding *sodium* salt, $C_{17}H_{18}O_4N_3SNa \cdot 2H_2O$, which is reduced by stannous chloride and hydrochloric acid to 4-hydroxy-1-*p*-aminophenylpiperidine, colourless leaflets, m. p. 158° (*dibenzoyl* compound, colourless leaflets, m. p. 195°). *Di-4-hydroxypiperidino-4-phenylmethane*, $CH_2(C_6H_4 \cdot C_5NH_9 \cdot OH)_2$, colourless leaflets, m. p. 162°, is prepared from the base by the action of formaldehyde and hydrochloric acid.

The oxidation of 4-hydroxy-1-phenylpiperidine to 1-phenyl-4-piperidone has not been effected in a satisfactory manner; the latter substance has been prepared in small quantity by hydrogenation of 1-phenyl-4-pyridone by Skita's method and is identified as the compound, $NPh \langle \begin{smallmatrix} CH_2 \cdot CH_2 \\ CH_2 \cdot CH_2 \end{smallmatrix} \rangle C:N \cdot NH \cdot CO \cdot NHPh$, yellow leaflets, m. p. 199° (decomp.). H. W.

Benzyl Ester of 2-Phenylquinoline-4-carboxylic Acid. A. GAMS and O. KAISER (U.S. Pat., 1378343).—Benzyl 2-phenylquinoline-4-carboxylate is prepared as follows: Sodium 2-phenylquinoline-4-carboxylate is heated in acetone and treated with benzyl chloride, gradually added, the acetone is distilled off, the residue is mixed with water and extracted with ether or benzene. The solution in the volatile solvent thus obtained is washed with sodium carbonate and with water and dried with calcium chloride and then treated with dry gaseous hydrogen chloride. The hydrochloride of the benzyl ester thus formed is a fine, crystalline, yellow powder. It is dissolved in alcohol, decomposed by adding solid sodium carbonate, and separated by filtration from the sodium chloride. By concentrating the solution the ester crystallises. It may be purified by recrystallisation from alcohol or ether. It has m. p. 77—78° and is citron-yellow. CHEMICAL ABSTRACTS.

Certain Derivatives of Arylated Cinchonic Acids. KARL W. ROSENMUND (*Ber.*, 1921, 54, [B], 2893—2896).— α -Phenylcinchonic acid (2-phenylquinoline-4-carboxylic acid) is extensively used in pharmacy under the name "Atophan." In this connexion its allyl ester is particularly useful by reason of its low melting point, solubility in fat, and ready absorption by the skin. A number of unsaturated esters of differently substituted cinchonic acids are described, which, however, do not possess these properties.

2-Phenylquinoline-4-carboxylic acid is converted by boiling thionyl chloride into 2-phenylquinoline-4-carboxyl chloride, m. p. 81—82°. *Allyl α-phenylcinchonate* is a pale yellow liquid, b. p. 265°/15 mm., 215°/0.8 mm., m. p. 30°. The corresponding *cinnamyl* ester has m. p. 83°. *Allyl 2-phenyl-6-methylquinoline-4-carboxylate* forms pale yellow needles, m. p. 75—76°. *Allyl 2-piperonylquinoline-4-carboxylate*, m. p. 61°, *βγ-dibromo-n-propyl 2-phenylquinoline-4-carboxylate*, m. p. 75°, *βγ-dibromo-α-phenyl-n-propyl 2-phenylquinoline-4-carboxylate*, needles, m. p. 103°, and *βγ-dibromopropyl 2-piperonylquinoline-4-carboxylate*, m. p. 102—103°, are also described. H. W.

Isomerism of the isoOxazolecarboxylic Acids. VI.

M. BETTI and S. BERLINGOZZI (*Gazzetta*, 1921, **51**, ii, 229—238).—It has been shown (Betti and Alessandri, A., 1915, i, 713; Betti, A., 1915, i, 896; Betti and Berlingozzi, A., 1915, i, 996, 997; Betti and Pacini, A., 1916, i, 222) that two 3:5-diphenylisooxazole-4-carboxylic acids, m. p. 153° and 233° respectively, and two 5-phenyl-3-methylisooxazole-4-carboxylic acids, m. p. 157° and 189° respectively, may be obtained. It is now found that, in either case, the acid with the lower melting point represents the unstable form and may be converted by boiling concentrated alkali hydroxide solution into the less readily fusible, stable isomeride; the inverse change has not been found possible.

These results explain (1) why the amide obtained from 3-phenyl (or methyl)-4-benzylideneisooxazolone may yield the one acid when treated with dilute alkali hydroxide solution and the other when treated with the concentrated alkali, it being the amide of the unstable acid, and (2) why the ethyl ester obtained by the action of hydroxylamine on ethyl benzoyl- (or acetyl-)acetoacetate is hydrolysable only to the stable isomeric acid, with which it corresponds. The amides of the stable acids, and the ethyl esters of the unstable acids, have now been prepared.

The isomerism of these acids may be due to the presence in the one form of a double ring, thus $\text{O} \begin{array}{c} \diagup \text{C} \text{Ph} \cdot \text{C} \cdot \text{CO}_2\text{H} \\ \diagdown \text{N} \text{---} \text{CR} \end{array}$; as this formula

contains an asymmetric carbon atom, experiments are being made on the optical resolution by means of alkaloids.

The stable form of 3:5-diphenylisooxazole-4-carboxylic acid, m. p. 233°, gives the following derivatives: *chloride*, which was obtained slightly impure in long, silky, almost white needles, m. p. 88—89°. *Amide*, $\text{C}_{16}\text{H}_{12}\text{O}_2\text{N}_2$, which forms opaque, white, spherical, crystalline aggregates, m. p. 223°. *Anilide*, $\text{C}_{22}\text{H}_{16}\text{O}_2\text{N}_2$, crystallising in groups of small, yellow needles, m. p. 188°. The isomeric unstable acid, m. p. 153°, gives an *anilide*, crystallising in lustrous, deep yellow leaflets, m. p. 236°; the *ethyl* ester, obtained as an orange-yellow oil, and the *chloride*, obtained as a viscous, orange-yellow substance, could not be purified.

The stable form of 5-phenyl-3-methylisooxazole-4-carboxylic acid, m. p. 189°, yields: a dense, oily, yellow *chloride*, difficult to purify; an *amide*, $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_2$, crystallising in opaque, white,

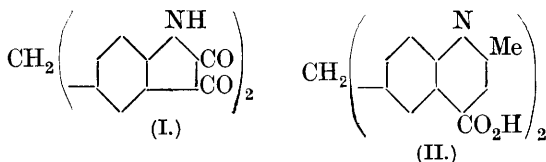
mammillary aggregates, m. p. 205°; and an *anilide*, which crystallises in groups of silky, white needles, m. p. 160°. The isomeric unstable modification, m. p. 157°, forms an oily, uncrystallisable *chloride*; an *anilide*, separating in lustrous, brown crystals, m. p. 179°, and an *ethyl ester*, which was obtained as a dense, intractable oil. T. H. P.

2:4-Diketo-5-phenyl-5-ethyltetrahydro-oxazole. J. ALTWEGG and D. EBIN (U.S. Pat., 1375949).—2:4-Diketo-5-phenyl-5-ethyltetrahydro-oxazole is prepared by dissolving 450 grams of α -phenyl- β -methyl-lactamide in 3 litres of boiling toluene, adding 700 grams of anhydrous potassium carbonate with stirring, slowly adding 300 grams of ethyl chloroformate, heating the mixture for an hour, adding cold water, decanting, and treating the liquid with sulphuric acid. An oily substance separates, which after some time solidifies to a crystalline mass, from which crystals, m. p. 63°, b. p. 176°/3 mm., are obtained after cooling. The aqueous solution has an acid reaction and forms salts with alkali or alkaline-earth metals and magnesium. The 5-methyl derivative, m. p. 70°, may be similarly produced from α -phenyl-lactamide.

CHEMICAL ABSTRACTS.

A New Synthesis of Oxazines. ARTHUR FAIRBOURNE and HAROLD TOMS (T., 1921, 119, 2076—2078).

Isatin and its Derivatives. III. 5:5'-Di-isatylmethane and its Conversion into Quinoline Derivatives. W. BORSCHÉ and R. MEYER (Ber., 1921, 54, [B], 2841—2843; cf. Borsche and Sander, A., 1915, i, 299).—*p*-Diaminodiphenylmethane is readily converted by Sandmeyer's method (A., 1919, i, 318) through 4:4'-di(oximinoacetyl-amino)-diphenylmethane, yellow plates, m. p. 212°, into 5:5'-di-isatylmethane (I), a reddish-yellow powder which does not melt at 300°.

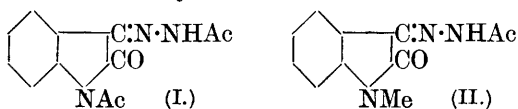


The latter compound readily combines with ketones, thus with acetone it yields 6:6'-methylene-di-(2-methylquinoline-4-carboxylic acid) (II), a yellow powder, m. p. above 320°, and this when distilled with lime, is converted into 6-diquinaldylmethane, colourless plates, m. p. 142°, which forms a yellow *picrate*, darkens at 215°, m. p. 234° (decomp.). With acetophenone 5:5'-di-isatylmethane forms 6:6'-methylenedi-(2-phenylquinoline-4-carboxylic acid), m. p. 265° (decomp.), which when distilled with lime yields *diquinolylmethane*, silvery, glistening plates, m. p. 205°. F. M. R.

Isatin and its Derivatives. IV. The Action of Hydrazine on Isatin and 1-Methylisatin. W. BORSCHÉ and ROBERT MEYER (Ber., 1921, 54, [B], 2844—2853).—The interaction of hydrazine

and isatin should result, according to the conditions, in the formation of isatin hydrazone or di-isatinazine, but Curtius and Thun (A., 1891, 1360) obtained only the former, and regarded it as a hydrazo-compound ($\text{C} \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix}$). Staudinger and Kupfer (A., 1911,

i, 751), on the other hand, concluded that the reaction products of hydrazine with aldehydes or ketones are hydrazones, and this view is supported by the investigation of the action of hydrazine on isatin and 1-methylisatin. If the products are hydrazo-compounds, the derivative of isatin should yield a triacetyl compound and the derivative of 1-methylisatin a diacetyl compound. Actually they yield diacetyl (I) and monoacetyl (II) compounds respectively, identical with the condensation products of acetylhydrazine with 1-acetylisatin and 1-methylisatin:



Isatinhydrazone can be condensed with isatin or aldehydes under suitable conditions, the reaction being facilitated in most cases by the presence of a trace of mineral acid, but condensation does not occur with ketones.

Isatinhydrazone, small, flat, yellow needles, m. p. 237—238° (Curtius and Thun gave 229°), sublimes without decomposition in a vacuum, dissolves in hot dilute sodium hydroxide with an orange-red colour, and on cooling slender, dark yellow needles (*o*-aminophenylglyoxylic acid-hydrazone sodium salt?) separate, from which isatinhydrazone is regenerated by acetic acid. 1-Acetyl-isatin-acetylhydrazone, yellow needles, m. p. 178°, is obtained by the action of acetic anhydride on isatinhydrazone, or by the action of acetylhydrazine on 1-acetylisatin in alcoholic solution. Benzylideneisatinazine, orange-red needles, m. p. 195° (decomp.), is obtained by the interaction of isatinhydrazone and benzaldehyde in alcoholic solution.

Piperonylideneisatinazine, small, orange-red needles, m. p. 250—251° (decomp.), is obtained by the interaction of isatinhydrazone and piperonaldehyde in alcoholic solution in presence of a drop of fuming hydrochloric acid.

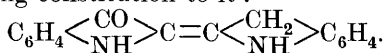
p-Nitrobenzylideneisatinazine forms orange-red plates, m. p. 250—251° (decomp.). Di-isatinazine, glistening, dark red needles, decomposing at 295—296°, is best prepared by boiling an alcoholic solution of isatinhydrazone with isatin in presence of a few drops of fuming hydrochloric acid; it is hydrolysed by acetic acid and fuming hydrochloric acid to isatin and hydrazine, and with acetic anhydride it forms only a monoacetyl derivative, dark yellow, flat needles, decomposing at 220°. In continuation of a former investigation (A., 1902, i, 186), an attempt was made to convert Marchlewski's semicarbazone of isatin (A., 1896, i, 449) into the azine by boiling with aniline. The product was, however, the phenyl-carbamylhydrazone, $\text{C}_8\text{H}_5\text{ON:N·NH·CO·NHPh}$, yellow needles,

m. p. 233° (decomp.). 1-*Methylisatinhydrazone* forms small, yellow, glistening needles, m. p. 107—108°, is soluble in most organic solvents, but insoluble in dilute sodium hydroxide; it forms a red *picrate*, m. p. 112°, and a red *hydrochloride*, m. p. 182°. 1-*Methylisatinacetylhydrazone* crystallises in thin, yellow needles, m. p. 143°. *Benzylidene-1-methylisatinazine* forms red plates, m. p. 156°. *p-Nitrobenzylidene-1-methylisatinazine* forms small orange-yellow needles, m. p. 245—246°. *Di-1-methylisatinazine* crystallises in light red needles, decomposing at 240—245° after darkening at about 235°.

There is a great similarity between the behaviour of isatin and that of 1-methylisatin with hydrazine, but the corresponding isatic acids (*o*-aminophenylglyoxylic acids) in acetic acid solution exhibit a remarkable difference in their behaviour when treated with hydrazine. *o*-Aminophenylglyoxylic acid yields an intermediate product, $C_{16}H_{14}O_4N_4 \cdot 2H_2O$, a pale yellow, crystalline powder, which is instantaneously converted into di-isatinazine by alcohol containing some hydrochloric acid. 1-*o*-Methylaminophenylglyoxylic acid, on the other hand, under similar conditions, yields a second hydrazone, oblique-angled, red prisms, m. p. 162—163°, believed to be a stereoisomeride of that already described. F. M. R.

Octabromindigotin. EUG. GRANDMOUGIN (*Compt. rend.*, 1921, **173**, 982—985).—Tetrabromoanthranilic acid, by the action of formaldehyde, gives a *formalide*, $C_8H_3O_2NBr_4$, which yields a nitrile and the latter on hydrolysis yields the *glycine* of *tetrabromoanthranilic acid*. The glycine when boiled with acetic anhydride gives acetyltetrabromindoxyllic acid, which in ammoniacal solution is readily saponified and oxidised, giving *octabromindigotin*. On oxidation in acetic acid solution with chromic acid, octabromindigotin gives tetrabromoisatin, and on reduction a leuco-derivative, the yellow *sodium* salt of which is only sparingly soluble. The original indigotin has a redder colour than the hexabromindigotin. W. G.

Deoxyindigotin. W. BORSCHÉ and ROBERT MEYER (*Ber.*, 1921, **54**, [B], 2854—2856).—An alcoholic suspension of indigotin is unaffected by boiling with hydrazine, but on adding sodium hydroxide and boiling for several hours, a deep green solution is obtained which deposits a yellow, crystalline precipitate on oxidation by air. This product, $C_{16}H_{12}ON_2$, crystallises from 200 times its weight of glacial acetic acid in small, greenish-yellow needles, m. p. 317°. The authors name the product *deoxyindigotin*, and ascribe the following constitution to it:



Neither deoxyindigotin nor the solution from which it is obtained are suitable for dyeing, but when deoxyindigotin is sulphonated with 36 times its weight of sulphuric acid for three-quarters of an hour at 40—45° it yields a *monosulphonic acid*, the *sodium* salt of which dyes wool or silk in golden-yellow shades which are very

fugitive to light. Similar deoxy-compounds are obtained by the action of hydrazine and sodium hydroxide on 5:5'- or 7:7'-dimethylindigotin, or dibromoindigotin, but thioindigo red is only converted into its leuco-compound.

F. M. R.

Benzoylation and Benzylation of 2:5-Diketopiperazine.

TAKAOKI SASAKI and TOKUDJI HASHIMOTO (*Ber.*, 1921, **54**, [B], 2688—2693).—2:5-Diketo-1:4-dibenzoylpiperazine is prepared by the gradual addition of benzoyl chloride to a suspension of glycine anhydride in pyridine and subsequent heating of the mixture on a water-bath; it forms colourless crystals, m. p. 239—240°, whereas Scheiber and Reckleben (*A.*, 1913, i, 969) record m. p. 116°. It is smoothly converted into hippuric acid by means of sodium hydroxide solution at 37°. 2:5-Diketo-1:4-dibenzylpiperazine (cf. Mason and Winder, *T.*, 1894, **65**, 190; Mannich and Kuptal, *A.*, 1912, i, 217) cannot be prepared by the action of sodium ethoxide and benzyl chloride on glycine anhydride but is readily formed from diacetylglycine anhydride under similar conditions; it has m. p. 173—174°. The stability of the ring system is remarkably increased by the introduction of the two benzyl groups.

H. W.

Diketopiperazines. XI. 3:5-Diketo-1-benzylhexahydro-1:4-diazine. J. V. DUBSKY and E. DINGEMANSE (*Ber.*, 1921, **54**, [B], 2659—2667; cf. *A.*, 1919, i, 289).—Iminodiacetonitrile, $\text{NH}(\text{CH}_2\cdot\text{CN})_2$, m. p. 78°, is conveniently prepared by the action of aqueous hydrocyanic acid (10%) on hexamethylenetetramine and is benzylated by the gradual addition of the nitrile and pyridine to benzyl chloride, which is heated at the temperature of boiling water. *Benzyliminodiacetonitrile*, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CH}_2\cdot\text{CN})_2$, large, prismatic crystals, m. p. 45—45.5° (the unstable *hydrochloride*, m. p. 105°, is described), is hydrolysed by boiling aqueous barium hydroxide solution to *benzyliminodiacetic acid*, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CH}_2\cdot\text{CO}_2\text{H})_2$, colourless, matted needles, m. p. 197—198° (decomp.). The substance behaves definitely as a monobasic acid and yields only a *monopotassium* salt even when treated with two molecular proportions of potassium hydroxide. The colourless *zinc* salt, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{NZn}$, and the pale blue *copper* salt, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{NCu}$, are described. The latter gives an azure blue additive *product*, $\text{C}_{11}\text{H}_{11}\text{O}_4\text{NCu}\cdot\text{NH}_3\cdot 2\text{H}_2\text{O}$, with ammonia. *Benzyliminodiacetic acid* gives a *nitrate*, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}\cdot\text{HNO}_3$, colourless needles, m. p. 117° (decomp.), and a *hydrochloride*, $\text{C}_{11}\text{H}_{13}\text{O}_4\text{N}\cdot\text{HCl}$, decomp. 197°. *Benzyliminodiacetonitrile* is transformed by methyl-alcoholic hydrogen chloride into *methyl benzyliminodiacetate hydrochloride*, m. p. 210°, which, however, could not be isolated in the homogeneous condition. The corresponding *dimethyl* ester could only be obtained as a pale yellow, viscous liquid which decomposes when distilled under diminished pressure. The corresponding *diethyl* ester is a brownish-yellow, viscous liquid with similar properties; in the form of its hydrochloride, the latter is converted by ammonia into its *ethyl hydrogen* ester and, finally, into the *diamide*, $\text{CH}_2\text{Ph}\cdot\text{N}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$.

pale yellow, glistening needles, m. p. (anhydrous) 166° ($+1\text{H}_2\text{O}$), m. p. 159° , which can also be prepared by the action of hydrogen peroxide on the nitrile. The anhydrous *hydrochloride* and its *monohydrate*, m. p. 222° (decomp.), are described. When heated at $180\text{--}190^{\circ}$ under 8 mm. pressure, the diamide is transformed into *benzyliminodiacetamide* [*3:5-diketo-1-benzyl-1:4-hexahydrodiazine*], $\text{CH}_2\text{Ph}\cdot\text{N}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO}\end{smallmatrix}\rangle\text{NH}$, yellowish-white crystals, m. p. 106° . H. W.

Diketopiperazines. XII. Attempted Preparation of 1-Benzoyl-3:5-diketo-hexahydro-1:4-diazine. J. V. DUBSKY and E. HOHER (*Ber.*, 1921, **54**, [B], 2667—2673; cf. preceding abstract).—A record of unsuccessful attempts to prepare 3:5-diketo-1-benzoylhexahydro-1:4-diazine from benzoyliminodiacetamide by elimination of ammonia or from the corresponding monoamide by loss of water.

Benzoyliminodiacetonitrile, colourless, lustrous leaflets, m. p. $131\text{--}132^{\circ}$ (cf. Bailey and Snyder, A., 1915, i, 389), is prepared conveniently by heating iminodiacetonitrile with a solution of benzoyl chloride in benzene at $110\text{--}120^{\circ}$; it is formed in small amount by the benzoylation of the iminodinitrile according to the Schotten-Baumann method. It could not be hydrolysed with hydrogen peroxide; it is converted by barium or potassium hydroxide almost exclusively into benzoyliminodiacetomonoamide,

$\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NBz}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2$, m. p. $190\text{--}191^{\circ}$. *Methyl benzoyliminodiacetate*, $\text{NBz}(\text{CH}_2\cdot\text{CO}_2\text{Me})_2$, transparent prisms, m. p. $73\text{--}76^{\circ}$, is prepared by the action of benzoyl chloride on methyl iminodiacetate or, preferably, from the hydrochloride of the ester, benzoyl chloride, and sodium hydrogen carbonate. It is hydrolysed by aqueous barium hydroxide solution at the atmospheric temperature to *benzoyliminodiacetic acid*, $\text{NBz}(\text{CH}_2\cdot\text{CO}_2\text{H})_2\cdot\text{H}_2\text{O}$, glassy prisms, m. p. $88\text{--}90^{\circ}$; the *barium salt*, colourless leaflets ($+1\cdot5\text{H}_2\text{O}$), and the *copper salt*, pale blue powder ($+ \text{H}_2\text{O}$), are described. Benzoyliminodiacetodiamide, $\text{NBz}(\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$, m. p. $225\text{--}227^{\circ}$, is obtained by the action of ammonia on a solution of the methyl ester in alcohol. H. W.

Diketopiperazines. XIII. J. V. DUBSKY, E. HOHER, and E. DINGEMANSE (*Ber.*, 1921, **54**, [B], 2674—2678; cf. preceding abstracts).—2:5-Diketopiperazine-1:4-diacetodi- α -naphthalide, $\text{C}_{10}\text{H}_7\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{N}\langle\begin{smallmatrix}\text{CO}\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CO}\end{smallmatrix}\rangle\text{N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_{10}\text{H}_7$, decomposing above 313° , is obtained by the action of methyl iminodiacetate hydrochloride on α -naphthylamine at $170\text{--}175^{\circ}$. In spite of manifold variations in the experimental conditions, it was not found possible to conduct the operation in such a manner as to lead to the production of the ketopiperazine, $\text{NH}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CO} \\ \text{CH}_2\cdot\text{CO}\end{smallmatrix}\rangle\text{N}\cdot\text{C}_{10}\text{H}_7$.

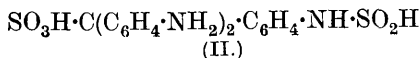
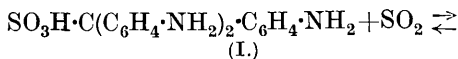
The preparation of phenyliminodiacetamide from aniline and chloroacetamide has been recorded previously (Dubsky and

Gränacher, A., 1918, i, 188); attempts to prepare the corresponding 2:6-dimethyl derivative by the use of α -chloropropionamide yielded a mixture of α -anilinopropionamide, $\text{NHPh}\cdot\text{CHMe}\cdot\text{CO}\cdot\text{NH}_2$, colourless, lustrous leaflets, m. p. 141° , and α -anilinopropionanilide, slender, silky needles, m. p. $126\cdot5^\circ$.

Hexaethylenetetramine is highly resistant towards hydrocyanic acid. H. W.

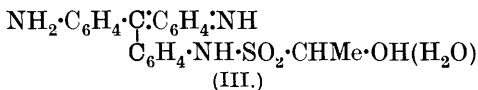
Rosaniline-sulphurous Acid and its Colour Reactions with Aldehydes. HEINRICH WIELAND and GEORG SCHEUING (*Ber.*, 1921, **54**, [B], 2527—2555).—The hydrochloride of pararosaniline-leucosulphonic acid prepared by Hantzsch and Osswald (A., 1900, i, 256) was regarded as the substance which produces the well-known colour reactions with aldehydes. Subsequently, Dürsch-nabel and Weil (A., 1905, i, 947) obtained the free sulphonic acid, and products described as “neutral and acid sulphites” of pararosaniline. The latter authors’ product is the free base of the former authors’ hydrochloride, and is actually a *trihydrate* of *pararosanilineleucosulphonic acid*, crystallising in needles, whilst the so-called “acid sulphite” is the *monohydrate* of *pararosanilineleucosulphonic acid*, crystallising in oblique-angled plates. This sulphonic acid possesses an amphoteric character, and its hydrochloride has been described by Hantzsch and Osswald (*loc. cit.*). It forms a *sodium* salt, plates ($2\text{H}_2\text{O}$), and an *ammonium* salt, fine needles ($2\text{H}_2\text{O}$). Similar products are obtained from other dyes, namely, *Döbner’s-violet-leucosulphonic acid*, small, quadrangular monoclinic, yellow crystals (H_2O), and *Crystal-violet-leucosulphonic acid*, faintly violet powder ($3\text{H}_2\text{O}$), which is extremely unstable.

The so-called “neutral sulphite” is the *pararosaniline salt* of *pararosanilineleucosulphonic acid*, metallic glistening crystals, $\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_3\cdot\text{SO}_3\cdot\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{NH}_2)_2$. Similar colour salts of a mixed type have also been prepared, namely, the *Crystal-violet salt* of *pararosanilineleucosulphonic acid*, black, crystalline powder with a green, metallic lustre, and the *pararosaniline salt* of *Malachite-green-leucosulphonic acid*, black, microcrystalline powder with a green lustre. Pararosanilineleucosulphonic acid is not the substance which gives rise to colour reactions with aldehydes, for no reddish-violet colour is produced when acetaldehyde is added to a very dilute hydrochloric acid solution of pararosanilineleucosulphonic acid, and the latter can be isolated unaltered from the solution after removing the acetaldehyde in a vacuum. The colour reaction only occurs when the solution contains sulphurous acid. The solution of pararosanilineleucosulphonic acid (I) in sulphurous acid is regarded as containing the *N*-sulphinic acid (II), thus:

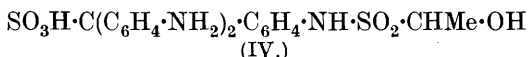


The sulphur dioxide attached to the amino-group in II can be

removed completely by iodine, which distinguishes it sharply from the sulphonic group attached to the carbon atom. The first stage in the reaction is the formation of the *N*-sulphinic acid, and the sulphonic group is introduced subsequently. When an aldehyde is added to the colourless dilute solution of the rosaniline-sulphurous acid an intense bluish-red colour is produced owing to the conversion of the benzenoid triphenylmethane derivative into a quinonoid compound by some hitherto unknown means. It was not known definitely whether the aldehyde colouring matter still contains sulphurous acid in some form, or whether it is identical with the reaction product obtained by the interaction of rosaniline and one or two molecular proportions of aldehyde. Actually the aldehyde colouring matter contains SO_2 . When a solution of pararosaniline reacts with one molecular proportion of sulphur dioxide and one molecular proportion of acetaldehyde, an insoluble colouring matter (III) separates in bluish-red flocks after a short time :



With an excess of sulphurous acid, a colourless, crystalline product ($4\text{H}_2\text{O}$) is formed :



This *N*-aldehyde-sulphurous acid pararosanilineleucosulphonic acid (IV) is also formed by the addition of acetaldehyde to a concentrated solution of pararosanilineleucosulphonic acid in a slight excess of aqueous sulphurous acid.

The colouring matter (III) is insoluble, whereas the colouring matter produced in the ordinary colour reaction with aldehydes is readily soluble, and is only formed when a further molecular proportion of sulphur dioxide is used, and the quantity of aldehyde is also increased. It would appear, therefore, that the latter colouring matter, when acetaldehyde is used, has the constitution : $\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{C} (\text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO} \cdot \text{O} \cdot \text{CHMe} \cdot \text{OH})_2$. The instability of this colouring matter on keeping is due to the hydrolysis of the aldehyde-sulphurous complex as such, for that does not give rise to colour reactions.

F. M. R.

Trypaflavin [3 : 6-Diamino-1-methylacridinium Chloride].

HANS THIEME (*Ber. deut. Pharm. Ges.*, 1921, **31**, 323—344).—Normal trypaflavin is composed of equimolecular quantities of two stereoisomeric forms, one of which on treatment of the sulphate in aqueous solution with barium hydroxide is converted into the true stable quaternary ammonium base, whilst the other breaks down into diaminoacridine with loss of methyl alcohol. The trypaflavin sulphate which is formed on adding sulphuric acid to the aqueous solution of the base after filtering off the diaminoacridine, no longer behaves as a dual substance when the treat-

ment with barium hydroxide is repeated, as no diaminoacridine is formed, but, instead, the theoretical quantity of the quaternary base. The different behaviour of the normal sulphate and the above salt was also demonstrated by conductivity measurements of the two salts in reaction with barium hydroxide. Whilst in the one case a very rapid fall in conductivity during the first few minutes was observed, in the latter case, where no diaminoacridine was formed, no such rapid fall in conductivity occurred. In each case there was a slow continuous decline, but this was due to absorption of carbon dioxide by the free base. G. F. M.

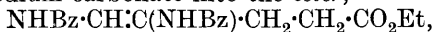
The Behaviour of certain Bisacylaminoethylene Derivatives prepared from Glyoxalines. A. WINDAUS, W. DÖRRIES, and H. JENSEN (*Ber.*, 1921, **54**, [B], 2745—2755).—A series of examples is given of the fission of the glyoxaline ring by *isovaleryl* chloride with the product of bisacylaminoethylenes, the catalytic hydrogenation of the latter to the ethane derivatives, and the conversion of these into the corresponding amines. The bisbenzoylaminoethylene compounds lose a molecule of benzoic acid and one of ammonia under the influence of alcoholic hydrogen chloride and pass into benzoylamino-ketones which are transformed by further action of the same reagent into aminoketones.

A well-cooled aqueous solution of glyoxaline is converted by alternate addition of small amounts of *isovaleryl* chloride and potassium hydroxide solution into *bisisovalerylaminoethylene*, which is conveniently characterised as its *dibromide*, slender needles, m. p. 164—165° (decomp.). Hydrogenation of the ethylene derivative in the presence of spongy palladium gives *bisisovalerylaminoethane*, $C_2H_4(NH \cdot CO \cdot C_4H_9)_2$, lustrous needles, m. p. 182°, which is converted by concentrated hydrochloric acid at 140° into ethylenediamine dihydrochloride. Bisbenzoylaminoethylene is transformed by boiling methyl alcoholic hydrogen chloride solution (10%) into aminoacetaldehyde, which is identified as glyoxalosazone.

4(5)-Methylglyoxaline is converted by *isovaleryl* chloride and reduction of the initial product into $\alpha\beta$ -*diisovalerylamino*propane, colourless, slender needles, m. p. 172—173°, which is transformed into $\alpha\beta$ -diaminopropane (*dipicrate*, yellow needles, m. p. 237° after previous darkening; dibenzoyl derivative, m. p. 192—193°). $\alpha\beta$ -Dibenzoylaminoethylene is transformed by alcoholic hydrogen chloride into aminoacetone.

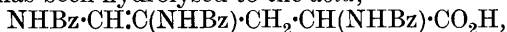
Hydrogenation of the product of the fission of histamine with *isovaleryl* chloride leads to the formation of $\alpha\beta\delta$ -*triisovalerylamino*butane, slender needles, m. p. 196—197°, which is converted in the usual manner into $\alpha\beta\delta$ -*triaminobutane trihydrochloride*, needles, m. p. 209—210° (corresponding *picrate*, small, yellow needles, decomp. about 225°). The fission of histamine with benzoyl chloride and sodium hydroxide has been described previously (Windaus and Vogt, A., 1907, i, 978); the product thus obtained is converted by alcoholic hydrogen chloride into $\alpha\delta$ -*dibenzoylamino*- β -*ketobutane*, $NHBz \cdot CH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot NHBz$, small, colourless needles, m. p. 151° (*semicarbazone*, needles, m. p. 172—173°).

Ethyl glyoxaline-4-propionate oxalate is transformed by benzoyl chloride and sodium carbonate into the *ester*,



slender needles, m. p. 132—133° (the corresponding *acid* crystallises in needles, m. p. 156—157°); it is converted by boiling alcoholic hydrogen chloride into *ethyl δ-benzoylamino-γ-ketovalerate*, $\text{NHBz} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, coarse prisms, m. p. 101° (*semicarbazone*, needles, m. p. 171°).

The fission of histidine methyl ester has been described by Kossel and Edlbacher (A., 1915, i, 285); the unsaturated ester thus produced has been hydrolysed to the *acid*,



small needles, m. p. 241°. The unsaturated ester is converted by hydrogen chloride dissolved in methyl alcohol into *methyl αδ-di-benzoylamino-γ-ketovalerate*, $\text{NHBz} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}(\text{NHBz}) \cdot \text{CO}_2\text{Me}$, lustrous needles, m. p. 173—174°; it gives a *phenylhydrazone*, pale yellow leaflets, m. p. 221—222°.

H. W.

The Nitro- and Amino-derivatives of 4-Phenyglyoxaline.

REGINALD LINDSAY GRANT and FRANK LEE PYMAN (T., 1921, 119, 1893—1903).

Aziminobenzene (1:2:3-Benztriazole). G. CHARRIER and A. BERETTA (*Gazzetta*, 1921, 51, ii, 267—269).—Attempts were made to prepare *o*-benzoylamino-phenyldiazonium chloride by the action of nitrous acid on benzoyl-*o*-phenylenediamine, but it was found that, under the most varied conditions, this reaction yields the *benzoyl* derivative of 1:2:3-benztriazole, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{NBz} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{N}$,

which crystallises in long, colourless needles, m. p. 112°. When dissolved in 95% alcohol and boiled in a reflux apparatus with 30% sulphuric acid for nine hours, this compound is hydrolysed to 1:2:3-benztriazole, which is conveniently prepared by this method.

T. H. P.

Preparation of Triazoles of the Aromatic Series (ψ-Az-imides). KALLE & Co., AKT. GES. (D.R.-P., 338926; from *Chem. Zentr.*, 1921, iv, 709).—*o*-Aminoazo-dyes, in particular those which contain amino- and hydroxyl-groups in addition to the amino-group present in the ortho-position to the azo-group are treated with cuprammonium salts. The product from diazotised sulphanilic acid and *m*-tolylenediamine is dissolved in water and treated with ammonia. An aqueous solution of copper sulphate and 25% aqueous ammonia solution is added and the mixture is heated at 90° for a few hours. On cooling, the ammonium salt of 5-amino-2-*p*-sulphophenyl-6-methyl-ψ-aziminobenzene crystallises out.

5-Amino-2-phenyl-ψ-aziminobenzene, $\text{PhN} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \text{C}_6\text{H}_3 \cdot \text{NH}_2$, is similarly obtained from benzeneazo-*m*-phenylenediamine. It crystallises from glacial acetic acid and has m. p. 183°. The dye from diazotised 5-aminosalicylic acid and *m*-tolylene diamine gives

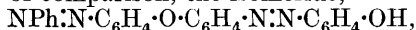
similarly 5-amino-2-p-hydroxy-m-carboxyphenyl-6-methyl-ψ-azimino-benzene, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_3(\text{OH})\cdot\text{N}<\underset{\text{N}}{\underset{|}{\text{N}}}>\text{C}_6\text{H}_2\text{Me}\cdot\text{NH}_2$. G. W. R.

Structure and Colour of the Azine Scarlets. JULIUS BEREND COHEN and HERBERT GRACE CRABTREE (T., 1921, 119, 2055—2070).

Ring Closure with Hydrazinededicarbonamides containing Sulphur. Dithiourazole and Iminothiourazole. EMIL FROMM (*Ber.*, 1921, 54, [B], 2840).—The author has prepared previously many of the compounds described by Arndt and Milde in their recent publication (A., 1921, i, 813), and the account of the work will appear shortly in the *Annalen*. In general, the results obtained are in good harmony except in so far as the preparation of dithiourazole and iminothiourazole is concerned, for which the author prefers the older process. H. W.

The Electrochemical Oxidation of Azobenzene. FR. FICHTER and WOLFGANG JAECK (*Helv. Chim. Acta*, 1921, 4, 1000—1009).—Text-books of electrochemistry, in dealing with the question of the introduction of hydroxyl groups into the benzene nucleus by anodic oxidation, quote the conversion of azobenzene into tetrahydroxyazobenzene (Heilpern, A., 1898, i, 249) as a smooth reaction. Heilpern's analytical figures for the so-called tetra-acetyl derivative of tetrahydroxyazobenzene, however, represent a triacetyl derivative as regards the carbon content, although the hydrogen content does not agree with this. Repetition of the oxidation shows that the product resembles that obtained by Heilpern, and is formed by the hydroxylation of azobenzene, although it is not tetrahydroxyazobenzene, but a complex mixture. Two of the reaction products have been isolated in the form of their acetyl derivatives from this mixture by means of their different solubilities in benzene; pp'-diacetoxyazobenzene, readily soluble in benzene, m. p. 193·5°, which on hydrolysis yields pp'-dihydroxyazobenzene, brown crystals, m. p. 204°; diphenyl-pp'-bisazophenyl acetate, sparingly soluble in benzene, glistening orange-red crystals, m. p. 257°, which on hydrolysis yields diphenyl-pp'-bisazophenol, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, small, brown needles, m. p. 265°; the constitution was confirmed by synthesis from tetrazotised benzidine and phenol.

For purposes of comparison, the isomeric,



for which the name 4'-hydroxy-4:4''-bisazo-benzoyl ether is suggested, in which azobenzoyl represents the group $\text{C}_6\text{H}_5\cdot\text{N}:\text{N}\cdot\text{C}_6\text{H}_4$, was synthesised; p-hydroxyazobenzene condensed with p-nitrochlorobenzene for twelve hours at 240° yields azobenzoyl-p-nitrophenyl ether, small, brown crystals, m. p. 125°, which is reduced in aqueous-alcoholic solution by sodium sulphide to azobenzoyl-p-aminophenyl ether, pale brown, glistening scales, m. p. 100—101°. Prolonged reduction converts the latter compound into its hydrazo-derivative, m. p. 212°, which is reoxidised by air to the azo-compound. When

azobenzoyl-*p*-aminophenyl ether is diazotised and coupled with phenol, 4'-hydroxy-4:4''-bisazobenzoyl ether, brown crystals, m. p. 198°, is formed; its *acetyl* derivative crystallises in plates, m. p. 183°.

F. M. R.

Action of Diazo-salts on Aromatic Sulphonamides. I. PAVITRA KUMAR DUTT, HUGH ROBINSON WHITEHEAD, and ARTHUR WORMALL (T., 1921, 119, 2088—2094).

Separation of the Proteins of the Serum. M. PIETTRE and A. VILA (*Bull. Soc. Chim. Biol.*, 1921, 3, 483—489).—A simplified method for the separation of serum-albumin and serum-globulin is described. Serum is neutralised with hydrochloric or sulphuric acid and the proteins are precipitated by addition of acetone or alcohol. Treatment of the precipitate with water removes the albumin, which is again precipitated, after filtration from the globulin, by addition of acetone.

E. S.

The Electric Charge of Hæmoglobin. L. MICHAELIS and Y. AIRILA (*Biochem. Z.*, 1921, 118, 144—149).—Cataphoretic experiments show that hæmoglobin behaves as a complex ampholyte. At the isoelectric point, the cataphoretic movement is nil, and with increasing or decreasing P_H there is a continuous increase in the cataphoretic velocity. These results disprove Straub and Meier's contentions (A., 1921, i, 72).

H. K.

Viscosity of Gelatin Solutions. CLARKE E. DAVIS, EARLE T. OAKES, and HAROLD H. BROWNE (*J. Amer. Chem. Soc.*, 1921, 43, 1526—1538).—Three kinds of gelatin have been examined to ascertain the effect on the viscosity of gelatin solutions of (a) the ageing of the solution, (b) the method of producing the solution, (c) the hydrogen-ion concentration, (d) the concentration of the gelatin, and (e) the hydrolysis of the solution. It is shown that viscosity determinations of gelatin solutions can be made by an Ostwald viscosimeter with a maximum error of 0.5%. Gelatin solutions increase in viscosity with age at different rates, depending on the concentration of the gelatin, the type of gelatin, and the hydrogen-ion concentration. For any given gelatin solution a maximum viscosity is attained at an age of solution of about twenty-four hours. A decrease in viscosity after the maximum is reached indicates bacterial decomposition. Gelatin solutions show a maximum viscosity at a hydrogen-ion concentration represented by $P_H=3.0-3.5$ at 25°. The viscosity of gelatin solutions is not a simple function of the concentration of the gelatin. Both the hydrogen and hydroxyl ions catalyse the hydrolysis of gelatin in solution, but the hydroxyl ion is more powerful in this respect than the hydrogen-ion. Excessive temperatures accelerate the hydrolysis of gelatin, whilst actual boiling of the solutions causes very rapid hydrolysis.

J. F. S.

An Unidentified Base among the Hydrolytic Products of Gelatin. DONALD D. VAN SLYKE and ALMA HILLER (*Proc. Nat. Acad. Sci.*, 1921, 7, 185—186).—The non-amino-nitrogen precipitable from the products of the acid hydrolysis of proteins is

assumed to be entirely in the histidine and arginine. When arginine is estimated directly, the remaining non-amino-nitrogen is assumed to be histidine. A comparison of the histidine obtained on this assumption with that obtained by Koessler and Hanke's direct colorimetric method (A., 1920, ii, 67) gave satisfactory results for casein, edestin, and fibrin, but not for gelatin. A hitherto unknown base must therefore be present among the products of the hydrolysis of gelatin which are precipitable by phosphotungstic acid. This was obtained by successive removal of the other bases from the phosphotungstate fraction, after removal of phosphotungstic acid. Attempts to crystallise the free base were unsuccessful. It is hygroscopic and decomposes slowly at 100°. The ratio of total nitrogen to amino-nitrogen is 2:1 and is not increased by prolonged boiling with 20% hydrochloric acid or by heating in a bomb tube with 25% sulphuric acid. It is concluded that it is not a peptide. G. W. R.

Origin of Melanin from Pyrrole. II. Action of Organ Extracts on Pyrrole. The Sepia of the Cuttlefish. PIETRO RONDONI (*Sperimentale*, 75, 33—44; from *Chem. Zentr.*, 1921, iii, 887).—An aqueous extract of the ink-sac of cuttlefish (previously freed from secretion) gives a distinct blackening with pyrrole. It is weaker in the case of an extract heated for ten minutes, but is deepened by addition of ferrous sulphate solution. Similar results are obtained with extract from the skin of frogs. The phenomenon is confined to melanogenic organs and is of colloidal character. A pyrrole oxydase may be present. The inky secretion (sepia) appears to be a suspensoid associated with a protective colloid which prevents precipitation by the electrolytes in sea-water. From the similar properties of sepia and Angeli's "pyrrole-black" it is concluded that a pyrrole ring occurs in the former. G. W. R.

Action of Hydrolytic Enzymes. II. MARC H. VAN LAER (*Bull. Soc. Chim. Belg.*, 1921, 30, 261—265; cf. A., 1921, ii, 445).—The author's hypothesis, that a hydrolytic enzyme owes its activity to its capacity for adsorbing substrate and hydrogen ions, involves the possibility of an enzyme acting on all hydrolysable substances which it adsorbs. In such a case, the optimal concentration of hydrogen ions should be independent of the particular substrate acted on, for this optimum is regarded as a characteristic of the enzyme itself, being the point beyond which the coagulating effect of further increases in the concentration of hydrogen ions, on the enzyme particles, preponderates over their catalytic effect on hydrolysis. Among the hydrolytic transformations effected by malt extract, those relating to starch, proteins, esters, and amygdalin (cf. A., 1921, i, 488) are all subject to the same optimal reaction, and may accordingly be due to one enzyme. J. H. L.

Some Errors in the Study of Invertase Action. WARREN C. VOSBURGH (*J. Amer. Chem. Soc.*, 1921, 43, 1693—1705; cf. Nelson and Vosburgh, A., 1917, ii, 252).—Invertase solutions are

subject to loss in activity when diluted, the magnitude of the loss varying with the invertase preparation and the substances present in the water used for the dilution. Dilution with distilled water results in less loss than is the case if very dilute acids are used and for practical purposes is consistent if the dilution is not too great. When an invertase solution is added to solutions containing sucrose, losses in activity are less than when the sucrose is absent. The velocity of hydrolysis of sucrose by invertase is greater when a citrate or acetate buffer is used as the source of hydrogen ions than when citric or acetic acid respectively is so used. Both dilute and stock solutions of invertase lose strength on keeping, the former faster than the latter. W. G.

Toxicity. I. The Action of Quinine on Invertase. PETER RONA and ERNST BLOCH (*Biochem. Z.*, 1921, **118**, 185—212).—The inhibitory action of quinine hydrochloride on invertase is dependent on the P_H of the solution. The more alkaline, the greater the toxic effect. This indicates that the free base is the active agent. The same applies to the action on paramœcia. Optochin, eucupin, and vuzin behave similarly, the two former being equivalent to quinine; vuzin is considerably more active. Quinidine has a greater toxic effect than quinine. H. K.

Toxicity. III. The Action of *m*- and *p*-Nitrophenols on Invertase. PETER RONA and EMERICH BACH (*Biochem. Z.*, 1921, **118**, 232—253).—The inhibitory action of these phenols is a time process. There is also a distinct threshold value for each, beyond which only a relatively small variation of concentration is possible without producing complete inhibition. The process is not reversible, this being attributed to an irreversible destruction of the ferment. H. K.

The Action of Metallic Copper and Silver on Diastase. The so-called Oligodynamic Phenomena. A. LUGER (*Biochem. Z.*, 1921, **117**, 153—160).—Diastase inactivated by contact with metals is more or less reactivated by treatment with certain salts such as potassium cyanide and sodium thiosulphate. H. K.

Enzymes. VIII. Conditions of Action of Amylases. W. BIEDERMANN and AMIN RUEHA (*Fermentforsch.*, 1921, **5**, 56—83; cf. A., 1921, i, 11, 468).—The results of previous investigators on the hydrogen- or hydroxyl-ion concentrations under which amylases act are fully discussed and their bearing on the different theories which have been advanced to explain enzyme action is considered.

As regards the retarding influence of hydroxyl ions on diastatic action, there exists always an upper limiting amount of enzyme for which the optimum activity persists in spite of the alkaline reaction. For less quantities of the enzyme, the action is retarded to an extent which increases as the amount of enzyme diminishes. Such "subliminal" amounts of enzyme may, however, be rendered active under the same reaction conditions if the degree of activity

and therewith the diastatic power is raised by addition of suitable ionic mixtures to the solution.

Similarly, the action of diastatic enzymes is prevented by a certain definite hydrogen-ion concentration, this depending, however, on the amount of enzyme present in the solution. Malt diastase is far more "acid-proof" than the ptyalin of saliva, the former exerting its optimum activity when the acidity is such that the action of the latter is prevented. T. H. P.

Chemical Investigation of Amylases and Related Enzymes.

H. C. SHERMAN (*Carnegie Inst. Washington Yearbook*, 1919, **18**, 328—330).—A neutral solution of sodium aspartate corrected the abnormally low results obtained by the action of purified pancreatic amylase on potato starch which had previously been purified by washing with very dilute alkali and subsequent thorough washing with specially purified water. The neutral solution of sodium aspartate also accelerated the rate of hydrolysis of wheat, maize, rice, and potato starches by purified pancreatic amylase, by purified malt amylase, by commercial pancreatin, or by saliva, but had no such action on their hydrolysis by a simple extract of malt, or by either the commercial or a laboratory preparation of the amylase of *Aspergillus oryzae*. When soluble starch was used as the substrate and the reducing sugar produced was estimated gravimetrically, similar results were obtained. When this technique was used, and asparagine was substituted for sodium aspartate, essentially similar results were obtained; however, the asparagine apparently produced a slight increase in the activity of taka-diastase. When both asparagine and a neutral solution of sodium aspartate were added to a digestion mixture, the results were such as were obtained by use of either of the two compounds in its optimum concentration. Thus the activating effects of aspartic acid and asparagine were interchangeable rather than additive; their effect was not due to a change in the hydrogen-ion concentration, or to the sodium ion, or to the mere concentration of electrolyte, since optimum concentrations of chlorides and phosphates were already present. The effect was, in a sense, specific, since neutral sodium aspartate increased the enzymic activity when the optimum amounts of chlorides and phosphates were present, but could not completely replace chlorides in the activation of pancreatic amylase. CHEMICAL ABSTRACTS.

Importance of Acidity for Cyanohydrin Synthesis and the Non-existence of Rosenthaler's *syn*-Emulsin.

E. NORDEFELDT (*Biochem. Z.*, 1921, **118**, 15—33).—The formation of benzaldehyde-cyanohydrin is largely conditioned by the P_H of the solution, the synthetic action increasing rapidly with increase of P_H . The enzymatic nature of emulsin in this reaction is an unnecessary assumption, the increased velocity in its presence being due to removal of hydrogen-ions by adsorption of benzoic acid. The specificity of emulsin in producing optical activity in the hydroxy-nitrile formed is not necessarily enzymatic, as the results of Fajans (A., 1908, ii, 268) with quinine and quinidine have shown. H. K.

Toxicity. II. The Action of Quinine on Serum-lipase.

PETER RONA and DORA REINICKE (*Biochem. Z.*, 1921, **118**, 213—231).—Quinine hydrochloride inhibits the action of lipase similarly to the inhibition produced by atoxyl (A., 1921, i, 69). The action depends on the \bar{P}_{II} of the medium, being more pronounced with increasing P_{II} , and is independent of the particular salt of quinine used. The inhibiting action on animal sera is only obtained at concentrations of quinine one hundred to one thousand times that observed with human sera.

H. K.

The Enzyme Phosphatase-Phosphatase. H. P. BARENDRECHT (*Biochem. Z.*, 1921, **118**, 254—255).—Euler and Ohlsen's experiments (A., 1912, i, 61) support the radiation hypothesis of enzyme action.

H. K.

Additive Reactions of Phosphorus Haloids. II. The 1:4-Addition of Phosphenyl Chloride.

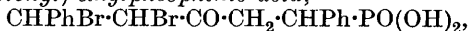
JAMES B. CONANT and S. M. POLLACK (*J. Amer. Chem. Soc.*, 1921, **43**, 1665—1669; cf. A., 1920, i, 454).—Dichlorophenylphosphine reacts with phenyl styryl ketone in acetic acid solution to give *phenyl-β-benzoyl-α-phenylethylphosphinic acid*, $\text{COPh}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{PPhO}\cdot\text{OH}$, m. p. 220—225° (decomp.). In acetic anhydride as a solvent, the product is an unsaturated cyclic *anhydride*, $\text{CH}\begin{smallmatrix} \text{CHPh} \\ \text{CPh}\cdot\text{O} \end{smallmatrix} \text{PPhO}$, which

readily reacts with water to give the ketophosphonic acid. The structure of the anhydride is shown by the fact that it combines with one equivalent of bromine and the product reacts with water to give two stereoisomeric *phenyl-β-bromo-β-benzoyl-α-phenylethylphosphinic acids*, $\text{CHBzBr}\cdot\text{CHPh}\cdot\text{PPhO}\cdot\text{OH}$, which may also be prepared by bromination of the ketophosphinic acid. One has m. p. 150° and the other m. p. 195° (decomp.). They are both decomposed by aqueous alkali, giving phenyl styryl ketone, hydrogen bromide, and phenylphosphonic acid.

W. G.

Addition Reactions of Phosphorus Haloids. III. The Reaction with Distyryl Ketone and Phenyl Cinnamylidenemethyl Ketone.

JAMES B. CONANT, ALBERT H. BUMP, and HAROLD S. HOLT (*J. Amer. Chem. Soc.*, 1921, **43**, 1677—1684; cf. preceding abstract).—Phosphorus trichloride acts on distyryl ketone in acetic acid solution to give *β-cinnamoyl-α-phenylethylphosphonic acid* (cf. A., 1918, i, 74), which, when acted on by bromine in chloroform solution, yields *α-phenyl-β-(α'β'-dibromo-β'-phenylpropionyl)-ethylphosphinic acid*,



m. p. 180—182°. This compound readily loses hydrogen bromide under the influence of alcoholic potassium hydroxide, giving *α-phenyl-β-(α'-bromocinnamoyl)-ethylphosphinic acid*,



m. p. 130—132°, which on oxidation with ozone gives hydrogen bromide, benzoic acid, and *α-phenyl-β-glyoxyethylphosphinic acid*, $\text{CO}_2\text{H}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{PO}_3\text{H}_2$, m. p. 183° (decomp.), and this phosphonic acid on heating loses carbon monoxide, yielding *α-phenyl-β-carboxyethylphosphinic acid*.

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A similar series of reactions occurred when the phosphorus trichloride was replaced by phosphenyl chloride. The products obtained were *phenyl- α -phenyl- β -cinnamoyl-ethylphosphinic acid*, $\text{CHPh}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{PPhO}\cdot\text{OH}$, m. p. 235—236°; *phenyl- α -phenyl- β -carboxyethylphosphinic acid*, m. p. 212°; *phenyl- α -phenyl- β -(α' β' -dibromophenylpropionoyl)-ethylphosphinic acid*, m. p. 195° (decomp.); *phenyl- α -phenyl- β -(α' -bromocinnamoyl)-ethylphosphinic acid*, m. p. 200°.

Phenyl cinnamylidenemethyl ketone condensed with phosphorus trichloride in acetic anhydride to give a poor yield of *β -benzoyl- α -styrylethylphosphinic acid*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{CH}_2\text{Bz})\cdot\text{PO}_3\text{H}_2$, m. p. 159—161°, and with phosphenyl chloride in acetic acid solution to give *phenyl- β -benzoyl- α -styrylethylphosphinic acid*, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}(\text{CH}_2\text{Bz})\cdot\text{PPhO}\cdot\text{OH}$, m. p. 200°, which on oxidation with ozone gave benzaldehyde as one of the products, the combination thus taking place in the 1 : 4-position.

W. G.

New Organic Compounds of Phosphorus. IV. Phosphineimines. H. STAUDINGER and ERNST HAUSER (*Helv. Chim. Acta*, 1921, 4, 861—886).—It has been shown previously (Staudinger and Meyer, A., 1920, i, 106) that phosphines react with azides to give phosphazides which decompose spontaneously into phosphineimines: $\text{NPh}\cdot\text{N}:\text{N} + \text{PPh}_3 \rightarrow \text{NPh}\cdot\text{N}:\text{N}:\text{PPh}_3 \rightarrow \text{NPh}\cdot\text{PPh}_3$. By operating at a low temperature, it has now been found possible to effect the isolation of certain phosphazides. The behaviour of phosphines towards azides has been more fully examined.

The greatest reactivity towards phenyl- and benzoyl-azides is exhibited by tertiary phosphines, among which the alkyl compounds are the most active. Triphenylstibine, triphenylarsine, and a number of tertiary amines are found to be indifferent towards azides, and the substances thus conform to the general rule that phosphorus shows the most pronounced tendency to pass into the quinquivalent state. Triphenylphosphine and triethylphosphine react readily in cold dilute solution with a number of azides, and the reaction does not appear to be influenced to a marked degree by the presence of substituents in the latter. It therefore appears probable that the azides, the aliphatic diazo-compounds, and nitrous oxide, all of which behave in the same manner towards phosphines, are to be regarded as substances possessing the unsaturated group, $\text{:N}:\text{N}$, for which the name "azen" is proposed. The independence of the reaction on the presence of substituents in the nitrogenous component thus receives an explanation, since it is unlikely that the behaviour of the terminal nitrogen atom would be influenced greatly by a change in group at the third nitrogen atom.

The reactivity of the phosphineimines depends greatly on the presence of substituents. In general, derivatives of triethylphosphine are more active than those of triphenylphosphine and *N*-alkylated phosphineimines react more readily than the corres-

ponding *N*-arylated compounds. Benzoylated phosphineimines are relatively very stable. Generally, the phosphineimines are readily hydrolysed in accordance with the scheme $\text{NR}:\text{P}(\text{R})_3 + \text{H}_2\text{O} \rightarrow [\text{R}_3\text{P}(\text{OH})\cdot\text{NHR}] \rightarrow \text{R}_3\text{P}(\text{OH}) + \text{NH}_2\text{R}$. They yield salts with acids, some of which are stable towards cold water. They react readily with carbonylene derivatives containing twin double bonds (carbon dioxide, carbimides, and ketens), giving oxides of the tertiary phosphines, and a similar change is observed with thio-carbonylene compounds and other substances with twin double bonds (sulphur dioxide, etc.). On the other hand, they do not react in the cold with substances containing a simple carbonyl group even if the latter is unusually activated. Similarly, simple reactions are not observed with other substances containing an unsaturated bond, such as nitrosobenzene.

Phosphine does react with an ethereal solution of phenylazide or benzoylazide. Phenylphosphine and phenylazide evolve nitrogen violently after some time, but the other products have not been examined.

The following substances are described. *Triphenylphosphineimine azide*, $\text{PPh}_3\cdot\text{NH}\cdot\text{N}_3\text{H}$ (from triphenylphosphine and hydrogen azide in benzene solution), a colourless, crystalline powder, m. p. 196° (decomp.), which is stable in dilute aqueous solution, but is hydrolysed by dilute acids to triphenylphosphine oxide. *Triphenylphosphinemethylimine*, $\text{NMe}:\text{PPh}_3$, a colourless, crystalline mass which is very sensitive towards moisture, m. p. (about) $62\text{--}65^\circ$; it is converted by carbon dioxide into triphenylphosphine oxide and methylcarbimide and by carbon disulphide into triphenylphosphine sulphide and methylthiocarbimide. *Ethylazide*, a colourless, mobile liquid, b. p. 48° . *Triphenylphosphine-ethylimine*, a colourless, crystalline substance, m. p. (indefinite) 90° , which is transformed by ethyl iodide into the compound, $\text{C}_{22}\text{H}_{25}\text{NPI}$, m. p. $164\text{--}165^\circ$. Ethyl azidoacetate and triphenylphosphine give a glassy mass which is hydrolysed to triphenylphosphine oxide and glycine ester hydrochloride and is transformed by methyl iodide into the compound, $\text{C}_{23}\text{H}_{25}\text{O}_2\text{NPI}$, m. p. $103\text{--}104^\circ$.

Triphenylphosphinephenylimine is transformed by phenylcarbimide into triphenylphosphine oxide and carbodiphenyldi-imide, and by benzophenone, after prolonged heating at 150° , into triphenylphosphine oxide and benzophenoneaniline. Benzaldehyde at 100° gives triphenylphosphine oxide and benzylideneaniline. Sulphur dioxide very readily gives thionylaniline, whereas a reaction is not observed with nitrobenzene, diphenyl-*N*-phenylnitron, iodobenzene, or diphenylsulphoxide. *Triphenylphosphine- α -naphthylazide*, $\text{C}_{10}\text{H}_7\cdot\text{N}:\text{N}:\text{N}:\text{PPh}_3$, a yellow, crystalline powder, decomp. $63\text{--}65^\circ$. *Triphenylphosphine- α -naphthylimine*, a yellow, crystalline powder, m. p. $141\text{--}143^\circ$. *Triphenylphosphinebenzoylimine*, colourless crystals, m. p. $193\text{--}194^\circ$, which is unusually stable and exhibits very feebly basic properties. *Phenyldiethylphenylphosphazide*, $\text{NPh}:\text{N}:\text{N}:\text{PPhEt}_2$, a pale yellow, crystalline powder, m. p. $51\text{--}52^\circ$ (decomp.). *Phenyldiethylphosphinephenylimine*, $\text{NPh}:\text{PPhEt}_2$, a colourless, crystalline powder, m. p. $69\text{--}70^\circ$,
*d** 2

which has only feebly basic properties. *Phenyldiethylphosphinebenzoylimine*, colourless crystals, m. p. 73—74°, which decomposes into phenyldiethylphosphine oxide and benzonitrile when distilled. *Triethylphosphineimine azide*, $\text{PEt}_3\cdot\text{NH}\cdot\text{N}_3\text{H}$ (from triethylphosphine and hydrogen azide in light petroleum solution). *Triethylphosphinemethylimine*, $\text{NMe}\cdot\text{PEt}_3$, a colourless liquid, b. p. 94—96°, which is extremely sensitive to moisture. *Triethylphosphine-ethylimine*, a colourless liquid, b. p. 93.5°/11 mm., is highly reactive towards unsaturated compound; with carbon dioxide or ethyl thiocarbimide it gives *diethylcarbodi-imide*, $\text{NEt}\cdot\text{C}\cdot\text{NEt}$, a colourless liquid, b. p. 24.5°/11 mm. *Triethylphosphinephenylimine*, a pale yellow, oily liquid, b. p. 116°/0.08 mm. *Triethylphosphinebenzoylimine*, colourless crystals, m. p. 62.5—63°. Boiling triethylphosphine is readily acted on by nitrous oxide with formation of triethylphosphine oxide and nitrogen. *Triisoamylphosphine*, b. p. 131—132°/11 mm., combines with phenyl azide to yield *triisoamylphosphinephenylphosphazide*, $\text{P}(\text{C}_5\text{H}_{11})_3\cdot\text{N}\cdot\text{N}\cdot\text{NPh}$, a yellow, crystalline precipitate, m. p. 57—58°, which decomposes readily with formation of *triisoamylphosphinephenylimine*, a colourless liquid, b. p. 161°/0.04 mm. *Triisoamylphosphine-ethylimine*, a colourless liquid, b. p. 119°/0.23 mm.; the immediately formed phosphazide appears to be relatively stable, but it was not isolated. H. W.

Organic Compounds of Phosphorus. V. Action of Carbonylene Derivatives on Phosphazines. H. STAUDINGER and W. BRAUNHOLTZ (*Helv. Chim. Acta*, 1921, 4, 897—900).—It has been shown previously that phosphineimine derivatives, phosphinemethylene derivatives, and phosphine sulphides react with carbonylene or thiocarbonylene compounds to give phosphine oxides and substances of the types $\text{R}\cdot\text{N}\cdot\text{C}\cdot\text{X}$, $\text{CR}_2\cdot\text{C}\cdot\text{X}$, and $\text{S}\cdot\text{C}\cdot\text{X}$ respectively, and that the compounds just named are particularly reactive (cf. Staudinger and Meyer, A., 1920, i, 106; Staudinger, Rathsam, and Kjelsberg, A., 1921, i, 33). The work has now been extended to the phosphazines, but the results are generally unsatisfactory.

Triphenylphosphinebenzophenoneazine reacts readily with phenylcarbimide, but the primary product polymerises rapidly to a colourless product of high molecular weight which evolves phenylcarbylamine freely when heated. Reaction appears to occur thus: $\text{PPh}_3\cdot\text{N}\cdot\text{N}\cdot\text{CPh}_2 + \text{O}\cdot\text{C}\cdot\text{NPh} \rightarrow \text{PPh}_3\text{O} + \text{CPh}_2\cdot\text{N}\cdot\text{N}\cdot\text{C}\cdot\text{NPh} \xrightarrow{(\text{not } \text{N}_2 + \text{CPh}_2\cdot\text{C}\cdot\text{NPh} + \text{N}_2)} \text{polymeride} \rightarrow \text{C}\cdot\text{NPh} + (?)\text{CPh}_2\cdot\text{N}\cdot\text{N}$. Reaction proceeds similarly, but more slowly, with phenylthiocarbimide. With carbon disulphide the phosphazine gives polymerides of high molecular weight, which could not be purified instead of the desired compound, $\text{CPh}_2\cdot\text{N}\cdot\text{N}\cdot\text{C}\cdot\text{S}$, which might decompose into nitrogen and $\text{CPh}_2\cdot\text{C}\cdot\text{S}$. Carbon dioxide reacts very slowly with the phosphazine and does not appear to give diphenylketen. Sulphur dioxide gives a well-defined additive compound with triphenylphosphinebenzophenoneazine, from which the unchanged phosphazine can be regenerated by very cautious heating; at a slightly higher temperature, fission of the phosphazine

occurs with evolution of nitrogen and formation of triphenylphosphine oxide, benzophenone, and sulphur, probably in accordance

with the scheme:
$$\begin{array}{c} \text{PPh}_3 \cdot \text{N} \vdots \text{N} \vdots \text{CPh}_2 \\ | \qquad \qquad | \\ \text{O} \text{---} \text{S} \vdots \text{O} \end{array} \rightarrow \text{PPh}_3\text{O} + \text{N}(\text{S} \vdots \text{O}) \cdot \text{N} \vdots \text{CPh}_2$$

$\rightarrow \text{CPh}_2 \cdot \text{S} \vdots \text{O} \rightarrow \text{CPh}_2 \cdot \text{O} + \text{S}$. The reaction is highly complicated, since the phosphine sulphide and small amounts of thiobenzophenone are also produced. A complex change takes place also with thionylaniline, yielding the phosphine oxide and sulphide and an oil which gives benzophenone and many other products when heated. H. W.

Organic Compounds of Arsenic. VI. Fission of Alkylated or Arylated Arsenic Hydroxybromides. WILHELM STEINKOPF and GUSTAV SCHWEN (*Ber.*, 1921, **54**, [B], 2802—2811).—Under the influence of heat, the hydroxy-bromides of tertiary arsines suffer, in part, decompositions analogous to those experienced by the trialkylhalogenoammonium hydroxides and on this account appear to have the constitution $[\text{AsR}_3\text{Br}]\text{OH}$. On the other hand, their complete hydrolysis to trialkyl-(aryl)arsine oxides or their hydroxide and the pyrogenic fission to alkyl bromide and aryl and dialkyl-(aryl)-arsenious acid are more readily expressed by the formula $[\text{AsR}_3\text{OH}]\text{Br}$. The formulation with quinquevalent arsenic, $\text{AsR}_3\text{Br} \cdot \text{OH}$, gives a formal picture, but not an explanation of their reactions.

Phenyldimethylarsine hydroxybromide is decomposed when heated at 160—180° in a vacuum into phenyltrimethylarsonium bromide and phenylmethylarsenic acid, which remain in the flask, a distillate of higher boiling point which is converted by being heated with methyl iodide into phenyltrimethylarsonium iodide, phenyltrimethylarsonium tri-iodide, and (?) phenyldibromoarsine [which thus in accordance with the observations of Steinkopf and Schwen (A., 1921, i, 694) must contain phenyldimethylarsine and phenylmethylbromoarsine], and a distillate of lower boiling point containing methyl bromide, water, and methyl alcohol. Fission under atmospheric pressure at about 195° gives a distillate containing methyl bromide, methyl alcohol, and aqueous hydrobromic acid and a residue consisting of arsenious acid and phenyltrimethylarsonium bromide which are insoluble in ether together with phenyldimethylarsine and phenylmethylbromoarsine and diphenylbromoarsine, which dissolve in ether and are transformed by methyl iodide into phenyltrimethylarsonium iodide and tri-iodide, diphenyldimethylarsonium tri-iodide, and diphenyliodoarsine. The changes are represented by the schemes: (1) $\text{AsPhMe}_2\text{Br} \cdot \text{OH} \rightarrow \text{AsPhMe}_2 + \text{HOB}r \rightarrow \text{HBr} + \text{O}$; (2) $\text{AsPhMe}_2\text{Br} \cdot \text{OH} \rightarrow \text{AsPhMeBr} + \text{MeOH}$; (3) $2\text{AsPhMe}_2\text{Br} \cdot \text{OH} \rightarrow 2\text{MeBr} + 2\text{AsPhMe} \cdot \text{OH} \rightarrow (\text{AsPhMe})_2\text{O} + \text{H}_2\text{O}$. The phenylmethylarsine oxide reacts with the liberated hydrogen bromide thus, $(\text{AsPhMe})_2\text{O} + 2\text{HBr} = 2\text{AsPhMeBr} + \text{H}_2\text{O}$, whereas the phenyltrimethylarsonium bromide is a secondary product derived from methyl bromide and phenyldimethylarsine. The changes (1) and

(2) are similar to those suffered by trialkylhalogenoammonium hydroxides.

Triphenylarsine hydroxy-bromide is decomposed in a vacuum at about 250°, giving two distillates, the more volatile of which contains bromobenzene, water, and hydrobromic acid, whereas the less volatile is a mixture of bromobenzene, triphenylarsine, and diphenylbromoarsine, since it is converted by methyl iodide into triphenylmethylarsonium tri-iodide and diphenyldimethylarsonium tri-iodide. The presence of phenol could not be established. Fission, which is not quantitative, occurs in accordance with the schemes: $\text{AsPh}_3\text{Br}\cdot\text{OH} \rightarrow \text{AsPh}_3 + \text{HOBr} \rightarrow \text{HBr} + \text{O}$ and $\text{AsPh}_3\text{Br}\cdot\text{OH} \rightarrow 2\text{PhBr} + \text{H}_2\text{O} + (\text{AsPh}_3)_2\text{O} \xrightarrow{2\text{HBr}} 2\text{AsPh}_2\text{Br} + \text{H}_2\text{O}$.
H. W.

Organic Compounds of Arsenic. V. Action of Cyanogen Bromide on Phenylated Tertiary Arsines. WILHELM STEINKOPF and GUSTAV SCHWEN (*Ber.*, 1921, **54**, [B], 2791—2801; cf. A., 1921, i, 694).—Phenylated tertiary arsines unite with cyanogen bromide in much the same manner as do the trialkylarsines (Steinkopf and Müller, A., 1921, i, 404) to give cyanobromides which undergo normal fission into alkyl haloid and cyanoarsine except in the case of triphenylarsine cyanobromide, the decomposition of which follows a complex course, leading, in part, to regeneration of the initial material. The ability of the di- and tri-phenylarsines to form bromocyanides, whereas the corresponding amines appear to be indifferent towards cyanogen bromide, is attributed to the more positive character of the arsenic atom.

Phenyldimethylarsine bromocyanide, $\text{AsPhMe}_2\text{Br}\cdot\text{CN}$, a colourless, microcrystalline powder, m. p. 94—96°, is prepared by the gradual addition of a solution of bromocyanogen in dry light petroleum to phenyldimethylarsine dissolved in the same medium, the apparatus used being that described by Wolfram (A., 1921, ii, 395). It is converted by moisture into *phenyldimethylarsine hydroxy-bromide*, $\text{AsPhMe}_2\text{Br}\cdot\text{OH}$, lustrous needles, m. p. 162°, which is converted by silver oxide into *phenyldimethylarsine dihydroxide*. The latter is transformed readily into *phenyldimethylarsine hydroxy-chloride*, colourless needles, m. p. 163°, *phenyldimethylarsine hydroxy-picrate*, needles, m. p. 132°, and *phenyldimethylarsine hydroxy-iodide*, yellow needles, m. p. 117°. *Phenyldimethylarsine iodocyanide*, yellow, crystalline powder, m. p. 93°, is prepared from its components and is converted by moisture into the hydroxy-iodide just described. Phenyldimethylarsine bromocyanide is decomposed by heat into *cyanophenylmethylarsine*, $\text{AsPhMe}\cdot\text{CN}$, b. p. 127°/11 mm.

Diphenylmethylarsine bromocyanide, $\text{AsPh}_2\text{MeBr}\cdot\text{CN}$, a colourless, voluminous, crystalline powder, m. p. 61—62°, is prepared from its components; it is converted by moisture into *diphenylmethylarsine hydroxy-bromide*, transparent crystals, m. p. 118° (corresponding *picrate*, m. p. 137°). The bromocyanide is converted by heat into methyl bromide and *diphenylcyanoarsine*, $\text{AsPh}_2\cdot\text{CN}$, m. p. 31·5°, b. p. 191°/11 mm.

Triphenylarsine bromocyanide, colourless, relatively coarsely

crystalline powder, m. p. (indefinite) 130—140° after softening at 120°, is converted by moisture into triphenylarsine hydroxybromide, m. p. 168° (corresponding *picrate*, yellow needles, m. p. 162—163°).
H. W.

Aromatic Arsenic Compounds. IX. Diazoamino-compounds of *p*-Aminophenylarsinic Acid and its Derivatives.

WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1921, **43**, 1632—1645; cf. A., 1920, i, 107, 108, 110, 111, 114, 116, 117).—It has previously been observed by Ehrlich and Berthelm that *p*-aminophenylarsinic acid can be diazotised and the resulting diazo-compound coupled without difficulty, yielding azo-dyes (cf. A., 1907, i, 812). The authors now show that this reaction can be extended to the preparation of well-defined diazo-amino-compounds containing the arsenic acid residues, and several such groups of compounds have been prepared and are described. For the treatment of experimental trypanosomiasis these compounds possess certain inherent disadvantages, and their use has been discontinued. The following compounds are described.

Diazobenzene(4-arsinic acid)dimethylamine, m. p. 182° (decomp.), giving a *sodium* salt; *diazobenzene(4-arsinic acid)diethylamine*, m. p. 195—200° (decomp.), and its *sodium* salt; *diazobenzene(4-arsinic acid)piperidine*, m. p. 162—163°, and its *sodium* salt; *bisdiazobenzene(4-arsinic acid)pentamethylenetetramine*, m. p. 210—212° (decomp.), and its *sodium* salt.

Diazobenzene(4-arsinic acid)aniline, m. p. 112—113° (decomp.), and its *sodium* salt; *diazobenzene(4-arsinic acid)methylaniline*, m. p. 160—162° (decomp.), and its *sodium* salt; *diazobenzene(4-arsinic acid)-p-toluidine*, m. p. 130—132°, and its *sodium* salt; *diazobenzene(4-arsinic acid)-4'-chloroaniline*, m. p. 177° (decomp.), and its *sodium* salt; *diazobenzene(4-arsinic acid)-o-anisidine*, m. p. 95—99° (decomp.), and its *sodium* salt; *diazobenzene(4-arsinic acid)-p-anisidine*, m. p. 116—119° (decomp.), and its *sodium* salt; *diazobenzene(4-arsinic acid)-4'-aminoacetanilide*, m. p. 165—170° (decomp.), and its *sodium* salt; *diazobenzene(4-arsinic acid)-4'-aminophenol*, its *benzoic* ester, m. p. 155—158° (decomp.), and its *sodium* salt; *diazobenzene(4-arsinic acid)-4'-aminoacetophenone*, m. p. 177—178° (decomp.), and its *sodium* salt.

Diazobenzene(4-arsinic acid)-o-aminobenzoic acid, m. p. 160° (decomp.), and its *mono-* and *di-sodium* salts; *diazobenzene(4-arsinic acid)-m-aminobenzoic acid*, m. p. 141°, and its *mono-* and *di-sodium* salts; *diazobenzene(4-arsinic acid)-p-aminobenzoic acid*, and its *monosodium* salt; *methyl diazobenzene-4-arsinic acid-3'-amino-6'-methoxybenzoate*, m. p. 90—95° (decomp.), and the free acid, m. p. 140° (decomp.), and its *disodium* salt; *diazobenzene(4-arsinic acid)-3'-aminoanisic acid*, m. p. 150—155° (decomp.), its *methyl* ester, m. p. 150° (decomp.), and its *disodium* salt; *methyl diazobenzene(4-arsinic acid)-6'-aminopiperonylate* and the corresponding *sodium* salt; *diazobenzene(4-arsinic acid)-4'-aminocinnamic acid*, m. p. 155—160° (decomp.), its *ethyl* ester, m. p. 155—160° (decomp.), its *disodium* salt, and the *sodium* salt of the *ethyl* ester;

diazobenzene(4-arsinic acid)-4'-aminophenylarsinic acid, m. p. 154° (decomp.), and its *mono-* and *di-sodium* salts.

Diazobenzene(4-arsinic acid)phenylglycine and its *sodium* salt; *diazobenzene(4-arsinic acid)-p-tolylglycine*, m. p. 148—149° (decomp.), and its *sodium* salt; *diazobenzene(4-arsinic acid)benzylglycine*, m. p. 155—160° (decomp.); *diazobenzene(4-arsinic acid)-4'-methoxyphenylglycine*, its *sodium* salt, its *ethyl* ester and the *sodium* salt of the ester; *diazobenzene(4-arsinic acid)-4'-ethoxyphenylglycine*, its *sodium* salt, its *ethyl* ester, and the *sodium* salt of the ester.

Diazobenzene(4-arsinic acid)-4'-aminophenoxyacetic acid, m. p. 132° (decomp.), its *disodium* salt, its *ethyl* ester, m. p. 132—133° (decomp.), and the *sodium* salt of the latter; the *acetamide*, m. p. 162° (decomp.), and its *sodium* salt, and the *acetomethylamide*, m. p. 170° (decomp.), and its *sodium* salt; *diazobenzene(4-arsinic acid)-4'-methylaminophenoxyacetic acid*, m. p. 155—160° (decomp.); *diazobenzene(4-arsinic acid)-3'-methyl-4'-aminophenoxyacetic acid*, its *disodium* salt, its *methyl* ester, and the *sodium* salt of the latter; *diazobenzene(4-arsinic acid)-4'-amino-2'-methylphenoxyacetic acid*, its *disodium* salt, its *methyl* ester, m. p. 143—144° (decomp.), and the *sodium* salt of the latter; *methyl diazobenzene(4-arsinic acid)-4'-amino-2':5'-dimethylphenoxyacetate*, m. p. 120° (decomp.), and the *disodium* salt of the free acid; *methyl diazobenzene(4-arsinic acid)-4'-amino-2'-methyl-5'-isopropylphenoxyacetate*, m. p. 145° (decomp.), and the *disodium* salt of the free acid; *methyl diazobenzene(4-arsinic acid)-4'-amino-3'-methyl-6'-isopropylphenoxyacetate* and the *disodium* salt of the free acid; *diazobenzene(4-arsinic acid)-2'-bromo-4'-aminophenoxyacetic acid*, m. p. 120° (decomp.), its *methyl* ester, m. p. 154—155° (decomp.), and its *disodium* salt; *diazobenzene(4-arsinic acid)-6-bromo-4-amino-2-methylphenoxyacetic acid*, m. p. 155° (decomp.), its *disodium* salt, and its *methyl* ester, m. p. 188° (decomp.); *diazobenzene(4-arsinic acid)-4'-amino-6'-acetophenoxyacetic acid*, its *disodium* salt, and its *methyl* ester, m. p. 155° (decomp.); *6-diazo-o-toluene(3-arsinic acid)-p-aminophenoxyacetic acid*, its *disodium* salt, and its *methyl* ester, m. p. 130—132° (decomp.); *diazo-2-bromobenzene(4-arsinic acid)-p-aminophenoxyacetic acid*, m. p. 130° (decomp.), its *disodium* salt, its *methyl* ester, m. p. 123—125° (decomp.), and the *sodium* salt of the ester. W. G.

Aromatic Arsenic Compounds. X. Azo-dyes derived from *p*-Aminophenylarsinic Acid. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1921, **43**, 1646—1654; cf. preceding abstract).—It has been found that certain classes of aromatic amino-compounds yield aminoazo-dyes at once when coupled with diazotised arsanilic acid or give diazoamino-compounds which rapidly undergo rearrangement, giving the dyes. In most cases the reaction between the amino-compound and the diazotised arsanilic acid proceeded smoothly, but the isolation and purification of the resulting dyes was often difficult. The following compounds are described:—

1-*Amino-2-methoxynaphthalene-4-azobenzene-4'-arsinic acid*; 1-

amino-4-methoxynaphthalene-2-azobenzene-4'-arsinic acid, m. p. 195° (decomp.).

4-Methylamino-5-carboxybenzeneazobenzene-4'-arsinic acid and its mono- and di-sodium salts; 4-ethylamino-5-carboxybenzeneazobenzene-4'-arsinic acid and its monosodium salt; 4-isoamylamino-5-carboxybenzeneazobenzene-4'-arsinic acid, its hydrochloride, and its monosodium salt; 4-amino-2:3-dimethoxy-5-carboxybenzeneazobenzene-4'-arsinic acid, its hydrochloride, and its monosodium salt; 2-amino-4:5-dimethoxy-3-carboxybenzeneazobenzene-4'-arsinic acid, its hydrochloride, and its monosodium salt.

4-Benzene(4'-arsinic acid)azo-phenylglycine, m. p. 170—175° (decomp.), and its hydrochloride; 4-benzene(4'-arsinic acid)azo-2-methylphenylglycine, m. p. 157° (decomp.), and its hydrochloride; 4-benzene(4'-arsinic acid)azo-2-methoxyphenylglycine, m. p. 167° (decomp.), and its sodium salt; 4-benzene(4'-arsinic acid)azo-2-ethoxyphenylglycine, m. p. 245—250° (decomp.), and its sodium salt; α' -benzene(4-arsinic acid)azo- α -naphthylglycine, m. p. 275° (decomp.), and its disodium salt.

4-Benzene(4'-arsinic acid)azo-phenylaminomethanesulphonic acid, $\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{CH}_2 \cdot \text{SO}_3\text{H}$, m. p. 187—189°, and its disodium salt; 4-benzene(4'-arsinic acid)azo-2-methoxyphenylaminomethanesulphonic acid, m. p. 158—160° (decomp.), and its disodium salt.

6-Benzene(4'-arsinic acid)azo-3-aminophenoxyacetic acid,

$\text{AsO}_3\text{H}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{N} \cdot \text{N} \cdot \text{C}_6\text{H}_3(\text{NH}_2) \cdot \text{O} \cdot \text{CH}_2 \cdot \text{CO}_2\text{H}$,

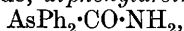
its hydrochloride, and its monosodium salt; 6-benzene(4'-arsinic acid)azo-3-amino-4-methylphenoxyacetic acid, m. p. 242—243° (decomp.), its hydrochloride, and its monosodium salt; 4-benzene(4'-arsinic acid)azo-5-amino-2-methylphenoxyacetic acid, m. p. 187—188° (decomp.), its hydrochloride, and its monosodium salt; 4-benzene(4'-arsinic acid)azo-3-amino-6-methoxyphenoxyacetic acid, and its hydrochloride; 4-amino-6-methoxy-3-[phenyl-(4'-arsinic acid)azo]-phenoxyacetic acid, its hydrochloride and its monosodium salt; 5-benzene(4'-arsinic acid)azo-4-amino-1:2-bisphenoxyacetic acid, and its monosodium salt; β -benzene(4-arsinic acid)azo- α -amino- α' -naphthoxyacetic acid, m. p. 285° (decomp.), and its disodium salt; α' -benzene(4-arsinic acid)azo- α -amino- β -naphthoxyacetic acid and its disodium salt; 5-benzene(4'-arsinic acid)azo-2-hydroxy-phenoxyacetic acid and its monosodium salt.

W. G.

Preparation of Dimethyl- and Diphenyl-arsinecarboxylic Acids. ANDRÉ JOB and HENRI GUINOT (Fr. Patents 521119 and 521469; from *Chem. Zentr.*, 1921, iv, 870—871).—Cacodyl cyanide, $\text{AsMe}_2 \cdot \text{CN}$, and diphenylarsine cyanide, $\text{AsPh}_2 \cdot \text{CN}$, respectively, are submitted to hydrolysis by the usual methods for the preparation of carboxylic acids from nitriles. By hydrolysis of cacodyl cyanide with dilute sulphuric acid and subsequent neutralisation with calcium hydroxide, the calcium salt of dimethylarsinecarboxylic acid is obtained, from which the free acid, $\text{AsMe}_2 \cdot \text{CO}_2\text{H}$, is formed by decomposition with acids and recrystallisation from an appropriate solvent. It reddens blue litmus and gives stable salts with

d**

a number of common metals and alkaloids. *Diphenylarsinecarboxylic acid*, $\text{AsPh}_2\cdot\text{CO}_2\text{H}$, is similarly prepared. By treatment of diphenylarsine cyanide with hydrogen peroxide or substances forming hydrogen peroxide, *diphenylarsinoformamide*,



is formed with evolution of oxygen and may be obtained by crystallisation from suitable solvents. It is decomposed by nitrous acid, giving nitrogen and diphenylarsinecarboxylic acid. G. W. R.

Organo-chromium Compounds. II. Abnormal Salt Formation of Chromium Pentaphenyl Hydroxide. Chromium Tetraphenyl Salts (Elimination of a Phenyl Group). FRANZ HEIN (*Ber.*, 1921, **54**, [B], 2708—2727; cf. A., 1921, i, 826).—It has been shown previously that chromic chloride or chromyl chloride is converted by magnesium phenyl bromide in cold ethereal solution into a mixture of bromides from which chromium pentaphenyl bromide can be isolated in small amount and in an impure state; the most definite compound of the series is chromium pentaphenyl hydroxide, $\text{CrPh}_5\cdot\text{OH}\cdot 4\text{H}_2\text{O}$. Attempts to isolate the pure pentaphenyl salts by the action of acids or salts on the crystalline base lead in a surprising manner to the loss of a phenyl group and formation of chromium tetraphenyl salts, the only exception to this regularity being found in the production of the pentaphenyl carbonate. The tetraphenyl salts, in so far as they are soluble in a mixture of alcohol and water, yield neutral solutions and are therefore not hydrolysed. Their normal behaviour is shown by the observation that the haloids give immediate precipitates with silver nitrate solution, and, with suitable acids, give precipitates of the corresponding sparingly soluble chromium tetraphenyl salts. They have also a marked tendency towards the formation of complex salts and polyiodides. Attempts to isolate chromium tetraphenyl hydroxide by the electrolysis of an alcoholic solution of the iodide were only partly successful. The author considers that the phenyl group is liberated in the nascent condition; it is present in the solutions largely in the form of phenol (the formation of which is attributed to the action of dissolved or atmospheric oxygen and, to some extent of water), of diphenyl and of a solid acidic substance which could not be characterised completely.

The action of a freshly-prepared, very dilute alcoholic solution of chromium pentaphenyl hydroxide on a dilute, aqueous alcoholic solution of Reinecke's salt leads to the precipitation of *chromium tetraphenylchromitetraethiocyanatodiammine*, $\text{Ph}_4\text{Cr}\left[\text{Cr}\begin{smallmatrix}(\text{CNS})_4 \\ (\text{NH}_3)_2\end{smallmatrix}\right]$, thin, golden-yellow leaflets, m. p. 175° (decomp.), when placed in a bath at 165° . The salt is also obtained from the β -modification of the base. It is somewhat sensitive to rise in temperature and to prolonged desiccation over concentrated sulphuric acid. It is extraordinarily stable when preserved beneath alcohol or mixtures of alcohol and water. Determinations of the molecular weight in freezing nitrobenzene indicate extensive dissociation, which is presumably ionic in character. A compound of chromium tetra-

phenyl iodide with chloroform, $\text{CrPh}_4\text{I} \cdot \text{CHCl}_3$, dark brownish-red, rhombic leaflets, is prepared conveniently by agitating the base with hydriodic acid or aqueous potassium iodide solution and chloroform, and is isolated from the chloroform extract. If the latter is treated with two to three times its volume of ether, a second salt ($+\frac{1}{2}\text{CHCl}_3$) separates. The solvent can be removed by gentle heating, leaving *chromium tetraphenyl iodide*, m. p. 178° (decomp.), after being placed in a bath at $165\text{--}170^\circ$. The salt appears to be somewhat associated in boiling chloroform, but dissociated in freezing phenol. It forms complex salts with silver iodide or mercuric chloride, which, however, are remarkably less stable than the parent substance. It gives a *periodide*, CrPh_4I_5 , chocolate-brown prisms, when its solution in alcohol or chloroform is slowly added to an alcoholic solution of iodine. *Chromium tetraphenyl bromide* is prepared in the same manner as the iodide; it forms orange-coloured, rectangular platelets ($+\frac{1}{2}\text{CHCl}_3$) which readily loses the chloroform and then has m. p. 136° , and is considerably less stable than the corresponding iodide. *Chromium tetraphenyl perchlorate*, $\text{CrPh}_4\text{ClO}_4$, is prepared from the pentaphenyl base and perchloric acid in aqueous alcoholic solution; it forms orange-red crystals which are very unstable when dry and explode when gently warmed or lightly struck. *Chromium tetraphenyl dichromate*, $(\text{CrPh}_4)_2\text{Cr}_2\text{O}_7$, golden-orange leaflets, is most conveniently prepared by mixing solutions of the base and ammonium dichromate in methyl alcohol; it is somewhat unstable and decomposes in a few days when exposed to the air or preserved over calcium chloride, very readily in the presence of phosphoric oxide. It explodes when heated.

Chromium pentaphenyl carbonate, $(\text{CrPh}_5)_2\text{CO}_3 \cdot 6\text{H}_2\text{O}$, orange-coloured leaflets, is most readily prepared by the preservation of the concentrated aqueous mother-liquors from the preparation of the base exposed to air and in an ice-chest. It has m. p. (indefinite) $118\text{--}119^\circ$, after softening at about 108° when placed in a bath pre-heated at 95° . A *dihydrate* and a *monohydrate* are also described.

H. W.

Organo-chromium Compounds. III. Chromium Triphenyl Hydroxide and its Salts. FRANZ HEIN (*Ber.*, 1921, 54, [B], 2727—2744; cf. A., 1921, i, 826 and preceding abstract).—Further examination of the solution of bases obtained by the action of silver oxide on the chromium polyphenyl bromide has disclosed the presence of chromium triphenyl hydroxide which remains dissolved after the separation of chromium pentaphenyl hydroxide. It is characterised by its extreme solubility in water. The solutions leave a strongly alkaline, syrupy, transparent, reddish-black mass when evaporated. In general, they are very unstable when highly concentrated, but may be preserved almost indefinitely when dilute and in the absence of light and air. Characteristic precipitates are obtained by the addition of many mineral acids or their alkali salts, but these are generally amorphous; it is remarkable that their colour resembles closely that of the corre-

sponding tetra- and penta-phenyl compounds. The most characteristic salt is *chromiumtriphenylchromitetra-thiocyanatodiammine*, $\text{CrPh}_3\left[\text{Cr}\left(\text{NH}_3\right)_2\left(\text{SCN}\right)_4\right]$, which is prepared by adding an aqueous alcoholic solution of Reinecke's salt to a similar solution of the base, until the precipitate commences to become distinctly flocculent, filtering and adding an excess of Reinecke's salt to the filtrate. The second amorphous precipitate becomes microcrystalline when preserved beneath the mother-liquor. It is preferably preserved beneath alcohol, when it remains unchanged for a long period, whereas, when washed with alcohol and ether and left exposed to air, it becomes discoloured and has an odour of diphenyl after three to four days. It crystallises with $2\text{H}_2\text{O}$, of which approximately $\frac{1}{2}$ molecule is lost on exposure to air, whereas a molecule is lost when it is dried immediately after its preparation over concentrated sulphuric acid. The monohydrate loses a further quantity of water when preserved over concentrated sulphuric acid, but decomposition occurs simultaneously. If, however, the freshly-prepared dihydrate is exposed to air in the absence of light and warmth for one to one and a half days and is then placed in a vacuum over concentrated sulphuric acid, it rapidly becomes completely dehydrated, giving a *salt* which can be preserved unchanged in the absence of air for a few hours, but which decomposes rapidly on exposure to air. The monohydrate and dihydrate have m. p. 168° when placed in a bath pre-heated to 155° . Like the corresponding tetraphenyl compound, they are transformed by great pressure into a viscous, resin-like mass. Determinations of the molecular weight of the dihydrate in freezing nitrobenzene gave abnormally low results, which are explained by the loss of one molecule of water; under similar conditions, the monohydrate behaves as if very extensively dissociated electrolytically.

Chromium triphenyl iodide, $\text{CrPh}_3\text{I}\cdot\text{Et}_2\text{O}$, is prepared by the addition of potassium iodide or hydriodic acid to an aqueous solution of the base in the presence of chloroform, into which the iodide passes. The concentrated chloroform solution is poured, after being dried, into ether; the iodide is thereby precipitated initially as an oil which gradually becomes solid. The hygroscopic salt can be preserved for a considerable period in a vacuum over concentrated sulphuric acid, but is unstable in the presence of dry or moist air. Like the corresponding tetraphenyl compound, the salt gives an amorphous additive *compound* with mercuric chloride and an amorphous *periodide*.

Chromium triphenyl perchlorate, $\text{CrPh}_3\text{ClO}_4$, can be prepared in the microcrystalline form by the fractional precipitation of a solution of chromium triphenyl hydroxide with dilute perchloric acid. It is preferably preserved in an ice-chest under a mixture of alcohol and ether; in the dry state, it is more labile and explosive than the corresponding tetraphenyl compound.

The results described in this and the preceding communication show that chromium pentaphenyl and triphenyl bromides are present in the "crude bromide." The latter greatly predominates

when the original action is too prolonged or when the temperature is allowed to rise; both bromides, however, appear to be primary products. In addition, small amounts of chromium phenyl compounds are formed which are insoluble in alcohol but readily soluble in chloroform to intensely olive-green solutions. They appear to be highly complex, probably containing several chromium atoms with differing valency within the molecule. They are formed invariably by the auto-decomposition of the orange chromium phenyl compounds, particularly when the process is oxidative. This fact appears to explain the greater extent of their formation when chromyl chloride in place of chromic chloride is treated with magnesium phenyl bromide.

H. W.

Physiological Chemistry.

Subcutaneous Absorption of Oxygen in Mountain Climbing and Aviation. RAOUL BAYEUX (*Compt. rend.*, 1921, 173, 937—939).—The resistance to subcutaneous injection of oxygen diminishes as the height increases in the ascent of a mountain. That this is not due to the fatigue of climbing is shown by experiments conducted in a decompression chamber. In the latter experiment, the decrease in resistance was accompanied by a slight increase in the beat of the pulse and a very slight increase in the velocity of respiration. The reverse process occurs as the altitude decreases or the pressure in the chamber increases. The injection of oxygen was not accompanied by formation of a gaseous tumour and the oxygen was rapidly absorbed. W. G.

Influence of Temperature on the Reaction of the Blood. JOSÉ M. DE CORRAL (*Biochem. Z.*, 1921, 117, 1—9).—The reaction of blood at 38° is $P_H=0.22$ lower than at 18°, in agreement with Michaelis and Davidoff's findings (*A.*, 1912, ii, 1184), provided that the blood is in equilibrium with carbon dioxide at 38° and then measured at 18°. If the blood is in equilibrium with carbon dioxide at both temperatures, then the P_H is independent of temperature as found by Hasselbalch (*A.*, 1917, i, 490). The results with serum still show discrepancies. H. K.

Excretion of Sweat and the Composition of the Blood. EBERHARD WILBRAND (*Biochem. Z.*, 1921, 118, 61—66).—Heavy perspiration is followed by a thickening of the blood; parallel with this there is a loss of protein and sodium chloride from the serum. The residual (non-precipitable) nitrogen of the blood and the content of fat are unaltered. H. K.

Concentration of the Blood. II. The Action of Diuretics of the Purine Group on the Exchange of Substances between the Tissues and the Blood. W. NONNENBRUCH (*Arch. exp. Path. Pharm.*, 1921, 91, 332—341).—Theophylline, theocine, and

euphylline cause the blood to lose water, which is soon replaced. The serum proteins increase often to a very large extent, not only relatively, but absolutely, and this stream of protein from the tissues into the serum even occurs after extirpation of the kidneys.

G. B.

An Effect of the Ingestion of Colostrum on the Composition of the Blood of New-born Calves. PAUL E. HOWE (*J. Biol. Chem.*, 1921, 49, 115—118).—The blood of the new-born calf does not contain euglobulin or pseudo-globulin I, but after ingestion of colostrum relatively large amounts of these proteins are present. If no colostrum is given, they are only formed slowly. The function of colostrum seems to be to supply them rapidly.

G. B.

Calcium Content of Blood Plasma and Corpuscles in the New-born. MARTHA R. JONES (*J. Biol. Chem.*, 1921, 49, 187—192).—The whole blood contains 8.8 mg., the corpuscles 5.0 mg., the plasma 12.3 mg. of calcium per 100 c.c. The average for plasma is higher and for corpuscles and whole blood less than for older children. In the first twelve days of life, the average percentage of red cells dropped from 55 to 42%.

G. B.

Action of Pilocarpine on the Composition of the Blood. A. BORNSTEIN and ROBERT VOGEL (*Biochem. Z.*, 1921, 118, 1—14).—Pilocarpine administered to dogs alters the distribution of water in the body, the blood showing increased content of hæmoglobin, corpuscles, and serum proteins. This change is only partly to be attributed to excretion of water from the body. In addition, pilocarpine produces hyperglycæmia in dogs and rabbits. Extirpation of the pancreas has no inhibiting action on these results, but atropine is antagonistic to all.

H. K.

Blood and Metabolism Studies with Radium Emanations. J. HAUSENSTEIN (*Munch. med. Woch.*, 1921, 68, 809—810; from *Chem. Zentr.*, 1921, iii, 795).—Observations were made of the effect of radium radiations on the numbers of red and white blood corpuscles and on the behaviour of the individual leucocyte forms in cases of carcinoma of the uterus. Red corpuscles disintegrate and decrease in amount under the influence of γ -rays. Leucocytes increase in number. There is a relative and absolute increase in neutrophiles and a relative although not absolute decrease in lymphocytes. No effect was observed on the large, white blood cells, and the mononuclear, eosinophile, and basophile cells.

The metabolism experiments showed that the nitrogen content of the urine decreased markedly during and after treatment. Similar results were obtained for uric acid. Acetone and acetoacetic acid were not found. The figures for indican were abnormal and slight albuminuria was observed.

G. W. R.

Permeability of the Red Corpuscles of Human Blood for Anions. ERNST WIECHMANN (*Pflüger's Archiv*, 1921, 189, 109—125; from *Chem. Zentr.*, 1921, iii, 895).—In native human blood the chlorine ion is distributed between corpuscles and plasma in

the ratio 1 : 2.1. This distribution is unaltered by isotonic sodium chloride solution. In the presence of sodium sulphate solution, chlorine ions pass out from the corpuscles. The partition ratio between corpuscles and suspending liquid is found to be 1 : 19.7 for the sulphate ion, 1 : 9.7 for the phosphate ion, and 1 : 3.1 for the bromine ion and the chlorine ion, under similar conditions of experiment. The permeability for the phosphate ion increases with the temperature. Permeability for the bromine ion is decreased by the presence of calcium. "Cyanol," "light green-F.S.," "setopalm," and "ponceau 2R" were scarcely absorbed after two hours.

G. W. R.

Quinine Hæmolysis. ALFRED LUGER (*Biochem. Z.*, 1921, **117**, 145—152).—When treated with quinine, blood corpuscles show a diminished resistance to acids and an increased resistance to alkalis. In the presence of saline solution, such corpuscles show a diminished resistance to water, but an increased resistance to saponin.

H. K.

The Amino-acid Content of Plasma and Corpuscles according to Bang. A. COSTANTINO (*Biochem. Z.*, 1921, **117**, 140—144).—Polemical against I. Bang (cf. A., 1916, i, 528).

H. K.

Normal Sugar Content of the Blood. P. J. CAMMIDGE, J. A. C. FORSYTH, and H. A. HOWARD (*Brit. Med. J.*, 1921, ii, 586—590).—As the result of observations on the blood-sugar of man and animals, the authors hold the view that the liver contains a diastatic ferment the action of which is reversible. In the fasting state, the glycogenolytic activities of this enzyme are largely inhibited by an anti-ferment formed by the pancreas, the impermeability of the resting liver cells to sodium chloride, and the reaction of the blood and liver cells. After the taking of food, when acids enter the duodenum, the secretion formed stimulates the liver cells to produce bile, thus permitting the entrance of sodium chloride, which activates the diastatic ferment. At the same time, it causes a secretion of alkaline pancreatic juice which combines with the acid gastric contents, forming acid salts and sodium chloride, which pass to the liver and increase the activity of the diastatic ferment. It also interferes with the formation of the internal secretion of the pancreas, thus diminishing its inhibitory effect on glycogenolysis in the liver. Carbohydrates reaching the liver from the intestine or formed from proteins in the liver are converted into glycogen by the diastatic ferment, the efficiency of the process depending on the extent to which the glycogenolytic action of the enzyme is inhibited by the internal secretion of the pancreas. Unless the power of glycogen formation possessed by the liver is exceeded, sugar as such, or formed from starch in the intestine, does not pass into the general circulation or play any direct part in the rise of blood-sugar following food.

G. B.

Lactic Acid in the Blood of Dogs in Exercise. A. B. HASTINGS (*Proc. Soc. Exp. Biol. Med.*, 1921, **18**, 306—307).—Severe exercise of short duration increases the lactic acid, but prolonged

moderate exercise decreases it. The significance of lactic acid as a primary factor in physiological fatigue not carried to exhaustion seems to be an open question (cf. similar results in man, Ryffel, A., 1910, ii, 325). G. B.

Distribution of Uric Acid in the Blood. R. C. THEIS and S. R. BENEDICT (*J. Lab. Clin. Med.*, 1921, **6**, 680—683).—Uric acid was estimated in plasma and corpuscles in 104 cases, 51 of which showed equal distribution, 45 showed plasma uric acid greater than corpuscle uric acid, and 8 the converse. This relationship holds for oxalated and defibrinated blood, and does not depend on pathological conditions. G. B.

Use of Frogs to Demonstrate the Anticoagulating Action of Nucleic Acids. DOYON (*Compt. rend.*, 1921, **173**, 1120—1122).—The frogs are decapitated and sixty drops of their blood allowed to drop into 0.5 c.c. of a solution containing 0.0033 gram of nucleic acid, 0.0025 gram of sodium carbonate, and 0.002 gram of sodium chloride. No coagulation occurs. Other experiments with frogs are described. W. G.

Changes in the Blood after Oral Administration of Sodium Chloride. G. SAMSON (*Biochem. Z.*, 1921, **118**, 55—60).—Oral administration of sodium chloride is followed by increased sodium chloride content of the blood-serum, the major portion, however, passing into the tissues. There is also an increase of the protein content of the blood. H. K.

Are there Protective Enzymes against Polysaccharides? EMIL ABDERHALDEN (*Biochem. Z.*, 1921, **117**, 161—165).—Mainly polemical against Herzfeld and Klinger (cf. A., 1921, i, 286). H. K.

The Fate of some Polysaccharides in the Digestive Tract of Mammals. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, **117**, 227—240).—Fæcal constituents are able to convert inulin, lichenin, and hemicellulose into acetic, propionic, and butyric acids. Lactic acid also appears. The agent is probably bacterial, as pure cultures, for example, *Bacillus coli*, *B. lactis*, *B. proteus*, and *B. subtilis*, have the same power. H. K.

Hydrolysis of some Polysaccharides (Inulin, Lichenin, and Hemicellulose) in the Digestive Tract of Mammals. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, **117**, 241—244).—Macerated gut or pancreas, separately or combined, failed to liquefy or produce reducing sugars from the polysaccharides named. H. K.

Cellulose Fermentation in the Paunch of the Ox and its Importance for Metabolic Experiments. W. KLEIN (*Biochem. Z.*, 1921, **117**, 67—68).—A criticism of Krogh and Schmit-Jensen's results (*J. Physiol.*, 1921, Sept. 20) on the carbon dioxide-methane ratio, chiefly on the grounds of priority. H. K.

Basal Metabolism of Underweight Children. KATHARINE BLUNT, ALTA NELSON, and HARRIET CURRY OLESON (*J. Biol. Chem.*, 1921, **49**, 247—262).—The basal metabolism tends to be (up to 40%) higher than in the normal child. G. B.

Variations in Chloride-metabolism Due to Menstrual Processes. W. EISENHARDT and R. SCHAEFER (*Biochem. Z.*, 1921, **118**, 34—38).—As a rule, immediately before or during the menstrual period there is an increased content of chloride in the circulating blood, as estimated by Bang's micro-method. H. K.

Calcium and Phosphoric Acid Metabolism with Large Doses of Calcium and Sodium Phosphate. K. BLÜHDORN (*Z. Kinderheilk.*, 29, 43—55; from *Chem. Zentr.*, 1921, iii, 886).—No harmful effects followed the administration of large quantities of calcium. A portion of the calcium given as chloride or lactate is probably retained, but the greater part is excreted in the faeces. The phosphoric acid exchanges run parallel with the calcium exchanges. Addition of sodium phosphate increases the retention of calcium. When calcium chloride is administered, it is apparently retained as such at first. G. W. R.

Facilitation of Intermediary Sugar Metabolism. H. STAUB (*Biochem. Z.*, 1921, **118**, 93—102).—There is a diminished capacity for assimilating the first dose of dextrose in fasting persons, or after a diet of fat and protein, and also after hard work. In a fasting person, the assimilation increases to a maximum after ten hours, and then falls off after fifteen or more hours. To explain these and other results, "equilibrating ferments" (Gleichgewichtsfermente) are postulated as produced in the blood by foodstuffs to restore to equilibrium the sudden abnormal conditions produced by a high concentration of the food administered. H. K.

Influence of some Polysaccharides (Inulin, Lichenin, and Hemicellulose) on Protein Exchange. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, **117**, 245—251).—Feeding experiments on dogs show that the polysaccharides named have a protein-sparing action. H. K.

The Fate of Parenteral Administered Sulphur and its Influence on Metabolism. ROBERT MEYER-BISCH and E. BASCH (*Biochem. Z.*, 1921, **118**, 39—49).—Intramuscular injection of sulphur in oil is followed by increased protein breakdown, shown by increased nitrogen and sulphur output in the urine, the proportion of the latter element being greater than that administered. H. K.

Antiketogenesis. III. Calculation of the Ketogenic Balance from the Respiratory Quotients. PHILIP A. SHAFFER (*J. Biol. Chem.*, 1921, **49**, 143—162; cf. A., 1921, i, 754).—The author makes the following assumptions (not wholly justified by experiment). (1) Each molecule of fat gives 3 molecules of acetoacetic acid and 0.5 molecule of dextrose or its equivalent anti-ketogenic derivative. (2) Protein is convertible (a) into anti-ketogenic dextrose or its equivalent to the extent of 3.6 grams

for each gram of urine nitrogen, (b) into acetoacetic acid for each molecule of leucine, phenylalanine, and tyrosine, it being calculated that each gram of urine nitrogen corresponds with approximately 10 millimols. of ketogenic substance. (c) Valine, lysine, histidine, and tryptophan are neutral as to ketogenesis. (3) Carbohydrate exerts its antiketogenic function in the form of dextrose, 1 gram of which is therefore equivalent to $1000/180=5.56$ millimols. of antiketogenic substance.

A method is described by which the ratio of ketogenic to anti-ketogenic molecules in the metabolic mixture can be calculated from the respiratory quotient. The molecular ratio 1:1 corresponding according to the calculation with a respiratory quotient of 0.76, appears to be the limit for the avoidance of acetone substances. With a quotient >0.76 the katabolism of the antiketogenic dextrose or its equivalent from protein and glycerol is great enough to remove aceto-acetic acid as fast as it is formed. G. B.

The Minimum of Odour Perceptible in an Absolutely Inodorous Space (Camera Inodorata). K. KOMURO (*Arch. Néerl. Physiol.*, 1921, 6, 20—24).—The camera is a large glass box which can be made inodorous by means of a mercury vapour lamp and into which the head of the experimenter can be introduced. Inside this chamber the minimum necessary for perception of a number of odours is 20—25% less than outside, that is, the nose becomes more sensitive when all other odours are eliminated.

G. B.

Acid Taste. WOLFGANG OSTWALD and ALFRED KUHN (*Kolloid Z.*, 1921, 29, 266—271).—The connexion between the acid taste and the power of producing swelling is considered. It is shown that neither quantity is strictly proportional to the free hydrogen-ion concentration, nor is this quantity in any way a quantitative measure of either. The stronger the swelling action of an acid, the greater the hydrogen-ion concentration must be before an acid taste is detectable. Consequently, swelling action and acid taste are directly opposed to one another. Strongly swelling acids taste less acid than weakly swelling acids of the same hydrogen-ion concentration. The series of minimum hydrogen-ion concentrations which can be detected by taste and the series of swelling constants do not run parallel for the 13 acids examined, but may be connected by means of an experimental equation which contains two constants. Acid salts and buffer solutions exhibit the above-named relationship between acid taste and swelling power. Solutions of these substances taste much more acid than solutions of their acids of the same hydrogen-ion concentration. This is in keeping with the colloid-chemical rule that the addition of salts reduces the swelling power of acids. A tentative hypothesis is put forward that the acid taste is qualitatively due to the hydrogen ion, but quantitatively to the simultaneous swelling action of the colloids in the region of the nerve-endings which is not determined by the hydrogen-ion concentration. J. F. S.

Chemical Constituents of the Egg of the Common Frog (*Rana temporaria*) and their Rôle in its Embryonic Development. E. FAURÉ-FREMIET and (Mlle) DU VIVIER DE STREEL (*Bull. Soc. Chim. Biol.*, 1921, **3**, 476—482).—The ripe egg has the following composition: water 57·60%, glycogen 3·31%, lipoids 10·14%, vitellin tablets 26·51%, the remaining 2·44% consisting of pigment, nucleus, and cytoplasm. The vitellin tablets, which are partly soluble in alkalis, contain phosphorus, nitrogen, and sulphur. E. S.

Constitution of the Egg of *Sabellaria alveolata*, L. E. FAURÉ-FREMIET (*Compt. rend.*, 1921, **173**, 1023—1026).—The eggs of *Sabellaria alveolata*, L., contain 70% of water; 19·08% of protein; 6·80% of fats and lipoids; 1·27% of glycogen, and 1·53% of ash. The protein fraction consists of two distinct substances, one slightly acid, the other neutral. The fatty substances in the eggs exist in three principal forms, namely, neutral fats, soaps, and phosphatides. W. G.

Tetrodon Poison and some of its Chemical Characteristics. F. ISHIHARA (*Tōkyō Igakukai Zasshi*, 1917, **31**, 1—39).—The poison, which was extracted from eggs of the globe fish, is a tasteless, white powder containing sulphur and an amino-group; it gives a positive ninhydrin reaction and a positive reaction for creatinine. Dextrose is present, probably as a dextrose ester.

CHEMICAL ABSTRACTS.

The Chemical Composition of Brain. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, **117**, 252—262).—From 35 kilos. of ox-brain, fractions of a gram of most of the amino-acids were isolated, together with purine and pyrimidine bases and choline. Non-nitrogenous constituents identified were succinic acid, *d*-lactic acid, and inositol. H. K.

The Calcium-Potassium Action. K. SPIRO (*Schweiz. med. Woch.*, **51**, 457—460; from *Chem. Zentr.*, 1921, iii, 888—889).—Examples are given of the antagonistic physiological action of calcium and potassium. With isolated frogs' hearts, poisoning by potassium salts was neutralised by calcium salts. The effect of certain alkaloids may be influenced by the relative amounts of calcium and potassium present. Changes in the reaction of the medium influence the calcium-potassium action. G. W. R.

Choline as Hormone for Intestinal Movement. III. Participation of Choline in the Action of Various Organic Acids on the Intestine. IV. Effect of Choline on Normal Gastric Movement. J. W. LE HEUX (*Pflüger's Archiv*, 1921, **190**, 280—300, 301—310; cf. *Ann. Report*, 1919, 160).—III. The effect on the isolated intestines of salts of various organic acids is explained as being due to the formation from these acids of esters of choline from the choline present in the walls of the bowel, with the aid of a synthetic enzyme which is also there. The activity of these esters, compared with choline, as estimated by the contraction

produced, is: Acetic ester 1000, propionic 300, formic 100, *n*-butyric 40, *isovaleric* 15, benzoic 2, succinic 1. The sodium salts of the acids have no effect, if the intestine is first freed from choline by washing; in some cases the further addition of choline or of the washings restores the effect. Atropine antagonises the effect of these salts, as it does that of choline. The possibility that the stimulating effect of sugars on the intestine may be due to intermediate formation of a pyruvic ester is discussed. IV. X-Ray observations on cats showed that 4–10 mg. of choline chloride given intravenously accelerates the movements of the stomach and small intestine. G. B.

Liver Function. Benzoate Administration and Hippuric Acid Synthesis. G. D. DELPRAT and G. H. WHIPPLE (*J. Biol. Chem.*, 1921, **49**, 229–246).—A severe liver injury, for instance, extensive necrosis due to chloroform, delays but does not prevent the synthesis of hippuric acid. The authors attribute the synthesis in these cases to the subsidiary action of other cells of the body. The intravenous administration of benzoate always increases ammonia, urea, and total nitrogen of the urine. Under certain conditions benzoate injection causes a considerable breakdown of protein, due probably to the acute need of glycine. G. B.

The Part Played by Acid in Carbohydrate Metabolism. IV. The Relation between Acid and Alkali and Adrenaline-glycosuria. H. ELIAS and U. SAMMARTINO (*Biochem. Z.*, 1921, **117**, 10–40; cf. A., 1919, i, 54).—Glycosuria induced by injection of acids into rabbits does not cause congestion of the liver such as occurs in *piqûre* or adrenaline glycosuria. There is marked acidosis produced in rabbits by subcutaneous administration of adrenaline, the lactic acid content of the liver increasing threefold. The mobilisation of sugar produced by adrenaline in isolated tortoise liver is inhibited by alkali, but restored by neutralisation. H. K.

Energy Exchanges in Muscle. IV. Formation of Lactic Acid in Cut Muscle. OTTO MEYERHOF (*Pflüger's Archiv*, 1921, **188**, 114–160; from *Chem. Zentr.*, 1921, iii, 892; cf. A., 1921, i, 76).—In the estimation of lactic acid in frog's muscle, the material is extracted directly with 96% ethyl alcohol. The extract is evaporated to dryness, and the residue ground and washed with saturated sodium sulphate solution. The lactic acid maximum observed in cut muscle is attributed to inhibition of its production owing to increase of acidity. By varying the conditions, the whole of the glycogen may be changed into lactic acid. Addition of dextrose, hexosephosphoric acid, or glycogen to muscle suspended in a phosphate solution does not increase the rate of formation of lactic acid if the addition takes place in the first hour. Disappearance of lactic acid runs parallel with oxidation. Whilst under anaerobic conditions there is an equivalence between the disappearance of carbohydrate and the formation of lactic acid, the equivalence of the reverse process does not hold for cut muscle.

A correlation exists between respiration intensity and lactic acid formation. In cut muscle, respiration intensity is nearly equal to the maximal respiration intensity for uncut muscle. G. W. R.

The Oxidative Degradation of Dextrose in the Animal Body.

JULIUS HIRSCH (*Biochem. Z.*, 1921, **117**, 113—116).—By use of dimethylhydroresorcinol (dimedon) as a fixative for acetaldehyde, the presence of acetaldehyde in 900 grams of frog's muscle was detected by isolation of 0.3 gram of condensation product (aldomedon). H. K.

Fixation of Lime by Animal Tissues. III. E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1921, **118**, 50—54; cf. A., 1921, i, 382).

—Cartilage which has absorbed the alkaline-earth metals has also the power of fixing phosphate. The colloids of the cartilage are assumed to play a part in this chemical combination. H. K.

Zinc in the Human and Animal Organism. E. ROST (*Med. Klin.*, 1921, **17**, 123—124).

—In the human body zinc is to be found in almost all organs and tissues, particularly in the liver and in the muscles. In the liver of infants there is 39—82 mg. per kilo. of tissue, in adults, 52—145 mg. per kilo. Zinc is present in the secretions (milk, urine, fæces), and in epidermal structures such as hair. Human milk contains 1.3—1.4 mg. per litre; goat milk 2.3 mg.; cow milk 3.9 mg. In the urine 0.6—1.6 mg., and in the fæces 3—19 mg. are eliminated daily. Hair contains 9 mg. per kilo. The zinc is derived largely from the meat eaten but some is taken in as vegetable matter. In the tissues, the zinc exists in a more or less firm union with protein. CHEMICAL ABSTRACTS.

The Measurement of the Influence of Heat and Light on the Activity of Reduction of Animal Tissues, and Applications to Heliotherapy. J. VALLOT (*Compt. rend.*, 1921, **173**, 1196—1198).

—The rate of reduction of methylene-blue by animal tissues is markedly increased by rise in temperature or by an increase in the intensity of the illumination and the beneficial therapeutic effects of solar radiation are attributed to this increased activity of reduction. W. G.

The Chemical Composition of Starfish. GUSTAV HINARD

and ROBERT FILLON (*Compt. rend.*, 1921, **173**, 935—937).—The oil extracted from fresh starfish has d_{15}^{20} 0.9372; $n_D^{22} + 47^\circ$ (Amagat and Jean); brismer index 48° ; iodine value (Wijs) 132.7; saponification value 159.1; unsaponifiable matter 38.94%. W. G.

Inorganic Constituents of Milk. I. Chlorides in Human Milk. W. R. SISSON and W. DENIS (*Amer. J. Dis. Children*,

1921, **21**, 389).—The average chloride content of all specimens examined was 58.2 mg. Cl per 100 c.c. It is higher in the first weeks of lactation, and after the second week the average is 52.6 mg. Cl per 100 c.c. G. B.

The "Alkaline Tide" after Meals. I. CYRUS H. FISKE (*J. Biol. Chem.*, 1921, **49**, 163—170).—The author lays stress on the P_H of the urine, rather than on titration values. The influence of the food taken renders the interpretation of small variations of P_H uncertain, but after a full meal an undoubted increase in alkalinity occurs quite suddenly in the second or third hour. G. B.

Inorganic Phosphate and Acid Excretion in the Post-absorptive Period. CYRUS H. FISKE (*J. Biol. Chem.*, 1921, **49**, 171—181).—During the night the rate of excretion of inorganic phosphorus in the urine is greater ($1\frac{1}{2}$ times to twice) than during the day. This the author attributes to retention of phosphorus in the morning. The rate of phosphate excretion is to some extent parallel to the hydrogen-ion concentration, but does not wholly account for the variations in the latter (cf. preceding abstract).

G. B.

The Iodine Number of Urine. OSKAR WELTMANN (*Wiener Arch. inn. Med.*, 1921, **2**, 107—120).—The affinity of urines for iodine normally varies directly with the density and inversely with the amount of the urine. The amount of iodine with which 100 c.c. of urine combines is termed the "percentage iodine number," and the corresponding amount for twenty-four hours, the "absolute iodine number." When the iodine number and the density show wide variation, a relatively high iodine number indicates extra-renal factors, and a relatively low iodine number, a severe injury to the kidney. High iodine numbers have been noted in certain diseases of the liver, acute febrile conditions, and certain rapidly progressing malignant neoplasms.

CHEMICAL ABSTRACTS.

Amino-nitrogen in the Urine by the Formol Method. C. CIACCIO (*Arch. Sci. med.*, 1920, **43**, 177—181).—This nitrogen is considered to be present, not as amino-acids, but as polypeptides. This conclusion is based on a comparison of results by the Henriquez method and those obtained by a preliminary treatment with mercuric acetate, or by tannin and lead acetate. G. B.

Quantitative Measurement of the Transient Excretion of Caffeine in Man by a New Biological Method. EDUARD FRIEDBERG (*Biochem. Z.*, 1921, **118**, 164—184).—The method depends on the observation that there is a sharp contraction of the transversely striped musculature of the frog at a concentration of caffeine of 1 in 3,500. The caffeine in urine is isolated from the dried residue by extraction with chloroform. In man, diuresis is not solely dependent on the dose of caffeine, but partly on the water content of the tissues. The cessation of excretion of caffeine is early, possibly due to degradation of the caffeine to a methyl-xanthine. The smallest proportion of caffeine taken by the mouth and recognisable in the urine is 10 mg. H. K.

A Red Colouring Matter Produced by the Action of *p*-Dimethylaminobenzaldehyde on Normal Urine. PAUL HÁRI (*Biochem. Z.*, 1921, **117**, 41—54).—When *p*-dimethylamino-

benzaldehyde is added to a hot concentrated urine which has previously been treated with lead acetate, a dark red coloration is produced. On cooling, and careful addition of ammonia, the colouring matter is precipitated and may be purified by crystallization from dilute alcohol. Ten to 12 litres of fresh urine yield 0.02 to 0.06 gram of pure substance, m. p. about 220°. The spectral behaviour of the substance has been examined and its extinction coefficient used as a measure of purity. Its tinctorial power is very great. The substance is apparently not identical with the colouring matter of Ehrlich's reaction on pathological urine. H. K.

Origin and Destiny of Cholesterol in the Animal Organism.

XII. The Excretion of Sterols in Man. JOHN ADDYMAN GARDNER and FRANCIS WILLIAM FOX (*Proc. Roy. Soc.*, 1921, [B], 92, 358—367).—The present paper revises earlier results (Ellis and Gardner, A., 1913, i, 222). It is now shown that, in man, the amount of sterols excreted in the faeces is in excess of that taken in with the food. The intake, however, of unsaponifiable matter not precipitated by digitonin (cf. A., 1921, i, 639) is larger than the output. It is concluded from the results that the human organism is capable of synthesising cholesterol. E. S.

Experimental Toxic Hæmatoporphyria. PIETRO BINDA (*Arch. Farm. speriment. Sci. aff.*, 1921, 31, 184—191).—The results of the author's experiments with rabbits indicate that chronic sulphonal poisoning does not determine elimination of hæmatoporphyrin by the kidneys, that animals poisoned by sulphonal keep their power of retaining and elaborating injected hæmatoporphyrin, and that in the organs of animals killed by chronic sulphonal poisoning, the original property of reducing hæmatoporphyrin in vitro is preserved. T. H. P.

Blood Fat in Diabetes. N. R. BLATHERWICK (*J. Biol. Chem.*, 1921, 49, 193—199).—Cases of mild and moderate diabetes can utilise satisfactorily large amounts of fat as indicated by the blood fat level and the absence of acetone substances from the urine. G. B.

Lipæmia. W. R. BLOOR (*J. Biol. Chem.*, 1921, 49, 201—227).—In most cases a sequence in the appearance and disappearance of fat, lecithin, and cholesterol is perceptible, fat being the first to increase and to disappear. In most cases the ratio lecithin/cholesterol is distinctly below normal, as the cholesterol is increased in greater proportion than the lecithin. The increase in fat is generally in still greater proportion. G. B.

Action of certain Bismuth Derivatives on Syphilis.

R. SAZERAC and C. LEVADITI (*Compt. rend.*, 1921, 173, 1201—1204).—It is shown that ammoniacal bismuth citrate, bismuth lactate, bismuth subgallate, and bismuth oxyiodogallate are all active against syphilis, but vary in their toxic power. For human

therapeutics sodium or potassium bismuthotartrate are the best bismuth preparations to use. W. G.

The Action of Polished Metals on Toxins. F. ERDSTEIN and L. FÜRTH (*Biochem. Z.*, 1921, **118**, 256—258).—A confirmation of Luger and Baumgarten's results (*Wien. klin. Woch.*, 1912, 1222) that copper and to a very slight extent silver have a harmful effect on toxins. An actual destruction of the toxin takes place in the sense that a complex metal-toxin compound is formed. H. K.

Toxicity of Methyl Alcohol. ASTRID CLEVE VON EULER (*Svensk. Kem. Tidskr.*, 1921, **33**, 114—119; from *Chem. Zentr.*, 1921, iii, 740).—Methyl alcohol is considered by the author to be less poisonous in large doses than ethyl alcohol. Cases of poisoning by methyl alcohol are to be attributed to accompanying poisonous impurities. G. W. R.

The Action of Organic Kations on the Vascular System and its Modification by Inorganic Ions. WERNER TESCHENDORF (*Biochem. Z.*, 1921, **118**, 267—285).—The action of a number of salts of strong organic bases was examined on the frog's vascular system. Acetylcholine had the most powerful constricting action. Nitrosocholine was much less active and guanidine still less so. In the homologous series of quaternary ammonium bases, tetramethylammonium chloride was intermediate between acetylcholine and nitrosocholine, the tetraethyl derivative resembled guanidine, whilst the tetrapropyl derivative depressed the vascular tonus. The action of the above organic kations was inhibited by the bivalent inorganic kations in the order: Mg, Ca, Sr, Ba. H. K.

Degradation of Fatty Acids in the Animal Organism. P. WORINGER (*Bull. Soc. Chim. Biol.*, 1921, **3**, 311—450).—A review on much the same lines as Dakin's monograph. Here and there the author puts forward independent views. Thus he argues against Dakin's conception of the breakdown of tyrosine and phenylalanine, and considers that the fundamental condition necessary for the combustion of an aromatic substance is its capacity of being transformed into homogentisic acid. He thus accepts Abderhalden's view (*A.*, 1912, ii, 585) that this acid is produced in the normal tyrosine metabolism.

The title of the review scarcely represents its full scope, as it also deals with hydroxy-, keto-, and amino-acids. A special feature is a tabulation of the transformations of acids hitherto observed in the animal, with a statement of the method employed and a literature reference. There is also a full bibliography. G. B.

A New Antianaphylactic Substance, Sodium Formaldehydesulphoxylate. P. BRODIN and P. HUCHET (*Compt. rend.*, 1921, **173**, 865—867; cf. *ibid.*, 1919, **168**, 369; **169**, 9).—Sodium formaldehydesulphoxylate, $\text{CH}_2(\text{OH})\cdot\text{SO}_2\text{Na}$, can be injected into dogs or rabbits to the extent of 1 gram per kilo. of live weight without any ill-effect and, like sodium chloride, it has an immunising action against an anaphylactic injection. W. G.

The Behaviour of Pyrrole in the Animal Body. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, **117**, 266—268).—Injection of an aqueous suspension of pyrrole into dogs is followed by its elimination in the urine as methylpyridine. H. K.

Behaviour of Phrenosine in the Animal Body. TOMIHIDE SHIMIZU (*Biochem. Z.*, 1921, **117**, 263—265).—Phrenosine administered to a dog appeared in the urine as sphingosine; the latter, when given either by the mouth or subcutaneously, to dogs or rabbits, appeared unchanged. H. K.

Chemistry of Vegetable Physiology and Agriculture.

The Nature of the Butyric Acid and Butyl Alcohol Fermentation. Fixation of Acetaldehyde as a Decomposition Product. Transformation of the Aldol of Pyruvic Acid into Butyric Acid. Production of Higher Fatty Acids from Sugar. CARL NEUBERG and BERNHARD ARINSTEIN (*Biochem. Z.*, 1921, **117**, 269—314).—Dextrose in a nutrient medium of inorganic materials and in the presence of a fixative, for example, sodium sulphite, is fermented by *Bacillus butylicus*, Fitz, with production of about 10% of acetaldehyde. By the use of a culture of *Amylobacter*, acetaldehyde could also be qualitatively recognised. Acetaldehyde or its condensation product, aldol, is not the intermediate stage in the butyric fermentation, but the aldol of pyruvic acid, α -keto- γ -valerolactone- γ -carboxylic acid, which gave butyric acid on fermentation. Starch syrup fermented by a culture of *B. butylicus*, Fitz, in an inorganic nutrient medium gave small quantities of the higher fatty acids of which decolic was identified. H. K.

Action of *Aspergillus glaucus* on Glycerol. F. TRAETTA-MOSCA and M. PRETI (*Gazzetta*, 1921, **51**, ii, 269—277).—When *Aspergillus glaucus* is grown in a nutrient liquid containing glycerol, the latter yields the compound, $C_6H_6O_4$, m. p. 154° , previously obtained from sucrose or invert-sugar by the action of the same mould (A., 1914, i, 1114). This compound forms a *methyl ether*, $C_6H_5O_3 \cdot OMe$, which crystallises in white needles, m. p. 165° , and, unlike the original compound, gives no coloration with ferric chloride solution. Hydrolysis of the methyl ether by means of barium or calcium hydroxide results in the formation of methyl-acetol ether and oxalic and formic acids, whilst the action of ammonia yields pyridone. The structure of the compound, $C_6H_6O_4$, is probably $CH \begin{smallmatrix} \diagup CH-CO \\ \diagdown O \cdot C(OH) \end{smallmatrix} \geq C \cdot CH_2 \cdot OH$, and is similar to Peratoner and Tamburello's maltol (A., 1905, i, 807). T. H. P.

The Longevity of certain Species of Yeast. ARTHUR R. LING and DINSHAW RATTONJI NANJI (*Proc. Roy. Soc.*, 1921, [B], 92, 355—357).—Cultures of eight different species of yeast were found to be still alive after thirty-four years' storage on dry cotton wool pads contained in sealed flasks. E. S.

Alcoholic Fermentation by means of Yeast-cells under Various Conditions. I. Influence of Animal Charcoal and other Adsorbents on the Course of the Fermentation: Formation of Acetaldehyde. EMIL ABDERHALDEN (*Fermentforsch.*, 1921, 5, 89—109).—The addition of animal charcoal to a solution containing sugar and yeast-cells effects acceleration of the fermentation, and such acceleration appears to be due to the formation of acetaldehyde, which is always detectable in the liquid under these conditions. It is uncertain if the acetaldehyde is a product of the degradation of the dextrose or a secondary product formed by oxidation of the ethyl alcohol, but it is found that addition of yeast and animal charcoal to aqueous alcohol results, after a time, in the appearance of an odour of acetaldehyde.

Since animal charcoal is an excellent adsorbent for acetaldehyde, it is possible, not only that it takes part in the secondary formation of acetaldehyde from ethyl alcohol, but that it concentrates on its surface and thus renders detectable acetaldehyde formed as a primary product of the fermentation of sugar. T. H. P.

Alcoholic Fermentation by means of Yeast-cells under Various Conditions. II. EMIL ABDERHALDEN (*Fermentforsch.*, 1921, 5, 110—118; cf. preceding abstract).—Further investigations show that acetaldehyde solutions which show no loss in weight when left in contact with either animal charcoal or yeast, immediately begin to evolve gas when both the charcoal and yeast are added. Experiments were made also with pyruvic acid and with methyl and ethyl alcohols, it being found that all the samples of animal charcoal tried accelerated the fermentation of sugar by means of yeast, caused formation of acetaldehyde, and induced formation of acetaldehyde and carbon dioxide from pyruvic acid, but that some samples were totally unable to effect transformation of acetaldehyde or alcohols. T. H. P.

Functions of the Yeast-cell. Zymase and Carboxylase Action. EMIL ABDERHALDEN and A. FODOR (*Fermentforsch.*, 1921, 5, 138—163).—The authors consider that the fermentations effected by zymase in its plasma form and by liberated zymase are, quantitatively and kinetically, different processes and have carried out various experiments with the object of ascertaining how dried yeast differs from the living cell and what substances are removed from living or dried yeast by pressing or maceration.

Dried yeast is found to contain cells which, in a fermentable solution, swell and resume their life functions. Like yeast juice, yeast sterilised by treatment with acetone or by age is incapable of fermenting dilute sugar solutions, all such preparations lacking the ability to concentrate peculiar to the living cells. Apparently

owing to its simpler and more independent relation to the protoplasm, the carboxylase of dried yeast is able to exert its activity before the whole of the water necessary for the complete vital functions has been absorbed.

The results of various experiments with maceration juice are described, these dealing with the kinetics of the fermentation, with the persistence, both of the fermentative activity and of the carboxylase of the juice, with the oxygen absorbed by the juice, and with kinetic measurements on mixtures containing pyruvic acid, dipotassium hydrogen phosphate, and maceration juice. The fermentative ability and the power to absorb oxygen fall gradually to zero together.

T. H. P.

Vitamine Content of Rice by the Yeast Method. Organic Nitrogen as a Possible Factor in Stimulation of Yeast.

WILLIAM D. FLEMING (*J. Biol. Chem.*, 1921, **49**, 119—122).—The stimulation of yeast growth is not due to water-soluble vitamin-B, for it persists after the rice extracts have been evaporated with 10% sodium hydroxide to inactivate the vitamin. The stimulation is due to organic nitrogen (cf. Fulmer, Nelson, and Sherwood, *A.*, 1921, i, 292).

G. B.

Comparative Experiments on the Inhibitive Action of some Chlorine Derivatives of Methane, Ethane, and Ethylene on Fermentation.

H. PLAGGE (*Biochem. Zeitsch.*, 1921, **118**, 129—143).— $\alpha\alpha$ -Dichloro- and $\alpha\beta$ -dichloro-ethane, dichloromethane, chloroform, and tetrachloroethane are toxic to the yeast-cell. The determining factor is not the concentration of the solution, but the actual dose administered.

H. K.

Fermentation without Yeast. EMIL BAUR and EUGEN HERZFELD (*Biochem. Z.*, 1921, **117**, 96—112).—Mixtures of substances in imitation of yeast press juice (peptone, dextrose, dextrin, sodium hydrogen carbonate, casein, lipid, and bile salts) produced carbon dioxide and alcohol (iodoform test) in small amounts. The formation of acid substances from dextrose, liberating carbon dioxide from the sodium hydrogen carbonate, only accounts for a portion of the gas formed.

H. K.

Behaviour of Diastase and other Enzymes under Unfavourable Conditions. Action of some Nitrogenous Compounds on Germination. TH. BOKORNY (*Bied. Zentr.*, 1921, **50**, 429—430).—Brief reference is made to the effect of acids, bases, salts of heavy metals, etc., on such enzymes as diastase, invertase, pepsin, myrosin, and trypsin.

From an examination of the effect of urea, hippuric acid, ammonium salts, and sodium nitrate on germination, it is shown that nutrient materials are injurious if used at too high a concentration.

W. G.

The Manganese Content of (Dutch) Seeds. D. H. WESTER (*Biochem. Z.*, 1921, **118**, 158—163).—The manganese content of the seeds of 48 species of plants was determined, the quantity of

metal generally present being between 2 and 6 mg. in 100 grams of dried material. H. K.

Is it Possible to Determine the Value of Seeds by a Biochemical Method? ANTOINE NÈMEC and FRANÇOIS DUCHOŇ (*Compt. rend.*, 1921, **173**, 933—935).—The activity of the various hydrolysing enzymes such as amylase, invertase, glycerophosphatase, lipase, urease, uricase, and phytoproteases of seeds diminishes with the germination capacity of the seeds, but is still marked when the latter has reached zero. Catalase is different, and there is some indication that the activity of the catalase, measured under comparable conditions, may represent a suitable means for determining rapidly and simply the agricultural value of seeds. W. G.

Corrosive Action of Roots on Marble. E. CHEMIN (*Compt. rend.*, 1921, **173**, 1014—1016).—Further experiments are given in support of the view that plant roots do not excrete any sensible amount of acids other than carbonic acid and that the excretion of the latter is sufficient to explain the corrosion of marble. W. G.

The Part Played by Lipoids in the Metabolism of Plant Cells. FRIEDRICH BOAS (*Biochem. Z.*, 1921, **117**, 166—214).—The influence of saponin and salts was investigated on the growth of yeast and the course of fermentation. The action of these agents is similar to their known action on animal cells, the combined action leading to destruction of the cell. The anions and kations of the salts influence the colloidal state of the cell wall and follow the lyotrope series. H. K.

The Effect of Neutral Salts on the Heat Coagulation of Plant Protoplasm. HUGO KAHHO (*Biochem. Z.*, 1921, **117**, 87—95).—Both ions of neutral salts play a part in the heat coagulation of the protoplasm of the epidermal cells of *Tradescantia zebrina*. The coagulation is accelerated by anions arranged in the lyotropic series. Neutral salts which penetrate the plasma membranes most readily have the greatest lowering effect on the temperature of coagulation. H. K.

The Relation between Fluorescent Substances which Act in the Dark and their Photodynamic Activity on Cells. A. JODLBAUER and F. HAFFNER (*Biochem. Z.*, 1921, **118**, 150—157).—A large number of fluorescent and non-fluorescent substances of known photodynamic action on cells (for example, paramoecia) have been examined in respect of their action in the dark, on the hæmolysis of erythrocytes at room temperature and at 56°, and in the flocculating property on the colloidal contents of hæmolysed corpuscles at 56°. In general there is a parallelism between the two actions. H. K.

Rhythmic Precipitation Phenomena in Cell Membranes of Plants. HANS PETER MÖLLER (*Kolloid Chem. Beihefte*, 1921, **14**, 97—146).—When wheat grains which have been cut are treated with a solution of silver nitrate, bands and layers are formed at

right angles to the direction of diffusion in the membranes of the aleurone cells and in the nucellus layer, which are identical with the zones discovered by Liesegang in artificial colloids. The identity between the rhythmic precipitation in plant cells and Liesegang's rings and zones is proved, (1) by the form and appearance of the bands and (2) by the fact that the effect of external agencies is the same in both cases. In both cases, the rhythmic precipitation of silver nitrate occurs after a region of formless precipitate; zones are produced which increase in width and distance apart with increasing distance from the centre of diffusion. With increasing width, the formation of grains occurs and the edges of the zones become indistinct, the space between the zones becomes turbid, and finally the rhythmic zone formation passes over into an irregular granular precipitate. Fick's law of diffusion is approximately applicable to the diffusion of silver nitrate in wheat grains, the water content of the membrane, its content on silver nitrate, and the concentration of silver nitrate have the same influence as in the diffusion into jellies. The formation of a rhythmic precipitation depends on the velocity of diffusion of silver nitrate. The zone formation commences so much nearer to the centre of diffusion the smaller the concentration of silver nitrate and the lower the temperature. The velocity of invasion of the silver is of equal importance, which apart from the concentration of silver nitrate is influenced by the content of the cell walls on silver precipitating salts and water. In wheat grains a larger and smaller rhythm cannot be detected. The dimensions of the width and distance between the bands are the same for plant cells which have had a previous treatment with silver nitrate and those which have not been so treated. The grains of other cereals, and the leaves of many plants show a similar zone formation when treated with silver nitrate, so that it may be assumed that the cellulose membranes of plants in general are capable of showing rhythmic precipitation when the necessary external conditions are obtained. From the experiments it follows that the pure cellulose membranes of the wheat grain which show rhythmic precipitation cannot be regarded as a selective permeable layer, and it further follows that the woody integument layer of the sheath of the wheat grain is the selective permeable membrane.

J. F. S.

The Distribution of Manganese in the Organism of Higher Plants. GABRIEL BERTRAND and (MME) M. ROSENBLATT (*Compt. rend.*, 1921, **173**, 1118—1120).—From a study of the distribution of manganese in the different parts of a dicotyledon, *Nicotiana rustica* L., and of a monocotyledon, *Lilium lancefolium rubrum*, it is shown that those organs in which chemical changes are the most intense contain the highest percentages of manganese. The seeds contain a high proportion of manganese, doubtless for the use of the future seedling.

W. G.

Lumbang Oil (Candlenut Oil). AUGUSTUS P. WEST and ZOILA MONTES (*Philippine J. Sci.*, 1921, **18**, 619—636).—The oil is obtained from the nuts of *Aleurites moluccana* and has the following

composition: glyceryl linolenate 6.5%, glyceryl linolate 33.4%, glyceryl oleate 56.9%, glycerides of solid acids 2.8%. It is insoluble in cold ethyl and methyl alcohols and acetic acid. The oil behaves in much the same manner as linseed oil on oxidation. It is an excellent drying oil. H. C. R.

The Odorous Constituents of Apples. F. B. POWER and V. K. CHESNUT (*J. Amer. Chem. Soc.*, 1921, **43**, 1741; cf. A., 1920, i, 653).—Inasmuch as esters derived from leucic acid do not occur in apples (*loc. cit.*), the title of a paper by Kodama on this subject (cf. A., 1921, i, 220) is misleading. W. G.

Characteristics and Utilisation of Beech Nut Oil. H. B. (*Mat. grasses*, 1921, **13**, 5860—5861).—The oil content of beech nuts varies from 14 to 22%. The constants of the oil are: d^{15}_4 0.9205, iodine number 104.4, bromine number 0.652, heat developed with sulphuric acid +65°, polariscope reading -0.8° in saccharimeter degrees, refractometer reading +16.5 to +18°. The oil is edible and may be kept without change for a long time. The cake from the nuts gave the following analysis: decorticated cake: water 12.5%, oil 7.5%, nitrogenous matter 37.1%, non-nitrogenous extract 29.7%, cellulose 5.5%, ash 7.7%; non-decorticated cake: water 19.1%, oil 8.34%, nitrogenous matter 18.15%, non-nitrogenous extract 28.39%, cellulose 20.89%, ash 5.13%. The non-decorticated cake is poisonous. CHEMICAL ABSTRACTS.

The Biology of the Alkaloids of Belladonna. JEAN RIPERT (*Compt. rend.*, 1921, **173**, 928—930).—Belladonna plants grown in obscurity show an increase in alkaloid content both in the leaves and in the stems, whilst the amount in the roots diminishes very slightly. When the plants are returned to sunlight the values for the leaves return to a practically normal figure after thirteen days. The protein content of the leaves also increases considerably when the plants are kept in the dark. W. G.

Anthocyanin of *Beta vulgaris*. F. M. ANDREWS (*Proc. Ind. Acad. Sci.*, 1917, 167).—The anthocyanin of *B. vulgaris* affords one of the examples where the pigment forms in the subterranean parts. A strong solution of such anthocyanin will preserve its normal colour in a test-tube placed in darkness for more than a week. In direct sunlight, it will retain its normal bright colour for a week or more, until disorganised by bacterial action, which change finally occurs in the anthocyanin solution in the dark. CHEMICAL ABSTRACTS.

Formation of the Red Pigment of *Beta vulgaris* by Oxidation of the Chromogens. ANTOINE KOZLOWSKI (*Compt. rend.*, 1921, **173**, 855—857).—Details are given for the extraction of the chromogens from beetroot by alcohol and for their subsequent purification and isolation. The chromogens extracted from the white sugar-beet resemble saponins in certain of their physico-chemical properties and on oxidation give a coloured pigment

having the same spectroscopic characteristics as the red pigment extracted from red beetroots and showing similar colour changes with acids and alkalis. W. G.

Transformation, by Oxidation, of the Chromogens of some Plants into a Red Pigment. ST. JONESCO (*Compt. rend.*, 1921, 173, 1006—1009).—The yellow chromogens extracted from such plants as *Cobæa scandens* and *Ampelopsis hederacea* on oxidation in amyl alcoholic solution with sulphuric acid and manganese dioxide at 50—60° give a violet-red pigment. In the case of the chromogens from *Ampelopsis* reduction was tried but red pigments were not obtained. The results obtained confirm those of Kozlowski on beetroot pigments (preceding abstract) that the appearance of red pigments in plants is due to oxidation and not to reduction phenomena. W. G.

Formation of Anthocyanin in the Flowers of *Cobæa scandens* at the Expense of Pre-existing Glucosides. ST. JONESCO (*Compt. rend.*, 1921, 173, 850—852).—Contrary to the results of Rosé (A., 1914, i, 639) experimental evidence is given to show that the anthocyanin glucosides in the flowers of *Cobæa scandens* are formed at the expense of pre-existing glucosides, and consequently Combes's hypothesis as to the formation of anthocyanin (cf. A., 1909, ii, 426) is incorrect. W. G.

The Effect of Daylight on the Content of Active Material in *Digitalis*. OTTO VON DAFERT (*Bied. Zentr.*, 1921, 50, 422—425).—The toxicity of the extract from *Digitalis* leaves depends on the time of day at which the leaves are gathered and how and when the leaves are killed. To obtain the most toxic extract the leaves should be gathered in the afternoon and immediately killed by plunging them into 96% alcohol. W. G.

The Occurrence of Methyl Anthranilate in Grape Juice. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1921, 43, 1741—1742).—Methyl anthranilate is a natural and apparently constant constituent of grape juice. Its presence, therefore, in a commercial grape juice must not necessarily be taken as an indication of adulteration. W. G.

Grape Oil from the Canadian Vine (*Vitis hederacea*). (*Boll. assoc. ital. piante med. aromat.* 2, 56—59; *Bull. Agr. Intelligence*, 1919, 10, 1004—1005).—Two oils were extracted, (1) from the pips, a dark yellow or green oil with sweet taste and nutty odour, d^{15} 0.9215, n^{15} 1.4778, saponification number 189.2—189.6, iodine number 131.4—141.6, fixed fatty acids 93.97%, volatile fatty acids 0%, and non-saponifiable substances 1.44%. The total fatty acids have iodine number 144.6 and mean molecular weight 281.2. Solid fatty acids consisting chiefly of palmitic acid do not exceed 3%, have a mean molecular weight of 261.4 and m. p. 57.6°. The liquid fatty acids are chiefly oleic and linoleic acids, with iodine number 148.8—149.9; (2) from the pulp and skin, an olive-green, soft, pasty oil with astringent taste and pleasant odour, turning rancid in the air, n^{15} 1.4722, saponification number 192.3—193.3, iodine

number 90.3, fixed fatty acids 94%, volatile fatty acids 0%, and unsaponifiable substances 1.67%. The total fatty acids have iodine number 94.4—94.6 and mean molecular weight 278.8. The solid fatty acids are about 10% of the pulp and skin oil, chiefly palmitic acid. The liquid fatty acids are mostly oleic and linoleic acids with iodine number 110.2.

CHEMICAL ABSTRACTS.

Oil from the Seeds of *Jatropha Curcas*, L. CLEMENS GRIMME (*Seifenfabr.*, 1921, **41**, 513—515; from *Chem. Zentr.*, 1921, iii, 1035).—The seeds of *Jatropha Curcas*, L., consist of 38% hard husk and 62% oil-bearing kernel. Analyses of the seeds are given. In spite of the high protein content, 48.13%, the seeds are unsuitable for use as a feeding stuff on account of the presence of highly poisonous *curcine*. A complete description is given, with constants, of the oil obtained by extraction, hot pressure, and cold pressure respectively. The principal constants are d^{15} 0.9213—0.9228; m. p. 5—8°; n_D^{20} 1.4610—1.4618; acid number 3.18—4.05; iodine number (Wijs) 96.7—98.8. The fatty acids are white to yellow in colour and have m. p. 15—18°. The oil belongs to the class of non-drying oils and consists of the glycerides of palmitic, myristic, and *curcanolic* acids. The latter is a hydroxy-acid like ricinolic acid. The seeds contain a lipolytic enzyme which, however, is not so energetic as the enzyme in *Ricinus* seeds.

G. W. R.

Iodine in the *Laminaria*. P. FREUNDLER, (MLLE) Y. MENAGER, and (MLLE) Y. LAURENT (*Compt. rend.*, 1921, **173**, 931—932).—An examination of the iodine content of certain species of *Laminaria* shows that they lose a certain amount of iodine during drying, the loss amounting in some cases to as much as 50%. The iodine content is dependent on the time of harvesting, being higher in July than in March. It is independent of the place of growth, but varies with the age of the tissues, being highest in the youngest tissues. The variations with different parts of the plant are not uniform, but differ with the species.

W. G.

The Composition of the *Laminaria*. P. FREUNDLER, (MLLE) Y. MENAGER, and (MLLE) Y. LAURENT (*Compt. rend.*, 1921, **173**, 1116—1118; cf. preceding abstract).—The authors have correlated the variation in iodine content of the *Laminaria* with their biological evolution and show that the maxima for iodine content as well as for the percentages of reserve carbohydrates and brown pigments coincide with the period of maximum sunshine. The *Laminaria* regularly restore to the sea a certain amount of their iodine under conditions which depend, for each species, on their mode of growth.

W. G.

Properties and Composition of Tohaku Oil. YOSHITORA IWAMOTO (*J. Chem. Ind. Japan*, 1921, **24**, 1143—1160).—A yellowish-brown oil is obtained by pressure or extraction of the seed of "Tohaku," *Lindera obtusiroba*, B. L., which is widely diffused in Corea. Its physical and chemical constants were determined. Decoic, lauric, and oleic acids and an acid, $C_{12}H_{22}O_2$, which occurs

in cochineal fat, were identified. Some of the lower unsaturated liquid, and solid fatty, acids seem to be present, but linolic, linolenic, stearic, and palmitic acids are probably absent. K. K.

The Proteins of the Alfalfa Plant [Lucerne]. THOMAS B. OSBORNE, ALFRED J. WAKEMAN, and CHARLES S. LEAVENWORTH (*J. Biol. Chem.*, 1921, **49**, 63—91).—The paper is mainly concerned with a technique for extracting plant proteins with as little change as possible. Fresh plants, or plants frozen soon after cutting, are ground very finely and pressed in a hydraulic press; the undiluted juice contains 10% of solids. The addition of 20% of alcohol precipitates a colloid, consisting of 70% of protein and calcium salts. The latter are extracted by dilute alcoholic hydrochloric acid, which forms an insoluble hydrochloride of the protein. The latter is further purified by heating with dilute alkali hydroxide, and reprecipitation. By successive extraction with water, alcohol, dilute aqueous alkali, and hot alkaline alcohol, practically all the cell contents can be extracted if the fresh plant is sufficiently thoroughly ground. Thirty-two per cent. of the solids of the plant, containing only 5.6% of its nitrogen, finally remains undissolved. G. B.

The Odorous Constituents of Peaches. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1921, **43**, 1725—1739).—An examination of the pulp of choice, ripe peaches shows that the odorous constituents of the fruit consist chiefly of the linalyl esters of formic, acetic, valeric, and octoic acids, together with a considerable proportion of acetaldehyde and a very small amount of an aldehyde of higher molecular weight. It is probable that the volatile acids are present to some extent in a free state. No trace of hydrocyanic acid or benzaldehyde could be detected in the distillate from peach pulp. The yield of essential oil was about 0.00074% of the fresh pulp, and the oil contained, in addition to the linalyl esters, a little acetaldehyde and furfuraldehyde, probably some cadinene and a very small amount of an unidentified paraffin hydrocarbon. The essential oil is very unstable and on exposure to air for any length of time is converted into a black, viscid mass and loses its original fragrance.

The emanation from the entire ripe fruit contains a minute amount of acetaldehyde. W. G.

Constituents of *Phellodendron Amurense*. KÔTARÔ SHIMO (*Sci. Rep. Tohoku Imp. Univ.*, 1921, **10**, 331—338).—The rind of *Phellodendron Amurense* contains berberine and fatty acids. These acids appear to exist uncombined with berberine and consist of palmitic acid, linoleic acid, and a small quantity of linolenic acid. A small quantity of a neutral substance was found in addition but was not identified. Two samples of phellodendron rind gave 2.473% and 3.75% respectively of berberine (estimated as berberine acetone). G. W. R.

The Cellulose Content of Pine Wood. PETER KLASON (*Zellstoffchem. Abhandlungen*, 1921, **1**, No. 5, 105—114).—Cross and Bevan's method cannot be used for the estimation of the cellulose

content of pine wood. The author has investigated the action of a solution of 80 grams of sodium hydrogen sulphite and 500 c.c. of *N*-hydrochloric acid in one litre of water for varying periods of time at 100°. After eight days the cellulose reaches a nearly constant value, and, with continued heating, only slowly decreases (1.7% in 13 days). He finds 53% of cellulose in pine wood. The composition of woods of various ages is also investigated.

CHEMICAL ABSTRACTS.

Chemical Constituents of Pine Leaves. II. ASTRID CLEVE VON EULER (*Tekn. Tidsk. Kem. Berg.*, 1921, **51**, 35—38, 47—52).—A study of the non-fatty impurities, insoluble in ethyl ether, present in the crude fat of pine leaves. The material is more conveniently extracted by means of 93% methyl alcohol, and is designated "crude gum." It readily changes into an insoluble substance, the change being facilitated by the presence of acids. A solution of the gum in sodium hydroxide showed marked changes when treated with carbon dioxide. Fractional precipitation of the alkaline solution of the gum with acids yielded coniferyl alcohol and dihydroxy- γ -phenylpropyl alcohol; the whole crude gum is tannin-like in character, and is considered to consist of intermediates in the plant synthesis of tannins. CHEMICAL ABSTRACTS.

The Organic Acids of *Pyrus coronaria*, L., *Rhus glabra*, L., and *Acer saccharum*, Marsh. CHARLES E. SANDO and H. H. BARTLETT (*J. Agric. Research*, 1921, **22**, 221—229).—The organic acids of the wild American crab apple, *Pyrus coronaria*, L., smooth sumac, *Rhus glabra*, L., and sugar maple, *Acer saccharum*, Marsh, were investigated. In all cases the acid found was malic acid, occurring in the form of the free acid in the first species, the acid calcium salt in the second species and both acid and normal calcium salts in the third species. A certain amount of gallic acid is also found in the second species. The substance known as "maple sand" obtained in the preparation of sugar from the sugar maple is crude calcium malate. It appears that succinic acid may be formed autolytically from the malic acid of *Pyrus coronaria*.

G. W. R.

Volatile Substances from the Bark of *Rhamnus frangula*. O. A. OESTERLE (*Schweiz. Apoth.-Zeit.*, 1921, **59**, 341—345; from *Chem. Zentr.*, 1921, iii, 734—735).—By steam distillation of the bark of *Rhamnus frangula*, 0.05—0.1% was obtained of a substance of unpleasant odour, which contained, in addition to dark coloured impurities, a white substance, insoluble in sodium carbonate, crystallising from chloroform—light petroleum in long needles, a compound obtained as a gelatinous precipitate from hot sodium hydroxide solution, a substance crystallising from hot water in slender, ray-like aggregates, and a main portion consisting of brownish-yellow platelets with a green tinge crystallising from dilute ethyl alcohol. The latter substance is tasteless and odourless, and has the empirical formula $C_{15}H_{12}O_4$. It is easily soluble in organic solvents, and has m. p. 100—101°. G. W. R.

Organic Chemistry.

Relation between the Molecular Properties and the Capacity for Fixation of Iodine of certain Hydrocarbons. PAUL WOOG (*Compt. rend.*, 1921, **173**, 1471—1473; cf. A., 1921, ii, 575).—Plotting the molecular weights of a homologous series of American oils against the corresponding iodine values reduced proportionately to the double linkings as calculated from the mean molecular surface area on water (*loc. cit.*), a regular curve was obtained, given by the equation $\log I_M + K = \log I_{M^{50}}$ where I_M is the iodine value for any molecular weight and $I_{M^{50}}$ the value for a molecular weight fifty units higher, and K is a constant equal to 0.0664. This progressive capacity for addition or substitution is apparently due to causes analogous to those responsible for the dissociations which occur in the "cracking" process. Benzene solutions of these oils rapidly undergo oxidation when exposed to sunlight and the velocity of oxidation increases with the number of double bonds in the molecule.

W. G.

A General Method for the Preparation of Carbides of Metalloids, and the Existence of Carbides of Phosphorus and Arsenic. E. DE MAHLER (*Bull. Soc. chim.*, 1921, [iv], **29**, 1071—1073).—The chloro-derivative of the metalloid is allowed to react in ethereal solution at the ordinary temperature with one of Iotsitsch's compounds (cf. A., 1914, i, 393) of the type $MgI \cdot C \cdot C \cdot MgI$, when the carbide of the metalloid is obtained. In this way, phosphorus trichloride gives *phosphorus carbide*, $P \begin{smallmatrix} \diagup C:C \diagdown \\ \diagdown C:C \diagup \end{smallmatrix} P$, an amor-

phous, white compound, which is spontaneously inflammable when gently warmed, and yields phosphoric anhydride and carbon dioxide. Arsenic chloride gives *arsenic carbide*, As_2C_6 , a brown, amorphous compound, which explodes when warmed or gently rubbed, arsenic and carbon being liberated.

W. G.

Some Aliphatic Fluorides. F. SWARTS (*Bull. Soc. chim. Belg.*, 1921, **30**, (ii), 302—315).—The following are described: *n-Amyl fluoride*, a volatile, mobile liquid, m. p. below -80° , b. p. 62.8° , $d^{10.5}_4$ 0.7960, d^{20}_4 0.7880, n^{20}_D 1.35622, n^{20}_B 1.36183, n^{20}_γ 1.36533. *n-Decyl fluoride*, a mobile liquid, which solidifies in a mixture of alcohol and solid carbon dioxide, b. p. about 183.5° , $d^{10.2}_4$ 0.792. *isoAmyl fluoride*, b. p. 53.5° . *n-Heptyl fluoride*, m. p. -73° , b. p. $119^\circ/755$ mm., d^{21}_4 0.8029, $n^{21.5}_A$ 1.38358, $n^{21.5}_B$ 1.3855, $n^{21.5}_\gamma$ 1.3899, $n^{21.5}_\gamma$ 1.39358. *n-Octyl fluoride*, b. p. $142.5^\circ/75$ mm., d^{14}_4 0.81200, d^{21}_4 0.8036, $n^{14.1}_A$ 1.3952, $n^{14.1}_B$ 1.3970, $n^{14.1}_\beta$ 1.40175, $n^{14.1}_\gamma$ 1.43565. *Cetyl fluoride* is solid at the ordinary temperature,

b. p. $287.5^{\circ}/760$ mm., $181^{\circ}/24$ mm., $d_{17.5}^{20} 0.809$. sec.-Octyl fluoride, b. p. 139.3° .

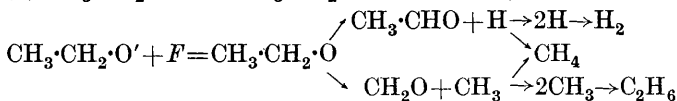
It is stated that mercury fluoride is preferable to silver fluoride for the preparation of the above, several reasons being given. The yield is diminished in each case by the formation of an ethylenic hydrocarbon and hydrogen fluoride; when silver fluoride is used, this may take place in such a way that two molecules of the alkyl haloid, containing C_n , condense to yield $C_{2n}H_{4n+1}F$; sometimes this represents the major reaction. The chemical properties of the substances are described; they are, in general, not so stable as the majority of organic fluorine compounds. The isoalkyl fluorides tend to decompose into ethylenic hydrocarbons and hydrogen fluoride on distillation; with straight-chain compounds this is not the case. The action of alkali hydroxides in aqueous or alcoholic solution is feeble; concentrated sulphuric acid reacts in the cold with formation of hydrogen fluoride.

H. J. E.

The Aliphatic Sulphonamides. I. PERCIVAL WALTER CLUTTERBUCK and JULIUS BEREND COHEN (T., 1922, **121**, 120—128).

The History of [Ethyl] Alcohol. EDMUND O. VON LIPPMANN (*Chem. Ztg.*, 1922, **46**, 4—5).—Historical.

Dehydroxidation of Alcohols. ERICH MÜLLER (*Z. Elektrochem.*, 1921, **27**, 563—567; cf. this vol., i, 109).—A number of alcohols, including ethyl alcohol, propyl alcohol, isobutyl alcohol, isopropyl alcohol, benzyl-alcohol, ethylene glycol, glycerol, and mannitol, in strongly alkaline solution on electrolysis or in the presence of oxidising agents such as potassium ferricyanide or in the presence of colloidal rhodium, give rise to hydrogen or hydrocarbons. The reaction is explained by the assumption that in the oxidation of alcohols to aldehydes a metastable intermediate product is formed which, in the presence of metals, breaks down to hydrogen or hydrocarbons according to the scheme: (1) $CH_3 \cdot CH_2 \cdot OH \rightleftharpoons CH_3 \cdot CH_2 \cdot O' + H^+$ and (2)



J. F. S.

The Influence of Potassium Hydroxide on the Formation of Vinyl Alcohol from Acetaldehyde. WILLIAM LLOYD EVANS and CLOYD D. LOOKER (*J. Amer. Chem. Soc.*, 1921, **43**, 1925—1928).—Poleck and Thummel's vinyl oxymercurochloride (A., 1890, 112) is obtained when alkaline solutions of acetaldehyde are treated with mercuric chloride, the yield of the oxymercurochloride being proportional to the concentration of the alkali present. Thus the production of vinyl alcohol is likewise proportional to the concentration of the alkali, and since vinyl alcohol is a necessary intermediate product in the formation of oxalic acid in the oxidation

of ethyl alcohol and acetaldehyde, the yield of oxalic acid must also be proportional to the concentration of the alkali used. A minimum concentration of about 1.40 grams of potassium hydroxide per litre is necessary for the formation of vinyl alcohol at 25°.

W. G.

Poly-ethers of Trimethylene Glycol. C. A. ROJAHN (*Ber.*, 1921, **54**, [B], 3118—3121).—During the purification of trimethylene glycol (this vol., i, 105) considerable quantities of residue are obtained in which the presence of poly-ethers of trimethylene glycol was suspected. Attempts to isolate a uniform substance therefrom by fractionation under diminished pressure did not give entirely satisfactory results owing to the continuous formation of resin, but the molecular weights of the individual fractions in boiling alcohol pointed to the conclusion that they contained di- to hexa-ethers. Further purification was attempted by conversion of the individual fractions into the corresponding phenylurethanes (which was only successful with the fraction of molecular weight corresponding with the di-ether), by acetylation and subsequent quantitative hydrolysis of the acetates and by fission of the ethers.

The *diphenylurethane* of *di-trimethylene glycol ether*, $C_{20}H_{24}O_5N_2$, crystallises in small, colourless needles, m. p. 104—105°.

The fraction, b. p. 130—170°/12 mm., yielded *di-trimethylene glycol ether diacetate*, $O(CH_2 \cdot CH_2 \cdot CH_2 \cdot OAc)_2$, a colourless, somewhat viscous liquid, b. p. 181—183°/52—54 mm., 265—270°/atmospheric pressure (slight decomp.), $d_{17.5}^{25}$ 1.0864, which was hydrolysed to the corresponding *di-ether*, a colourless, syrupy liquid, b. p. 155—160°/15 mm., $d_{17.5}^{25}$ 1.064. Similarly, the fraction b. p. 180—210°/12 mm., gave the *diacetate* of *tri-trimethylene glycol ether*, a colourless, viscous liquid, b. p. 238°/80 mm., $d_{17.5}^{25}$ 1.0546.

Di-trimethylene glycol ether is decomposed by a boiling saturated solution of hydrogen bromide in glacial acetic acid and subsequent treatment of the product with alkali hydroxide solution into trimethylene glycol, which was identified as the di-benzoate, needles, m. p. 60—61°, thus establishing the constitution of the ether.

Protracted ebullition of trimethylene glycol under the atmospheric pressure leads to the formation of poly-ethers. H. W.

Derivatives of Acetylenic Erythritol [*Hexinene- $\alpha\beta\epsilon\zeta$ -tetrol*], $HO \cdot CH_2 \cdot CH(OH) \cdot C \equiv C \cdot CH(OH) \cdot CH_2 \cdot OH$. R. LESPIEAU (*Compt. rend.*, 1921, **173**, 1367—1369).—Chloroacetaldehyde reacts with the dimagnesium derivative of acetylene in the presence of ether to give a black, viscous mass, which, when further treated with bromine in chloroform solution, gives a product which crystallises after several months. It is $\alpha\zeta$ -*dichloro- $\gamma\delta$ -dibromohexen- $\beta\epsilon$ -diol*, $CH_2Cl \cdot CH(OH) \cdot CBr \cdot CBr \cdot CH(OH) \cdot CH_2Cl$, m. p. 141—142.5°. The black, viscous mass mentioned above when treated with solid potassium hydroxide in ether gives the *dioxide*, $\begin{array}{c} CH_2 \\ \diagup \quad \diagdown \\ O \quad \quad O \end{array} > CH \cdot C \equiv C \cdot CH < \begin{array}{c} CH_2 \\ \diagdown \quad \diagup \\ O \quad \quad O \end{array}$,

b. p. 87.5—88.5°/10 mm., d_0 1.417.

W. G.

Alkylations. I. Alkylation of Sodium Sulphite. H. BAGGESGAARD-RASMUSSEN and SVEN WERNER (*Bull. Soc. chim.*, 1921, [iv], 29, 1073—1087).—A quantitative study of the interaction of methyl or ethyl iodide and sodium sulphite in 30% methyl alcohol shows that the reaction is essentially bimolecular, although the curve is somewhat irregular towards the end. The abnormal progress of the reaction may be explained on the basis that in solution sodium sulphite exists in two tautomeric forms, which are in equilibrium, $\text{NaSO}_2\cdot\text{ONa} \rightleftharpoons \text{SO}(\text{ONa})_2$, and that only the first undergoes alkylation, the atom of sodium attached to sulphur being replaced by the alkyl group. The results indicate that, in solution, 88% of the sodium sulphite is in the first form and 12% in the second. W. G.

Neutralisation of the Affinity of Main and Subsidiary Valencies in Compounds of a Higher Order. III. J. V. DUBSKY [with P. APTEKMANN] (*J. pr. Chem.*, 1921, [ii], 103, 109—128; cf. A., 1916, i, 541).—Investigation of the behaviour towards pyridine of nickel salts of various substituted xanthic acids shows that the ability of xanthates of the general formula, $\text{OR}\cdot\text{CS}\cdot\text{SX}$, to form additive compounds with pyridine is independent of the volume of the radicle R, although the stability of the additive product diminishes with the magnitude of R. Unlike the cobalt xanthates previously investigated, cobalt amyl, benzyl, and bornyl xanthates unite with two molecules of pyridine, giving additive compounds far less stable than those given by the corresponding nickel salts.

It is not found possible to convert either tertiary alcohols, such as dimethylethylcarbinol, or phenols into the corresponding xanthic acid derivatives (cf. Meyer, "Analyse und Konstitutionsermittlung organischer Verbindungen," 3rd ed., 474), but analogous secondary alcohols, such as cyclohexanol or borneol, readily yield xanthic acid compounds. These results are in accord with those of Bamberger and Lodter (A., 1890, 517), who found that 5 : 6 : 7 : 8-tetrahydro-2-naphthol acts as a true phenol and gives no xanthate, whereas the isomeric 1 : 2 : 3 : 4-tetrahydro-2-naphthol behaves as a secondary alcohol (cf. Lippmann and Fleissner, A., 1888, 296).

Nickel propyl xanthate, $\text{Ni}(\text{CS}_2\cdot\text{OPr})_2$, forms brown crystals and gives with pyridine the compound $\text{C}_8\text{H}_{14}\text{O}_2\text{S}_4\text{Ni}_2\text{C}_5\text{H}_5\text{N}$, which separates in pale green crystals and is unstable in the air. *Nickel butyl xanthate*, $\text{Ni}(\text{CS}_2\cdot\text{O}\cdot\text{CH}_2\text{Pr})_2$, forms brown crystals and gives a pale green compound with 2 molecules of pyridine. *Nickel amyl xanthate*, $\text{Ni}(\text{CS}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Pr})_2$, crystallises in brown leaflets with a greenish-yellow lustre and forms a pale green compound with 2 molecules of pyridine. Cobalt amyl xanthate gives an unstable, brown compound with 2 molecules of pyridine. *Nickel cetyl xanthate*, $\text{Ni}(\text{CS}_2\cdot\text{O}\cdot[\text{CH}_2]_{15}\cdot\text{CH}_3)_2$, crystallises in orange-yellow leaflets, and forms a very unstable, green compound with 2 molecules of pyridine. *Cobalt cetyl xanthate* forms green crystals. *Sodium benzyl xanthate*, $\text{NaCS}_2\cdot\text{O}\cdot\text{CH}_2\text{Ph}$, and the *potassium* salt, were prepared. *Cobalt benzyl xanthate*, $\text{Co}(\text{CS}_2\cdot\text{O}\cdot\text{CH}_2\text{Ph})_2$, forms lustrous, black crystals,

gives a deep green solution in benzene, and with 2 molecules of pyridine yields a brown *compound* which is highly unstable, even in an atmosphere of pyridine. *Nickel benzyl xanthate* forms black crystals and with 2 molecules of pyridine yields a *compound* which remains unchanged in an atmosphere of pyridine. *Potassium cyclohexyl xanthate*, $\text{KCS}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_{11}$, is crystalline, and the *nickel salt*, $\text{Ni}(\text{CS}_2 \cdot \text{O} \cdot \text{C}_6\text{H}_{11})_2$, forms brown crystals. *Sodium bornyl xanthate*, $\text{NaCS}_2 \cdot \text{O} \cdot \text{C}_{10}\text{H}_{17}$, is crystalline; the *nickel salt* forms brown crystals, and the cobalt salt forms with 2 molecules of pyridine a highly unstable, brown, crystalline *compound*. T. H. P.

$\beta\beta'$ -Dichlorodiethyl Ether. The Oxygen Analogue of Mustard Gas. OLIVER KAMM and JOHN H. WALDO (*J. Amer. Chem. Soc.*, 1921, **43**, 2223—2227).— $\beta\beta'$ -Dichlorodiethyl ether, b. p. 177—178° (corr.); d_{20}^{20} 1.213; n_{20}^{20} 1.457, may be prepared by the action of concentrated sulphuric acid on ethylene chlorohydrin. When condensed with aniline, it gives 4-phenylmorpholine. When condensed with ethyl malonate, the ether gives *ethyl tetrahydropyran-4 : 4-dicarboxylate*, $\text{O} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{C}(\text{CO}_2\text{Et})_2$, b. p. 260°/740—745 mm.; d_{20}^{20} 1.107, which with carbamide in the presence of sodium ethoxide yields *tetrahydropyran-4 : 5-spiro-2 : 4 : 6-triketohexahydropyrimidine*, $\text{O} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{C} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \text{CO} \cdot \text{NH} \end{array} \text{C} : \text{O}$, m. p. 218°.

$\beta\beta'$ -Dichlorodiethyl ether, unlike its sulphur analogue, exerts no deleterious action on the tissues of the animal body. Similarly, tetrahydropyran-4 : 5-spiro-2 : 4 : 6-triketohexahydropyrimidine, although closely related in structure to barbital, possesses no marked hypnotic properties. W. G.

$\gamma\gamma'$ -Dihalogenodipropyl Ethers. OLIVER KAMM and WALTER H. NEWCOMB (*J. Amer. Chem. Soc.*, 1921, **43**, 2228—2230).— $\gamma\gamma'$ -Dichlorodipropyl ether, b. p. 215°/745 mm.; d_{20}^{20} 1.140, was obtained by boiling trimethylene chlorohydrin with sulphuric acid under a reflux condenser.

Attempts to prepare trimethylene bromohydrin from trimethylene glycol by the action of hydrobromic acid and sulphuric acid gave a mixture of $\alpha\gamma$ -dibromopropane, the required bromohydrin and $\gamma\gamma'$ -dibromodipropyl ether, b. p. 128°/19 mm.; d_{20}^{20} 1.574. The products can be separated by fractional distillation. W. G.

Preparation of β -Chloro- and β -Bromo-propionic Acids from Trimethylene Glycol. C. A. ROJAHN (*Ber.*, 1921, **54**, [B], 3115—3118).—Trimethylene glycol is present in considerable amount in the sweet water concentrates obtained by the fermentation of sugar to glycerol by the method of Connstein and Lüdecke, particularly when the operation is conducted with insufficient care. It is purified by distillation, dilution of the fraction, b. p. 170—230°, with water, and treatment of the hot solution with lead oxide and barium hydroxide in a current of air. After removal of lead and barium by sulphuric acid, air is passed through

the hot solution whereby the bulk of the organic acids are removed and trimethylene glycol, b. p. 210° , d_{15}^{15} 1.0573, is ultimately isolated by repeated distillation, finally under diminished pressure. It is treated at the temperature of boiling water with about two-thirds of the calculated quantity of hydrogen chloride, and the product is fractionated, giving thereby (i) water and dichloropropane, (ii) γ -chloropropyl alcohol, (iii) unchanged trimethylene glycol, and (iv) a residue (see this vol., i, 103). β -Chloropropyl alcohol is added gradually to nitric acid (30%) at 0° , and the mixture maintained at below 5° during twenty-four hours, after which it is cautiously treated at 30 – 35° , allowed to remain during eight hours, and subsequently heated at 70 – 75° ; β -chloropropionic acid, colourless needles, m. p. 37 – 38° , is thus formed in 30 – 40% yield.

Trimethylene glycol is converted by boiling hydrobromic acid into a mixture of $\alpha\gamma$ -dibromopropane and γ -bromopropyl alcohol. The latter is oxidised by nitric acid to β -bromopropionic acid, b. p. 140 – $142^{\circ}/45$ mm., m. p. 62 – 63° ; the action proceeds less violently than with γ -chloropropyl alcohol.

H. W.

The Mixed Anhydrides of Sulphuric Acid and Carboxylic Acids. II. *n*-Butyrylsulphuric Acid. A. J. VAN PESKI (*Rec. trav. chim.*, 1921, **40**, 736–746; cf. A., 1921, i, 302).—*n*-Butyrylsulphuric acid, $C_3H_7\cdot CO\cdot O\cdot SO_3H$, is formed by the action of sulphur trioxide on *n*-butyric acid, and resembles acetylsulphuric acid in its general properties. When heated, it is transformed into α -sulphobutyric acid, and at 70° evolution of carbon dioxide takes place with sharp rise in temperature to about 110° , the other product being α -sulphobutyronone. Full experimental details are given as to the preparation of the acid, its sodium salt, and, from the latter, of butyric anhydride, the preparation of *isoamylsulphuric acid*, phenyl butyrate, *tribromobutyranilide* (long needles, m. p. 167.8°), *tribromobutyrophenol* (a pale yellow viscous liquid, m. p. 6 – 9° , b. p. $192.8^{\circ}/16$ mm. corr.) are described and also the sulphonation of benzene by the acid.

H. J. E.

C₁₈ Fatty Acids. II. The Relation of Oleic and Elaidic Acids to their Halogen Additive Products. BEN H. NICOLET (*J. Amer. Chem. Soc.*, 1921, **43**, 2122–2125; cf. A., 1921, i, 390).—Using the anilides of the various acids as means of characterising them, it is shown that there is no *cis-trans*-isomerisation when bromine is added to the double bond and later removed by zinc and alcoholic hydrochloric acid in the case of oleic or elaidic acids. These acids thus differ from linolic acid in this respect. *Oleanilide dibromide* has m. p. 67° ; *elaidanilide dibromide* has m. p. 88° .

W. G.

The Mechanism of the Oxidation of Drying Oils as Elucidated by a Study of the True Oxygen Absorption. III. The Action of Driers. SAMUEL COFFEY (*T.*, 1922, **121**, 17–23).

The Formation of Substituted Succinic Acids from Esters of $\alpha\beta$ -Unsaturated Acids. LUCY HIGGINBOTHAM and ARTHUR LAPWORTH (*T.*, 1922, **121**, 49–54).

Nitromalic Acid. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 2084—2091; cf. A., 1921, i, 303).—*Nitromalic acid*, m. p. 110—112°, is readily obtained by adding fuming sulphuric acid to a cooled solution of malic acid in nitric acid (*d* 1.42). It gives a *sodium* and a *silver* salt. When hydrolysed with sodium hydroxide in aqueous solution, it yields a mixture of nitric and nitrous acids, the percentage of nitrous acid being independent of the temperature, the concentration, or the presence of an excess of alkali. Similar results were obtained in methyl alcoholic solution, except that the amount of nitrous acid obtained was nearly twice that in aqueous solution. When alkali was excluded altogether and a substance such as sulphanilic acid, capable of reacting with the nitrous acid as fast as it is formed, was present, the production of nitrous acid was greatly increased and the rate under these conditions corresponded with a unimolecular reaction.

In the hydrolysis of nitric esters, two independent processes occur. One is the normal hydrolysis into alcohol or hydroxy-acid and nitric acid, and the second is isomerisation to a nitrous ester, which subsequently is hydrolysed to an aldehyde or a ketone. Each of these reactions proceeds at its own rate under given conditions. The action of alcohol in increasing the yield of nitrous acid is that it diminishes the rate of the normal hydrolysis of the nitric ester to nitric acid. The constant yield when alkali is employed is a false equilibrium. The real constant is the ratio of the velocities of the two reactions.

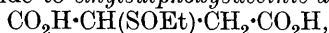
W. G.

Stereoisomeric Ethylthiolsuccinic Acids. PETER FITGER (*Ber.*, 1921, **54**, [B], 2943—2951).—*r-Ethylthiolsuccinic acid*, $\text{CO}_2\text{H}\cdot\text{CH}(\text{SEt})\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, small, colourless needles, m. p. 124—126°, is prepared from ethyl mercaptan, sodium bromosuccinate, and sodium hydroxide in aqueous solution or by the action of ethyl bromide and sodium hydroxide on sodium thiolsuccinate dissolved in water. The normal salts, with the exception of those of *silver*, *lead*, and *iron*, are generally freely soluble in water; the *sodium hydrogen*, *potassium hydrogen*, and *barium hydrogen* salts crystallise in colourless prisms. Attempts to resolve the racemic acid into its optically active components by means of the phenyl-ethylamines were unsuccessful, since a partly racemic salt is the least soluble. On the other hand, a partly active *d*-acid could be obtained by the action of ethyl mercaptan and sodium hydroxide on an aqueous solution of sodium *l*-bromosuccinate, and from this the pure *d*-variety could be isolated with the aid of *d*-phenyl-ethylamine. *d-Ethylthiolsuccinic acid*, m. p. 126—128°, forms lustrous aggregates of prisms or needles; it has $[\alpha]_D^{20} + 139.3^\circ$ in absolute alcohol, $[\alpha]_D^{20} + 149.8^\circ$ in ethyl acetate, $[\alpha]_D^{20} + 145.0^\circ$ in acetone, $[\alpha]_D^{20} + 107.7^\circ$ in water. Under certain conditions, it is possible to isolate the almost pure *d*-acid by the process described above in relatively good yield and without recourse to *d*-phenyl-ethylamine. *l-Ethylthiolsuccinic acid* is obtained in good yield by the action of ethyl bromide and sodium hydroxide on an aqueous

solution of sodium *l*-thiolsuccinate; it forms aggregates of lustrous needles, m. p. 126—128°, $[\alpha]_D^{19}$ —139·3° in absolute alcohol, $[\alpha]_D^{19}$ —150·0° in ethyl acetate, $[\alpha]_D^{20}$ —145·1° in acetone, $[\alpha]_D^{20}$ —108·0° in water. It was not found possible to isolate well-defined salts of the active acids.

H. W.

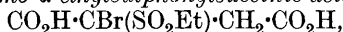
Certain Products of the Oxidation of Inactive Ethylthiol-succinic Acid. PETER FITGER (*Ber.*, 1921, **54**, [B], 2952—2963; cf. preceding abstract).—Ethylthiolsuccinic acid is oxidised by hydrogen peroxide to *ethylsulphoxysuccinic acid*,



which becomes discoloured at 120°, but does not exhibit a definite melting point when more strongly heated. The *ferric* and *silver* salts are described, but, in general, the normal salts do not appear to be sharply characterised. The acid is unstable when dissolved in water or ethyl acetate, and in boiling solution becomes decomposed into carbon dioxide, ethyl mercaptan, diethyl disulphide, fumaric acid, and β -*ethylthiolacrylic acid*, long, colourless, slender needles, m. p. 83—84°.

Sodium ethylthiolsuccinate is oxidised by potassium permanganate in aqueous solution, and in the presence of carbon dioxide to *r*-*ethylsulphonylsuccinic acid*, long, colourless prisms, m. p. 167—168°; the *sodium* salt, $\text{C}_6\text{H}_8\text{O}_6\text{SNa}_2\cdot 2\text{H}_2\text{O}$, colourless, rhombic plates, *barium* salt, pointed prisms, *silver* salt (+2H₂O), prisms, and *ferric* salt are described.

The action of bromine on an aqueous solution of *r*-ethylthiolsuccinic acid appears to lead to the initial formation of ethylsulphoxysuccinic acid (which is too unstable to permit its isolation in these circumstances), and then to ethylsulphonylsuccinic acid, which can only be prepared in poor yield in this manner. The use of three molecular proportions of bromine, on the other hand, readily gives α -*bromo- α -ethylsulphonylsuccinic acid*,



colourless, microscopic plates (+H₂O), m. p. 83—85° (decomp.); the *silver*, *ferric*, and *barium* (+3H₂O) salts are described. The acid readily eliminates carbon dioxide in hot aqueous acidic solution and passes into β -*bromo- β -ethylsulphonylpropionic acid*, colourless prisms, m. p. 142—143° (decomp.); the *ferric* salt and *silver* salt, needles, are described.

Ethylthiolsuccinic acid, when dissolved in glacial acetic acid, reacts vigorously with bromine, giving α -*bromo- β -ethylthiolmaleic acid*, $\text{CO}_2\text{H}\cdot\text{CBr}:\text{C}(\text{SEt})\cdot\text{CO}_2\text{H}$, pale yellow, thin plates or flattened prisms, m. p. 131° to 141° (decomp.), according to the mode of heating. The *barium* salt, voluminous needles, and the *anhydride*, long, pale yellow needles, m. p. 44—45°, are described.

Ethylthiolsuccinic acid is extensively decomposed by potassium permanganate in bicarbonate-alkaline solution, but the products formed have not yet been identified.

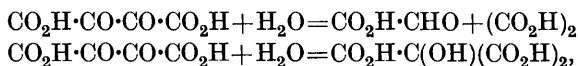
H. W.

Behaviour of Fehling's Solution in Light. A. BENRATH and J. OBERBACH (*Z. physikal. Chem.*, 1921, **98**, 498—501).—The

authors have been unable to confirm the statement of Bolin and Linder (A., 1920, ii, 144) that when Fehling's solution contained in glass vessels is exposed to ultra-violet light no reaction occurs. It is found that Fehling's solution exposed in a glass tube to sunlight is decolorised, with the evolution of hydrogen. Illumination of an alkaline solution of potassium sodium tartrate gives no evolution of gas, but if cuprous oxide is added, hydrogen is vigorously evolved; copper turnings and even massive copper have the same action. Fehling's solution to which copper has been added evolves hydrogen immediately it is exposed to light, and the action persists for some time after the light is removed. The oxidation products of tartaric acid, such as dihydroxytartaric acid, mesoxalic acid, and formic acid, when treated with alkali hydroxides and metallic copper, evolve hydrogen in light. Mesoxalic acid has the most pronounced action, and the insoluble sodium dihydroxytartrate passes into solution with the evolution of hydrogen. If dihydroxytartaric acid is added to Fehling's solution, it is decolorised more rapidly than if the addition has not been made. In all cases where the reaction was carried out in quartz vessels, a thin deposit of copper was found on the walls of the vessel. The reaction probably follows the course: the Fehling's solution decomposes in light, forming cuprous oxide and metallic copper, and these act catalytically on the tartaric acid, producing hydrogen and oxidation products of tartaric acid. Some of the oxidation products are further oxidised in the dark.

J. F. S.

Dihydroxytartaric Acid. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 2091—2097; cf. Fenton, T., 1898, **74**, 71; 1902, **81**, 426).—Dihydroxytartaric acid, considered as a diketone, has a structure similar to benzil, and when acted on by alkalis behaves like benzil, and thus its decomposition is represented by the equations



the carboxytartronic acid losing carbon dioxide and giving tartronic acid. It is shown that when sodium dihydroxytartrate is heated at 160°, carbon dioxide is evolved and glyoxylic acid and oxalic acid were identified along with tartronic acid in the products of decomposition.

In Fenton's method for the estimation of sodium by precipitation as sodium dihydroxytartrate and subsequent oxidation of this salt with standard permanganate, it is necessary to carry out the oxidation first in alkaline and then in acid solution in order to obtain consistent results.

W. G.

Internal or Catalytic Dehydroxidation of Formaldehyde. ERICH MÜLLER (*Z. Elektrochem.*, 1921, **27**, 558—563).—Alkaline solutions of formaldehyde, when treated with oxidising agents such

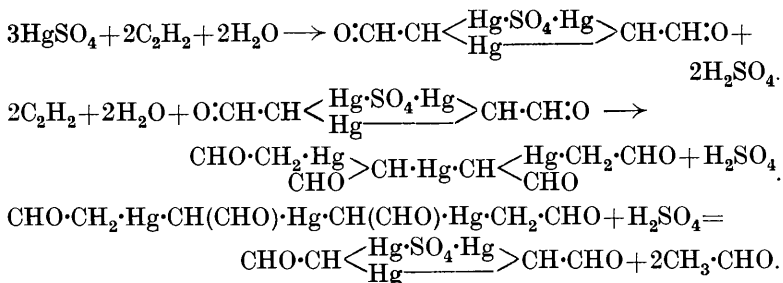
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as cuprous oxide, cupric oxide, silver oxide, potassium persulphate, hydrogen peroxide, or potassium ferricyanide, are converted into formic acid with evolution of hydrogen. The same reaction occurs on electrolysis of an alkaline solution of formaldehyde, and, finally, finely divided metals (Cu, Ag, Pd, Pt.), when added to alkaline solutions of formaldehyde, bring about a rapid evolution of hydrogen and formation of formic acid. The catalytic change is best shown with colloidal rhodium, thus: If to 30 c.c. of 15*N*-sodium hydroxide and 50 c.c. of 20% formaldehyde 20 c.c. of colloidal rhodium (0.05 gram) are added at 25°, there is an evolution of 3 litres of hydrogen in two hours. The author explains the electrolytic reaction as follows: In solution, formaldehyde exists in equilibrium as represented by the equations $\text{HCHO} + \text{H}_2\text{O} \rightleftharpoons \text{HCH}(\text{OH})_2 \rightleftharpoons \text{HCHO}'(\text{OH}) + \text{H}^+$, on the anode the reaction $\text{HCH}(\text{OH})\text{O}' + \text{F} = \text{HCH}(\text{OH})\text{O}$ takes place; this substance the author terms an O-aldehyde, and states that it may exist in the metastable condition in formaldehyde solution up to a definite concentration. Above this definite concentration, it spontaneously decomposes to give hydrogen and formic acid, $\text{H}\cdot\text{CH}(\text{OH})\text{O} \rightarrow \text{HC}(\text{OH})\text{O} + \text{H}$, but at lower concentrations it is decomposed only by oxidising agents or catalysts. This reaction the author terms "*dehydroxidation*." The course of the reaction with catalysts is represented as follows: In alkaline solution, a reaction similar to Cannizzaro's reaction occurs in two stages, (1) $3\text{HCHO} + 2\text{H}_2\text{O} = \text{CH}_3\text{OH} + 2\text{HCH}(\text{OH})\text{O}$ and in the presence of the catalysts (2) $2\text{HCH}(\text{OH})\text{O} = 2\text{HCO}_2\text{H} + \text{H}_2$. J. F. S.

Alcoholic Fermentation of Formaldehyde by Osmium.

ERICH MÜLLER (*Ber.*, 1921, **54**, [B], 3214—3216).—An aqueous solution of formaldehyde decomposes in the presence of osmium into carbon dioxide and methyl alcohol. The catalytic activity of the metal diminishes somewhat rapidly. At about 50°, and then only to a small extent, hydrogen is also evolved. H. W.

The Rôle of Mercury Salts in the Catalytic Transformation of Acetylene into Acetaldehyde and a New Commercial Process for the Manufacture of Paracetaldehyde. RICHARD R. VOGT and JULIUS A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1921, **43**, 2071—2081).—In the commercial preparation of acetaldehyde from acetylene and water by the use of mercury salts as catalysts, the chief drawback is the ease with which the mercury salt is reduced to metallic mercury, with consequent loss in activity. It is now shown that mercuric sulphate in sulphuric acid is the most suitable catalyst, on account of its activity and less ready reduction, but the difficulty attached to its use is the impossibility of separating acetaldehyde from the more concentrated acid solution and the rapid reduction of the mercury compounds in dilute acid solutions. In such solutions, the mercury is soon converted into an organic compound, and this compound acts as the catalyst. It is suggested that the reaction may be as follows:



It is considered that the reduction of mercury compounds by acetylene is in some way due to their hydrolysis in dilute acid solutions, and the only way in which acetaldehyde could be obtained without the reduction of any mercury salt whatever was by the action of a stream of moist acetylene at 70—120° on a dry mixture of the mercuric sulphate-acetylene compound and sodium, potassium, or ammonium hydrogen sulphates. This process was, however, so slow as not to be of practical value.

Owing to the difficulty of obtaining the acetaldehyde from these acid solutions, it was found advantageous to use the solutions in place of pure acetaldehyde in the preparation of quinaldine. For this purpose, aniline sulphate was dissolved along with the mercuric sulphate in sulphuric acid before passing in the acetylene, a concentration of 40% of sulphuric acid and a temperature of 60° being most advantageous.

For the preparation of paracetaldehyde, a large bottle or carboy was filled with dry fragments of glass on which a pasty mass of mercuric sulphate, sodium or ammonium hydrogen sulphate, and a very little water was distributed and the moist acetylene led in with shaking. The paracetaldehyde accumulated as a separate layer at the bottom of the bottle. The aldehyde-mercury ratio obtained was 17 : 1 with a steady production of paracetaldehyde. In this method no distillation process is necessary, there are no by-products or waste products, and there is no excess of acetylene to be recovered.

W. G.

Preparation of Aldol from Acetaldehyde. NATHAN GRÜNSTEIN (Brit. Pat. 147119).—Aldol condensation by means of a very small quantity of an alkaline catalyst proceeds, without the addition of ice or a neutral organic diluent, as a smooth and easily controlled reaction if the acetic acid contained in the acetaldehyde is first neutralised with the requisite quantity of sodium hydroxide solution, and the catalyst is then gradually added with cooling, the operation being preferably conducted in an atmosphere of nitrogen to prevent the formation of further quantities of acetic acid by atmospheric oxidation. As catalyst, aqueous alkali hydroxide, not exceeding in quantity 1 part of alkali to 100 parts of acetaldehyde, may be employed, or equally favourable results are obtained with alkali or alkaline-earth carbides or cyanides, or alkaline-earth hydroxides. In all cases, the presence of a small

quantity of water appears to be essential. To prevent the condensation proceeding too far with formation of resins, etc., it is stopped before all the acetaldehyde has been converted into aldol by adding sufficient hydrochloric or acetic acid to neutralise the alkali, separating the salt, and distilling the product in a vacuum.

G. F. M.

Preparation of Butaldehyde and Butyl Alcohol from Crotonaldehyde. NATHAN GRÜNSTEIN (Brit. Pat. 147118).—Butaldehyde and butyl alcohol are obtained in good yield by the catalytic hydrogenation of crotonaldehyde in presence of 20–25% of water or steam. The formation of undesirable by-products of high boiling point is greatly minimised by using a large excess of hydrogen, and the excess passing from the catalyst can be recirculated after suitable cooling to condense the reaction products. The catalyst is prepared by depositing in the usual manner 5–15 parts of nickel on 100 parts of pumice or kieselguhr, and the optimum temperature for the hydrogenation is 110–120°. Instead of using a mixture of pure crotonaldehyde and water, the product of the decomposition of aldol may be employed with equal advantage. The reaction may be carried out either in a tube charged with the contact material, or with the liquid substances in an autoclave, the hydrogen in the latter case being pumped in at 10–15 atm. pressure with vigorous agitation of the liquid. In either case, provision must be made for the periodical discharge of gas from the apparatus as the hydrogen becomes contaminated with propylene and carbon monoxide produced by the “cracking” of the crotonaldehyde, particularly at the higher temperatures.

G. F. M.

Benzyl Ethers of Carbohydrates. M. GOMBERG and C. C. BUCHLER (*J. Amer. Chem. Soc.*, 1921, **43**, 1904–1911).—Carbohydrates of all types are readily benzylated and various benzyl ethers obtained when the carbohydrate is heated with benzyl chloride and aqueous sodium hydroxide for several hours at about 90°. Thus α -methylglucoside yielded benzylglucoside, *dibenzylmethylglucoside*, and *tetrabenzylbenzylglucoside*. Sucrose gave a solid *dibenzyl* and a liquid *pentabenzyl* derivative. Dextrin gave a *benzyl*dextrin, $C_{12}H_{19}O_{10} \cdot C_7H_7$, m. p. 208–210°; potato starch gave a *monobenzyl* derivative, $C_{12}H_{19}O_{10} \cdot C_7H_7$, m. p. 200–203°, and maize starch gave a *dibenzyl* derivative, $C_{12}H_{18}O_{10}(C_7H_7)_2$, m. p. 203–205°. Cellulose, unless previously subjected to one of the several so-called “hydration” processes, underwent only slight benzylation, but after hydration a *monobenzyl*, a *tribenzyl*, and a *tetrabenzyl* derivative were obtained according to the conditions. Benzylated cellulose, unlike cellulose itself, is insoluble in Schweizer’s reagent.

W. G.

Biochemical Synthesis of α -Methyl-*d*-mannoside. H. HÉRISSEY (*Compt. rend.*, 1921, **173**, 1406–1407; cf. A., 1921, i, 306).—By the action of α -methyl-*d*-mannosidase, present in the

germinated seeds of lucerne, on a solution of mannose in 10% methyl alcohol, the author has synthesised α -methyl-*D*-mannoside and obtained it in a crystalline form. W. G.

The Formation of Osazones. MARC H. VAN LAER and R. LOMBAERS (*Bull. Soc. chim. Belg.*, 1921, **30**, 296—301).—A study of the formation of the osazones of l  vulose and dextrose shows that the difference in the time of the reaction has its origin at the second stage and is due to the fact that the oxidation by the second molecule of phenylhydrazine is, in the first case, that of a primary alcohol, and, in the second, that of a secondary one. H. J. E.

Pentosans. EMIL HEUSER (*J. pr. Chem.*, 1921, [ii], **103**, 69—102).—[With MARIA BRADEN.]—Salkowski's method for the preparation of xylan from wheat straw (A., 1902, i, 206) yields a product which gives at most 80% of the theoretical proportion of furfuraldehyde and contains appreciable amounts of ash. The author finds that application of a modification of Salkowski's method to bleached straw cellulose [*Strohzellstoff*] (cf. Heuser and Haug, *Z. angew. Chem.*, 1918, **31**, 99) is capable of yielding a product containing 96% of xylan, calculated on the dry ash-free material, and 0.35% of ash.

[With E. K  RSCHNER.]—By 43% hydrochloric acid solution (*d* 1.21) at the ordinary temperature, xylan cannot be hydrolysed completely to xylose, since part of the latter is destroyed before the hydrolysis is finished. The results obtained when the course of the hydrolysis is followed by measuring the copper-reducing power and by estimation of the furfuraldehyde obtained by treatment with hydrochloric acid show that no sugar other than xylose is formed during the hydrolysis, but fail to indicate the nature of the 4% of non-xylan in the preparation. [Cf. *J. Soc. Chem. Ind.*, 1922, Feb.] T. H. P.

Chemistry of Starch. IV. The Methylation of Polyamyloses. HANS PRINGSHEIM and WALTER PERSCH (*Ber.*, 1921, **54**, [B], 3162—3168; cf. A., 1912, i, 832; 1913, i, 1156; 1915, i, 382).—Tetra-amylose is not converted into a homogeneous product by sodium hydroxide and methyl sulphate. If, however, the material which is thus obtained, containing 28% OMe, is treated with methyl iodide and silver oxide, it gives a crystalline substance which contains two methoxyl groups in each dextrose residue. Very protracted treatment does not bring about methylation of the third hydroxyl group. The most important observation, however, is that the treatment does not cause depolymerisation, and that, in accordance with determinations of the molecular weight in freezing benzene or naphthalene, the product is to be regarded as *octamethyltetra-amylose*. It crystallises in colourless, hexagonal plates which do not decompose below 250   and has $[\alpha]_D^{20} + 141.5$ to $+148.2^\circ$ in ethyl alcoholic solution. The slight mutarotation is somewhat surprising, since the original tetra-amylose is not mutarotatory.

Fermentation of starch by a degenerated specimen of *Bacillus*

macerans has led to the isolation of a tetra-amylose which gives a dark green, crystalline, additive compound with iodine, and, after being freed from the latter, a crystalline, additive product with carbon disulphide. Removal of the latter gives a tetra-amylose crystallising in needles and having a specific rotation higher by a few degrees than that quoted for previous specimens. The substance is possibly a stereoisomeride, but its preparation is difficult and uncertain. H. W.

Preparation and Alkyl Interchange of Cellulose Esters; Cellulose Stearate and Laurate. AD. GRÜN and FRANZ WITTKA (*Z. angew. Chem.*, 1921, **34**, 645—648; cf. A., 1921, i, 222).—The attempt to find a simple method for the preparation of cellulose esters of the higher fatty acids has led to observations on the interchange of alkyl groups between cellulose esters and alcohols, and between alkyl esters and cellulose. Cellulose esters of the higher fatty acids are formed by acylation of cellulose with an acid chloride and pyridine. Preliminary experiments with stearyl chloride led to impure monostearate, and mixtures of cellulose mono- and di-stearate; the pure distearate was only obtained by the use of a large excess of the acid chloride, the reaction mixture being diluted with benzene. *Cellulose distearate* forms white fibres, m. p. 220° (decomp.), is insoluble in the usual cellulose solvents, even in an ammoniacal solution of copper oxide, but soluble in fatty acids and in glycerides on heating at about 200°. The fibres under the microscope are cylindrical and swollen to two or three times the original volume, and the lumen has partly disappeared. *Cellulose dilaurate* is a white, spongy, short-fibred mass, m. p. about 250°. The solubility in glycerides is greater than that of the distearate, and, when dissolved in triisovalerin and diluted with alcohol, a faintly coloured powder is obtained, m. p. 110°. Cellulose distearate and dilaurate exhibit a characteristic behaviour with fat colouring matters, for with Sudan-III an intense scarlet-red coloration is produced which is not removed by treatment with 50% alcohol, whereas cellulose or cellulose steeped in fatty acids is only faintly coloured, and the colour is completely removed by 50% alcohol. These cellulose esters may be distinguished further from cellulose by their behaviour with iodine and sulphuric acid, for they are coloured wine-red and the fibre swells but little, and is not disintegrated by the acid. The interchange of alkyl groups between ethyl esters of fatty acids and cellulose does not proceed as readily as with glycerol. Alkyl interchange between the cellulose esters of the lower fatty acids and alcohols proceeds readily, however, but the esters of the higher fatty acids react with difficulty. Thus, cellulose triacetate and ethyl alcohol yield cellulose monoacetate, whereas under similar conditions but little stearic acid is removed from cellulose distearate. The stability of the cellulose esters increases with their molecular weight. When isoamyl alcohol reacts with cellulose triacetate, alkyl interchange occurs, but is accompanied by a far-reaching degradation of the cellulose molecule. F. M. R.

Plant Colloids. XII. Action of Formaldehyde on Cellulose. M. SAMEC and S. FERJANČIĆ (*Koll. Chem. Beihefte*, 1921, **14**, 209—226; cf. A., 1921, i, 400, 707).—Purified sulphite cellulose has been heated under pressure with formaldehyde or formic acid at 143° for various periods of time and the products have been compared with the original cellulose. It is shown that formaldehyde reacts with cellulose and its derivatives when they have been converted into the emulsoid condition. The product does not give any iodine coloration, but after washing away the formaldehyde the colour can be obtained after the product has been emulsified by sulphuric acid. The sulpholysis of cellulose in the presence of formaldehyde takes place differently from the action in its absence and leads to low molecular derivatives. The charring of cellulose derivatives by strong sulphuric acid is strongly retarded by formaldehyde, and in the same way the esterification of cellulose derivatives is also retarded. Formaldehyde has a similar action on cellulose derivatives. The experimental results are explained by the assumption that the formaldehyde unites to the cellulose with the breaking of oxygen rings and the formation of oxymethylene groups, and that in the cellulose molecule an internal anhydride formation follows with the hydroxyl group of a neighbouring dextrose residue. J. F. S.

Alkaline Copper Hydroxide Solutions and Copper Oxide—Ammine—Cellulose Solutions. WILHELM TRAUBE (*Ber.*, 1921, **54**, [B], 3220—3232).—The term “alkaline copper hydroxide solutions” is applied to the aqueous solutions produced from polyhydroxy-compounds, copper oxide or hydroxide, and alkali hydroxides. The quantity of copper hydroxide dissolved by solutions of glycerol and potassium hydroxide in which the concentration of the latter is maintained constant increases with increasing molecular ratio of alkali to glycerol within certain limits; it diminishes with increasing dilution of the alkali. Since copper hydroxide is not soluble in glycerol or in alkali hydroxide solutions of the concentration used, it appears that the action depends on the initial formation of alkali glyceroxide and reaction of the latter with copper hydroxide to give an alkali-copper glyceroxide. The behaviour of polyhydroxy-alcohols and of polyhydroxy-compounds in general is similar to that of glycerol. The place of the fixed alkalis can be taken by the ethylenediamine hydroxide of copper (A., 1912, i, 9), since it is found that addition of glycerol enables a solution of ethylenediamine saturated with copper hydroxide to dissolve considerably further amounts of the substance. A similar effect is produced by mannitol or sucrose. The solubility of cellulose in a solution of the ethylenediamine hydroxide of copper is also to be attributed to the formation of an alkoxide compound of the polyhydroxy-compounds produced by the degradation of cellulose, since it is found that a solution of ethylenediamine saturated with copper hydroxide has the power of dissolving more of the latter after being treated with cellulose. The ability to dissolve cellulose is, however, a specific

property of the copper solutions, since the ammine compounds of other metallic hydroxides, which in all probability are able to give rise to alkoxide derivatives, do not possess this power. The same conception of the solution of cellulose must be extended also to Schweizer's solution. Since copper hydroxide is relatively but little soluble in aqueous ammonia, it is not possible to obtain concentrated solutions of cellulose directly. Such solutions can, however, be obtained by taking advantage of the fact that Schweizer's solution saturated with cellulose has the power of dissolving further amounts of both cellulose and copper hydroxide. The explanation of the phenomenon is found in the existence in solution of an equilibrium, $\text{Cu}(\text{OH})_2 + 4\text{NH}_3 \rightleftharpoons [\text{Cu}(\text{NH}_3)_4](\text{OH})_2$; in proportion as the ammine is removed in combination with cellulose or the products of its degradation, the equilibrium is displaced towards the right-hand side of the equation and further quantities of copper hydroxide can be dissolved. The insolubility of cellulose in copper ammine solutions which have been treated with glycerol is due to the fact that the copper is now present as the glyceroxide. The precipitation of cellulose from its solution in Schweizer's reagent by glycerol is likewise explained.

Soluble starch behaves towards alkaline copper hydroxide solution in the same manner as the other polyhydroxy-compounds. Ordinary starch swells and becomes intensely blue when brought into contact with ethylenediamine solution saturated with copper hydroxide; the colour is not removed by repeated washing with water. The substance contains nitrogen, and, possibly, is a well-defined compound of alkoxide nature. H. W.

Cellulose. VI. De-polymerisation of Ethyl-cellulose.

KURT HESS and WALTER WITTELSBACH (*Ber.*, 1921, **54**, [B], 3232—3241).—In a previous communication (*A.*, 1921, i, 710), the depolymerisation of ethyl-cellulose has been described and substances with a molecular weight in dilute solution of 800—900 have been isolated. Since, however, the molecular weight increased rapidly with increasing concentration owing to association, it remained doubtful whether still lower values would be observed in more dilute solution and the uncertainty was increased by the subsequent discovery (this vol., i, 12) of the ready conversion of cellulose by acetyl chloride into a compound of the composition and molecular weight of a biose-anhydride. It is now shown that the products of acetolysis of ethyl-cellulose, after action varying in its duration from two to one hundred and forty-four hours, have molecular weights in very dilute solution corresponding with those required for a tetraethylbiose anhydride. De-polymerisation of cellulose to "celluxose" occurs, therefore, with much greater readiness than has been assumed previously. H. W.

Mercury Fulminate. HANS RATHSBURG (*Ber.*, 1921, **54**, [B], 3185—3187).—The presence of unsaturated impurities in mercury fulminate can be detected by the behaviour of the

specimen towards potassium permanganate which is not affected by the pure compound. The amount of oxidising agent used by impure specimens depends on the medium in which they are suspended and, generally, is greatest in acid and least in aqueous suspension. On the other hand, the addition of halogen cannot be applied quantitatively, since pure mercury fulminate unites with halogen. Nevertheless, titration with iodine is a useful method of detecting the presence of more reactive mercury salts, which is judged by the presence of greater or less quantities of red mercuric iodide in the titrated mixture. The following process is more convenient than that advocated by Solonina for the estimation of oxalate in mercury fulminate. The specimen (about 3 grams) is dissolved in ammonia (20%) and the bulk of the fulminate, in so far as it is not decomposed, is re-precipitated with acetic acid. Oxalic acid is precipitated in the clear filtrate (or an aliquot portion thereof) with approximately *N*-calcium chloride and the calcium oxalate is weighed as such or as calcium oxide. H. W.

Preparation of Guanidine Nitrate. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1921, **43**, 2234—2238).—Guanidine nitrate may be obtained in excellent yield by heating dicyanodiamide with slightly more than two molecular proportions of ammonium nitrate for two hours at 160°, using either the dry materials alone or with water in an autoclave. At lower temperatures, diguanide nitrate is the main product. The reaction consists in the formation of diguanide nitrate by the action of one molecule of ammonium nitrate, and this then reacts with the second molecule of ammonium nitrate at the higher temperature to give guanidine nitrate.

The reaction is not therefore dependent on the depolymerisation of dicyanodiamide as suggested by Werner and Bell (*T.*, 1920, **118**, 1133) in their account of a similar preparation of guanidine thiocyanate. W. G.

The Synthesis of a Nitrogenous Principle of Plants, Hydrocyanic Acid, by the Oxidation of Ammonia and Carbohydrates, Glycerol, or Formaldehyde. R. FOSSE (*Compt. rend.*, 1921, **173**, 1370—1372; cf. *A.*, 1919, i, 152, 313, 459; 1920, i, 664, ii, 714, 779; 1921, i, 165, 321, 500, 652).—In the presence of a silver or a mercury salt, ammoniacal solutions of dextrose, sucrose, starch, dextrin, glycerol, or formaldehyde, on oxidation by potassium or calcium permanganate give cyanides as one of the products. W. G.

Synthesis of Hydrocyanic Acid by Oxidation, in Ammoniacal Silver Solution, of Alcohols, Phenols, and Amines. R. FOSSE and A. HIEULLE (*Compt. rend.*, 1922, **174**, 39—41).—It has been shown that, by the oxidation of a number of alcohols, phenols, and amines by potassium or calcium permanganate in ammoniacal solution in the presence of silver nitrate, hydrocyanic acid is always formed, but in variable amount. The highest yield of hydrocyanic acid was obtained from methylamine. W. G.

The Action of Aqueous Ammonia on Dicyanodiamide. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1921, **43**, 2230—2233).—When dicyanodiamide is heated in a sealed tube at 150° with aqueous ammonia (*d* 0.9) it gives, first, guanylcarbamide and then guanidine carbonate. If the reaction is prolonged, the guanidine carbonate reacts with ammonia and carbon dioxide, giving in turn ammelide, ammeline, and, finally, melamine. W. G.

Organic Compounds of Arsenic. VII. Additive Compounds of Iodoform and Salts of Organic Bases of Tervalent Elements. WILHELM STEINKOPF and GUSTAV SCHWEN (*Ber.*, 1921, **54**, [B], 2969—2975; cf. this vol., i, 71, 72).—Attempts to convert tetramethylarsonium tri-iodide into the corresponding monoiodide by means of alcoholic potassium hydroxide solution have led to the isolation of an additive compound of molecular proportions of the latter and iodoform. Similar products can be obtained from quaternary ammonium, phosphonium, and stibinium iodides and, in certain cases, from the corresponding bromides. These compounds may also be produced from their components or from a mixture of the tertiary arsine, methyl iodide, and iodoform. They are pale yellow to yellow, crystalline substances which can be recrystallised without decomposition from organic solvents, but are decomposed by water with separation of iodoform. They are for the most part odourless. Their physiological action appears to be attributable to iodoform poisoning.

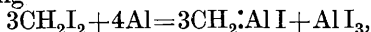
The following individual compounds are described. *Tetramethylarsonium iodide iodoform*, $I[Me_4As] \dots CHI_3$, m. p. 165° (discoloration). *Phenyltrimethylarsonium iodide iodoform*, yellow needles, m. p. 143—145°, prepared by the methods indicated above or from phenyltrimethylarsonium hydroxide and iodoform in alcoholic solution. *Triphenylmethylarsonium bromide*, colourless crystals, m. p. 195°. *Triphenylmethylarsonium bromide iodoform*, pale brownish-yellow leaflets, m. p. 124°. *Tetramethylammonium iodide iodoform*, yellow needles, m. p. 237° after previous darkening when rapidly heated. *Tetraethylphosphonium iodide iodoform*, m. p. 212—215° after previous darkening when rapidly heated. [Tetraethylphosphonium bromide crystallises in colourless needles, m. p. about 320° (decomp.).] *Tetraethylphosphonium bromide iodoform*, brownish-yellow powder, m. p. about 200° after incipient decomposition at about 180°. *Tetraethylstibinium iodide iodoform*, yellow powder, m. p. (indefinite) 162° after previous softening.

It was not found possible to isolate additive compounds from iodoform and phenyltrimethylarsonium bromide or chloride, tetraethylammonium chloride, or triphenylmethylarsonium chloride, respectively. H. W.

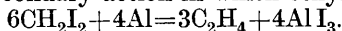
Some Recent Applications of Magnesium in Synthetic Organic Chemistry. HARRY HEPPWORTH (*J. Soc. Chem. Ind.*, 1922, **41**, 7—11).—A résumé of some of the recent applications of the Grignard reagents,

Organo-derivatives of Thallium. III. Some Thallium-dialkyl Salts and the Preparation of Thalliumdiaryl Haloids. ARCHIBALD EDWIN GODDARD (T., 1922, **121**, 36–40).

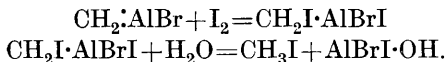
Mixed Organometallic Compounds of Aluminium. FAILLEBIN (*Compt. rend.*, 1922, **174**, 112–114).—Aluminium dissolves in an anhydrous mixture of ether and methylene iodide, the reaction being



but there is a secondary action in which ethylene is formed,



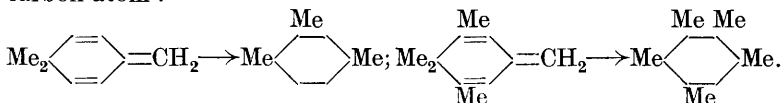
If the methylene iodide is replaced by methylene bromide, the action is more difficult to start and the secondary action is less marked. These complex compounds are obtained as dense liquids, which are readily decomposed by water, giving methane. A similar decomposition occurs with alcohol. The compounds are unsaturated and form additive compounds with iodine, which, when decomposed by water, no longer give methane but methyl iodide,



W. G.

Hydrocarbons of the Semibenzene Group. K. VON AUWERS and K. ZIEGLER (*Annalen*, 1921, **425**, 217–280).—In continuation of previous work (Auwers and Müller, A., 1911, i, 621), a number of homologous semibenzene hydrocarbons have been prepared and examined with respect to their physical properties and their capacity for passing into aromatic hydrocarbons by isomeric change. The principal physical distinction between the semibenzene hydrocarbons and their aromatic isomerides consists in the fact that the former group of compounds have lower densities, and therefore (since the refractive indices of the two series are comparable) higher molecular refractions and dispersions than the latter. In general, the semibenzene compounds are more volatile than their isomerides.

The conversion of semibenzene hydrocarbons into benzene derivatives takes place in the presence of acids with great ease in the case of the simpler members. Higher in the series polymerisation and other side reactions occur simultaneously. In general, the isomeric change involves the migration of one methyl group from the *gem*-dimethyl residue to an adjacent position in the nucleus; but if both the neighbouring positions are already occupied the mobile group may attach itself to some other nuclear carbon atom :



A new series of physical constants for carefully purified 1:1-dimethyl-4-methylene- $\Delta^{2,5}$ -cyclohexadiene is given: b. p. 38—

40°/15 mm., $d_4^{15.8}$ 0.8360, d_4^{20} 0.833, $n_D^{15.8}$ 1.50295, $n_\beta^{15.8}$ 1.51739, $n_\gamma^{15.8}$ 1.53009, n_D^{20} 1.5011. This hydrocarbon passes into ψ -cumene with development of heat when a drop of hydrochloric acid is added to its solution in two vols. of acetic acid.

1 : 1-*Dimethyl-4-ethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol*, large, transparent tablets, m. p. 46—47°, is prepared like the trimethyl compound (*loc. cit.*); on shaking with 10% sulphuric acid, it is converted into 1 : 1-*dimethyl-4-ethylidene- $\Delta^{2:5}$ -cyclohexadiene*, b. p. 71—74°/16 mm., 81.5—84°/25 mm., $d_4^{15.15}$ 0.8614, d_4^{20} 0.857, $n_a^{15.15}$ 1.51072, $n_D^{15.15}$ 1.51572, $n_\beta^{15.15}$ 1.53015, $n_\gamma^{15.15}$ 1.54300, n_D^{20} 1.5135 (another preparation gave slightly different constants, e.g. d_4^{20} 0.855, n_D^{20} 1.5124). This hydrocarbon is fairly stable at 160°; on oxidation by permanganate, it is converted into dimethylmalonic acid and acetic acid. When its solution in acetic acid is saturated with hydrogen chloride, it is converted in the course of one hour into 1 : 2-dimethyl-4-ethylbenzene (b. p. 186—187°, $d_4^{15.2}$ 0.8777, d_4^{20} 0.874, $n_a^{15.05}$ 1.50103, $n_D^{15.05}$ 1.50489, $n_\beta^{15.05}$ 1.51606, $n_\gamma^{15.05}$ 1.52531, n_D^{20} 1.5027), which was prepared for comparison from 4-*o*-xylyl methyl ketone by reduction with amalgamated zinc and hydrochloric acid. 1 : 1-*Dimethyl-4-n-propyl- $\Delta^{2:5}$ -cyclohexadien-4-ol* and 1 : 1-*dimethyl-4-n-propylidene- $\Delta^{2:5}$ -cyclohexadiene* could not be fully purified (b. p. 95—105°/10 mm. and 83—85°, respectively). The crude alcohol was converted into 1 : 2-dimethyl-4-*n*-propylbenzene by the addition of a drop of concentrated hydrochloric acid to a solution in acetic acid, and the hydrocarbon identified by comparing its physical properties (b. p. 201—203°, $d_4^{12.85}$ 0.8718, d_4^{20} 0.866, $n_a^{12.7}$ 1.49504, $n_D^{12.7}$ 1.49881, $n_\beta^{12.7}$ 1.50920, $n_\gamma^{12.7}$ 1.51784, n_D^{20} 1.4955) with those of a specimen prepared by reducing 4-*o*-xylyl ethyl ketone. This ketone, b. p. 258—262°, was obtained by the action of propionyl chloride and aluminium chloride on *o*-xylene, and was characterised by means of its *semi-carbazone*, m. p. 192—193°.

1 : 1 : 3 : 4-*Tetramethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol*, needles, m. p. 50.5—51.5°, was obtained like its lower homologues, but could not be converted into the corresponding semibenzene owing to the ease with which this substance passed into its aromatic isomeride, durene. From 1 : 1 : 3-*trimethyl-4-ethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol* (m. p. 47—48°), however, 1 : 1 : 3-*trimethyl-4-ethyl- $\Delta^{2:5}$ -cyclohexadiene* (b. p. 85—86°, $d_4^{12.7}$ 0.8844, d_4^{20} 0.879, $n_a^{12.7}$ 1.51470, $n_D^{12.7}$ 1.51931, $n_\beta^{12.7}$ 1.53230, $n_\gamma^{12.7}$ 1.54371, n_D^{20} 1.5160) was obtained by the usual means. It was converted by hydrochloric acid in the presence of acetic acid into 4-ethyl- ψ -cumene.

The following physical constants are recorded for 1 : 1 : 2 : 4-*tetramethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol*: b. p. 90—95°, m. p. below 20°, $d_4^{10.0}$ 0.9333, d_4^{20} 0.925, $n_a^{10.1}$ 1.48376, $n_D^{10.1}$ 1.48685, $n_\beta^{10.1}$ 1.49502, $n_\gamma^{10.1}$ 1.50176, n_D^{20} 1.4824. On treatment with acids it yields 1 : 1 : 2-*trimethyl-4-methylene- $\Delta^{2:5}$ -cyclohexadiene* (b. p. 60—65°/15 mm., $d_4^{10.7}$ 0.8735, d_4^{20} 0.866, $n_a^{10.7}$ 1.51331, $n_D^{10.7}$ 1.51813, $n_\beta^{10.7}$ 1.53213, $n_\gamma^{10.7}$ 1.54435, n_D^{20} 1.5139), which readily passes into a polymeride. The isomeric aromatic hydrocarbon *isodurene* is best obtained, therefore, from the alcohol.

1 : 1 : 3 : 4 : 6-*Pentamethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol*, b. p. 85—95°/12 mm., on dehydration gives 1 : 1 : 3 : 6-*tetramethyl-4-methylene- $\Delta^{2:5}$ -cyclohexadiene*, b. p. 77°/12 mm., $d_4^{15.2}$ 0.8809, d_4^{20} 0.877, $n_\alpha^{15.2}$ 1.51235, $n_D^{15.2}$ 1.51687, $n_\beta^{15.2}$ 1.53006, $n_\gamma^{15.2}$ 1.54172, n_D^{20} 1.5147, which isomerises, yielding pentamethylbenzene. 1 : 1 : 3 : 6-*Tetramethyl-4-ethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol* could not be purified by distillation owing to the ease with which it passes into 1 : 1 : 3 : 6-*tetramethyl-4-ethylidene- $\Delta^{2:5}$ -cyclohexadiene*. This hydrocarbon has the following constants: b. p. 100—103°/18 mm., $d_4^{15.4}$ 0.8837, d_4^{20} 0.880, $n_\alpha^{15.4}$ 1.51028, $n_D^{15.4}$ 1.51452, $n_\beta^{15.4}$ 1.52702, $n_\gamma^{15.4}$ 1.53796, n_D^{20} 1.5125.

The main product of the action of sodium hydroxide and chloroform on hemimellithenol is 1 : 2 : 6-*trimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one*, m. p. 107.5—108.5°, which gives a *semicarbazone*, m. p. 218°, and a *p-nitrophenylhydrazone*, m. p. 190—191°. 6-*Hydroxy-2 : 3 : 4-trimethylbenzaldehyde* is a by-product in the reaction. It melts at 77—78° and yields a *semicarbazone*, which turns yellow at 130° but does not melt at 280°. Magnesium and methyl iodide convert the chloro-ketone into 1 : 2 : 4 : 6-*tetramethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol*, which, however, is partly decomposed during the isolation, giving 1 : 2 : 3-*trimethyl-5-di- ω -chloroethylbenzene*, for which the following constants are recorded: b. p. 155—159°/19 mm., $d_4^{21.8}$ 1.1424, d_4^{20} 1.144, n_α 1.53900, n_D 1.54310, n_β 1.55494, n_D^{20} 1.5439. On reducing the above chloroalcohol, two substances are obtained, the normal product, 1 : 1 : 2 : 4 : 6-*pentamethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol*, having partly undergone dehydration with the formation of 1 : 1 : 2 : 6-*tetramethyl-4-methylene- $\Delta^{2:5}$ -cyclohexadiene*, which, when pure, has the following constants: b. p. 89—90°/15 mm., $d_4^{23.3}$ 0.8765, d_4^{30} 0.879, $n_\alpha^{25.2}$ 1.50884, $n_D^{23.3}$ 1.51350, $n_\beta^{23.2}$ 1.52660, $n_\gamma^{23.2}$ 1.53830, n_D^{20} 1.5149. When warmed with acetic acid and sulphuric acid, this hydrocarbon undergoes isomeric change with the formation of pentamethyl benzene.

C. K. I.

Constitution of Benzene. RONALD FRASER (T., 1922, 121, 188—196).

The Action of Sulphuryl Chloride on Organic Substances.
I. Simple Monosubstituted Benzenes. THOMAS HAROLD DURRANS (T., 1922, 121, 44—49).

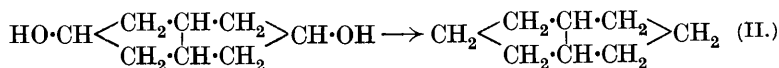
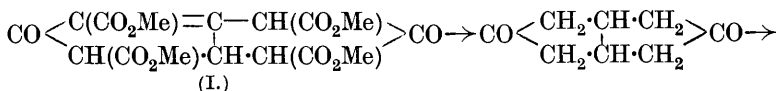
The Existence and Reactions of Positive Halogen attached to Carbon in Aromatic Compounds. BEN H. NICOLET (*J. Amer. Chem. Soc.*, 1921, 43, 2081—2084).—3-Iodo-*p*-toluidine, 4-iodoaniline, aceto-3-bromo-*p*-toluidide, and 3-iodo-4-hydroxybenzoic acid when boiled with 10% hydrochloric acid are hydrolysed with a readiness decreasing in the order named, in such a way that in part they replace their halogen by hydrogen and in part give di- or tri-halogenated derivatives. This is considered to be the best evidence yet offered for the existence of positive halogen attached to carbon in the benzene nucleus. It will be

noticed that, in all cases, the halogen is in a position ortho or para to a strongly negative group. In similar compounds, iodine is more positive than bromine, and more positive in ortho- than in para-compounds. Alkali is much less effective than acid in removing such positive halogens. In the presence of stannous chloride and acid, the halogen is abnormally readily removed, but reconstitution is prevented. W. G.

The Action of Pyrosulphuryl Chloride on Toluene. WILHELM STEINKOPF and KURT BUCHHEIM (*Ber.*, 1921, **54**, 2963—2968).—Pyrosulphuryl chloride reacts with toluene at 60° with evolution of hydrogen chloride and sulphur dioxide. The reaction product is a mixture from which the following substances have been isolated: Toluene-*p*-sulphonic acid, toluene-*p*-sulphonyl chloride, a mixture of dichlorotoluenes, and 4-*chloro-3:4'*-ditolylsulphone, fine needles, m. p. 136°, which is also formed by the interaction of *o*-chlorotoluene and toluene-*p*-sulphonyl chloride dissolved in light petroleum in presence of aluminium chloride at 55°.

A vigorous reaction ensues when toluene is added to a mixture of pyrosulphuryl chloride and aluminium chloride at -5° to 0°, with formation of toluene-*p*-sulphonic acid, *o*- and *p*-chlorotoluene, *pp*-ditolylsulphone, and a substance, needles, m. p. 215—217°, containing chlorine but no sulphur. F. M. R.

Hydrogenated Naphthalenes and their Transformations. I. G. SCHROETER (*Annalen*, 1922, **426**, 1—17).—[With G. VOSSEN.]—The condensation between chloral and methyl malonate leads to the formation of methyl 0:3:3-dicyclo- Δ^1 -octene-3:7-dione-2:4:6:8-tetracarboxylate (I), which can be converted by hydrolysis and reduction into 0:3:3-dicyclooctane-3:7-dione, 0:3:3-dicyclo-octane-3:7-diol, and, finally, 0:3:3-dicyclooctane (II) (b. p. 138°, d_4^{21} 0.8817, n_D^{20} 1.46632):



Closely related to this hydrocarbon (II) are the hydrogenated naphthalenes, certain of which, moreover, are more easily and cheaply prepared.

[With F. STAHL, H. HAEHN, and C. PRIGGE.]—Full working details are given of the preparation of tetrahydronaphthalene by reducing naphthalene by means of hydrogen at 180—200° and 5—15 atmospheres in the presence of nickel. The hydrocarbon, purified by regeneration from its sulphonie acid, has b. p. 100—101°/25 mm., 206.5° (corr.)/755 mm., d_4^{20} 0.971, n_D^{20} 1.5434.

C. K. I.

Hydrogenated Naphthalenes and their Transformations.

II. Nitro- and Amino-derivatives of Tetrahydronaphthalene.

G. SCHROETER [with E. KINDERMANN, C. DIETRICH, C. BEYSCHLAG, CL. FLEISCHHAUER, E. RIEBENSAHM, and C. OESTERLIN] (*Annalen*, 1922, **426**, 17—83).—This paper describes the nitration of tetrahydronaphthalene, the reduction of various mono-, di-, and tri-nitro-derivatives, and the nitration of the acetyl derivatives of the amines so obtained. The orientations of a considerable number of isomeric nitro-compounds, amines, and nitroamines are definitely established.

The mononitration of tetrahydronaphthalene, using a mixture of nitric and sulphuric acids, leads to the formation of both 1- and 2-nitro-*ar-tetrahydronaphthalene* which may be separated by fractional distillation and "freezing out" the fractions or by taking advantage of the fact that the 2-nitro-compound is more easily reduced than its isomeride to an amino-derivative. 1-Nitro-*ar-tetrahydronaphthalene* has m. p. 34°, b. p. 157°/13 mm., d_{40}^{20} 1.1757 and the 2-compound, m. p. 31.4°, b. p. 169°/13 mm., d_{40}^{20} 1.1762. On dinitration, tetrahydronaphthalene yields a mixture of 1:2-dinitro-*ar-tetrahydronaphthalene* (m. p. 102—103°) and 1:3-dinitro-*ar-tetrahydronaphthalene* (m. p. 95°) which may be separated by crystallisation from concentrated sulphuric acid, in which the former is less soluble. The orientation of the 1:2-compound rests on its reduction to *ar-tetrahydro-1:2-naphthylenediamine* and 1-nitro-*ar-tetrahydro-β-naphthylamine* (see below), and that of the 1:3-isomeride on its oxidation to 3:5-dinitrophthalic acid and its reduction to the 1:3-diamine and the 1-nitro-3-amino-compound (see below). Another oxidative fission which the 1:3-dinitro-compound undergoes with nitric acid leads to the formation of *β-o-carboxytrinitrophenylpropionic acid*, which decomposes violently on heating and is characterised by analysis of its potassium hydrogen salt. 1:3-Dinitro-*ar-tetrahydronaphthalene* cannot be further nitrated, but the 1:2-isomeride may be converted into 1:2:4-trinitro-*ar-tetrahydronaphthalene*, m. p. 94.5—95°, the structure of which is established by its conversion into the triamino-derivative (see below). The other possible isomeride, namely, 1:2:3-trinitro-*ar-tetrahydronaphthalene* is not produced by direct nitration.

1:1-*Hydrazo-ar-tetrahydronaphthalene*, which is obtained by reducing 1-nitro-*ar-tetrahydronaphthalene* by means of zinc dust and alkali, forms colourless, slender needles, m. p. 181—183°, and on oxidation by permanganate is converted quantitatively into 1:1-azo-*ar-tetrahydronaphthalene*. The latter, which crystallises in glistening, red needles, m. p. 190—191°, may also be obtained along with 1:1-azoxy-*ar-tetrahydronaphthalene*, yellow needles, m. p. 184°, by reduction of the nitro-compound with zinc and alkali hydroxide under less energetic conditions. The benzidine conversion applied to hydrazotetrahydronaphthalene gives rise to 4:4'-diamino-1:1'-di-*ar-tetrahydronaphthyl*, m. p. 153—154°, the *hydrochloride*, *hydrobromide*, *sulphate*, and *phosphate* of which are described. The corresponding diazonium salt gives substantive dyes on coupling

with naphthionic acid, Neville and Winthers's α -naphtholsulphonic acid, crocein acid, H-acid, salicylic acid, chromotropic acid, " β -aminonaphtholsulphonic acid" and G-acid, 4:4'-*dihydrazino*-1:1'-*di-ar-tetrahydronaphthyl*, on reduction by means of stannous chloride, and 4:4'-*diethoxy*-1:1'-*di-ar-tetrahydronaphthyl*, colourless needles, m. p. 173°, on decomposing with ethyl alcohol. A basic by-product, consisting of colourless needles, m. p. 216°, and giving a *hydrochloride* which is easily soluble in water, is obtained in the preparation of 4:4'-diamino-1:1'-*di-ar-tetrahydronaphthyl*. Apparently it is 1:1'-*diamino*-2:2'-*di-ar-tetrahydronaphthyl*, because when heated its hydrochloride yields ammonium chloride and a carbazole-like base which may be separated in the form of its picrate.

ar-Tetrahydro- α -naphthylamine and *ar*-tetrahydro- β -naphthylamine are obtained from the corresponding nitro-compounds by catalytic reduction, and may also be obtained by reducing the crude mononitration product of tetrahydronaphthalene and separating the isomeric bases by taking advantage of the differences of solubility of their hydrochlorides in water, their methanedisulphonates in 96% alcohol, and the difference in the ease with which the bases are acetylated. *ar*-Tetrahydro- α -naphthylamine, b. p. 146°/12 mm., gives a hydrochloride which is more easily soluble than that of the β -derivative, and a *methanedisulphonate* which forms colourless leaflets soluble in 20 parts of hot water, 60 parts of cold water, and about six times as soluble in alcohol as the β -compound. With phthalic anhydride, the base gives a *phthalamic acid*, $C_{10}H_{11}\cdot NH\cdot CO\cdot C_6H_4\cdot CO_2H$, colourless needles, m. p. 182—184° (decomp.), which on heating passes into the *phthalimide* (needles, m. p. 148—150°) by loss of water. *ar*-Tetrahydro- α -naphthylamine is more easily acetylated than the β -compound, and its acetyl derivative (m. p. 156°) on methylation by the action of methyl sulphate on its sodio-derivative gives the *acetyl* derivative of *ar-tetrahydro- α -naphthylmethylamine*, which has m. p. 70—72° and b. p. 182—185°/11 mm. The *hydrochloride* and *sulphate* of *ar-tetrahydro- β -naphthylamine* (b. p. 147—148°/13 mm., m. p. 38.5—39.5°) are sparingly soluble in cold water and the *methanedithionate* is rather sparingly soluble in alcohol. The *phthalamic acid* forms glistening needles, m. p. 156.5—158.5°, and the *phthalimide*, needles, m. p. 169—171°. The acetyl derivative (m. p. 102—104°) on methylation yields the *acetyl* derivative of *ar-tetrahydro- β -naphthylmethylamine*, needles, m. p. 67—69°.

The preparation of aceto-4-nitro-*ar-tetrahydro- α -naphthalide* by nitration of aceto-*ar-tetrahydro- α -naphthalide* has been described by Green and Rowe (T., 1918, **113**, 958), but it is now shown that aceto-2-nitro-*ar-tetrahydro- α -naphthalide* (colourless needles, m. p. 184—185°) and aceto-3-nitro-*ar-tetrahydro- α -naphthalide* (colourless needles, m. p. 193°) are formed as by-products. 2-Nitro-*ar-tetrahydro- α -naphthylamine*, which is obtained by hydrolysis of its acetyl derivative, forms orange needles, m. p. 87—88°. Its constitution rests on its relationship to *ar-tetrahydro*-1:2-naphthylenediamine (see later). 3-Nitro-*ar-tetrahydro- α -naphthylamine*, prepared

by hydrolysis of its acetyl compound, forms yellow leaflets, m. p. 78°. It is identical with the product obtained by regulated reduction of 1 : 3-dinitro-*ar*-tetrahydronaphthalene.

The course pursued by the nitration of aceto-*ar*-tetrahydro- β -naphthalide varies with the conditions. If glacial acetic acid is the solvent, aceto-3-nitro-*ar*-tetrahydro- β -naphthalide, long, yellow needles, m. p. 134—135·5°, is the main product, whilst aceto-1-nitro-*ar*-tetrahydro- β -naphthalide, colourless needles, m. p. 128—129°, is produced only in small amount. On the other hand, if the nitration is carried out in the presence of concentrated sulphuric acid, the main product is aceto-4-nitro-*ar*-tetrahydro- β -naphthalide, which forms long, colourless needles, m. p. 194°, whilst the 3-nitro-compound is a by-product. 3-Nitro-*ar*-tetrahydro- β -naphthylamine, the constitution of which follows from its reduction to the diamine (see below), forms long, red needles, m. p. 125—127°. 1-Nitro-*ar*-tetrahydro- β -naphthylamine, red needles, m. p. 96°, is obtained, not only by hydrolysis of its acetyl derivative, but also by partial reduction of 1 : 2-dinitro-*ar*-tetrahydronaphthalene. The structure assigned is based on its reduction to the diamine which is known. 4-Nitro-*ar*-tetrahydro- β -naphthylamine, m. p. 55°, obtained by hydrolysis of its acetyl compound, is identical with the substance produced by partial reduction of 1 : 3-dinitro-*ar*-tetrahydronaphthalene. 1-Nitro-*ar*-tetrahydronaphthalene is obtained when the amino-group is eliminated by diazotisation and subsequent reduction.

Aceto-1 : 3-dinitro-*ar*-tetrahydro- β -naphthalide, colourless needles, m. p. 189—191°, is produced by further nitration of aceto-1-nitro-*ar*-tetrahydro- β -naphthalide and aceto-3-nitro-*ar*-tetrahydro- β -naphthalide and as a by-product in the dinitration of aceto-*ar*-tetrahydro- β -naphthalide. When it is prepared from the 3-nitro-compound an isomeric, $C_{12}H_{13}O_5N_3$, of unknown constitution and having no definite melting point (decomp. at about 215°) is also formed. 1 : 3-Dinitro-*ar*-tetrahydro- β -naphthylamine, which forms yellow needles, m. p. 166—168°, is obtained by hydrolysing the acetyl compound. On reduction, it yields 1 : 2 : 3-triamino-*ar*-tetrahydronaphthalene (below).

Aceto-3 : 4-dinitro-*ar*-tetrahydro- β -naphthalide, needles, m. p. 175—177°, is the main dinitration product of aceto-*ar*-tetrahydro- β -naphthalide, and is also obtained by nitration of aceto-4-nitro-*ar*-tetrahydro- β -naphthalide. On hydrolysis, it yields 3 : 4-dinitro-*ar*-tetrahydro- β -naphthylamine, which melts at 157° and on reduction is converted into 1 : 2 : 3-triamino-*ar*-tetrahydronaphthalene.

ar-Tetrahydro-2 : 3-naphthylenediamine (for formation, see above) has m. p. 135—136° and b. p. 165°/13 mm. Its hydrochloride crystallises in glistening leaflets. With acetic acid it forms 2-methyl- $\beta\beta$ -*ar*-tetrahydronaphthiminazole (m. p. 251—252°) and with phenanthraquinone 2 : 3-*ar*-tetrahydronaphthylenphenanthrazine, $C_{10}H_8 \begin{smallmatrix} & N:C_6H_4 \\ & | \\ N:C_6H_4 \end{smallmatrix}$ (m. p. 214—216°). Acetyl-*ar*-tetrahydro-1 : 2-naphthylenediamine, m. p. 149—151°, on acetylation yields the

diacetyl derivative, and on hydrolysis gives the free diamine, which forms a *phenanthrazine*, m. p. 222·9—230°.

ar-Tetrahydro-1 : 3-naphthylenediamine, prepared by reduction of the dinitro-compound, forms pearly leaflets, m. p. 84—85°, b. p. 199—202°/10 mm. Its 1-*acetyl* derivative, obtained from 3-nitro-aceto-*ar*-tetrahydro- α -naphthalide, has m. p. 173°, and its 3-*acetyl* derivative, prepared from aceto-4-nitro-*ar*-tetrahydro- β -naphthalide, has m. p. 110—111°. The *diacetyl* derivative, obtained by acetylation of any of the above three substances, forms small, filamental needles, m. p. 245—246°. The *monoacetyl* derivative of *ar*-tetrahydro-1 : 4-naphthylenediamine is prepared by reducing aceto-4-nitro-*ar*-tetrahydro- α -naphthalide, and has m. p. 154—156°.

1 : 2 : 3-*Triamino-ar-tetrahydronaphthalene*, which is produced by reduction of 3 : 4-dinitro- or 1 : 3-dinitro-*ar*-tetrahydro- β -naphthylamine, is unstable in air, but yields a crystalline *hydrochloride*, and a *triacetyl* derivative which forms microscopic, white needles, m. p. 285°. 1 : 2 : 4-*Triamino-ar-tetrahydronaphthalene* is obtained by reducing the 1 : 2 : 4-trinitro-compound or the 2 : 4-dinitro-1-amino-derivative (see above). This base is also unstable, but its *triacetyl* derivative forms small needles, m, p. 315°.

C. K. I.

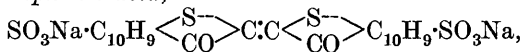
Hydrogenated Naphthalenes and their Transformations.

III. Tetrahydronaphthalenesulphonic Acids, Tetrahydronaphthols, and their Derivatives. G. SCHROETER [with SVANOE, H. EINBECK, H. GELLER, and E. RIEBENSAHM] (*Annalen*, 1922, **426**, 83—160).—Both *ar*-tetrahydronaphthalene-1-sulphonic acid, which has been prepared already by an indirect process by Morgan, Micklethwait, and Winfield (T., 1904, **85**, 736), and *ar*-tetrahydronaphthalene-2-sulphonic acid (hitherto unknown) are obtained as their chlorides when chlorosulphonic acid is allowed to react with tetrahydronaphthalene. On the other hand, concentrated sulphuric acid gives chiefly the 2-sulphonic acid, 4—7% of the 1-sulphonic acid being produced simultaneously. Both sulphonic acids on fusion with alkalis yield the corresponding tetrahydronaphthols, and the sulphonyl chlorides on reduction give the tetrahydronaphthylthiols. The sulphonation of tetrahydronaphthalene, therefore, opens the way to the preparation of a large number of new aromatic compounds.

ar-Tetrahydronaphthalene-2-sulphonic acid separates with 2H₂O (m. p. 75°), its *sodium* salt with 1H₂O, and its *lead* salt with 1H₂O, which is given off at 130°. The *barium* and *ammonium* salts crystallise in the anhydrous condition in glistening leaflets. The acid *chloride*, m. p. 58°, b. p. 197—200°/18 mm., is obtained when phosphorus pentachloride acts on the acid, and on treatment with 10% ammonia passes into the *amide*, m. p. 135—137°. The *anilide*, prepared in similar manner, has m. p. 155—156°.

The mixtures obtained when chlorosulphonic acid is used for the sulphonation may be separated by crystallisation of the acids from chloroform, the 1-sulphonic acid separating first, or by pre-

precipitating the *lead* salt of *ar*-tetrahydronaphthalene-1-sulphonic acid by adding aqueous lead acetate to a concentrated solution of the acids, or by dissolving the sulphonamides in warm *N*-sodium hydroxide, from which the sodium salt of the 2-sulphonamide separates on cooling. The mixture of acid chlorides may also be reduced by means of zinc and hydrochloric acid to the *ar*-tetrahydronaphthylthiols, the sodium salts of which on condensation with sodium chloroacetate give the sodium salts of the *ar*-tetrahydronaphthylthiolacetic acids. The *ammonium* salt of the 2-compound is sparingly soluble and is precipitated if ammonium chloride is added. *ar*-Tetrahydronaphthyl-2-thiolacetic acid forms colourless needles, m. p. 78—80°; it may be prepared from pure *ar*-tetrahydronaphthalene-2-sulphonyl chloride. *ar*-Tetrahydronaphthalene-1-thiolacetic acid crystallises as glistening plates, m. p. 133—135°. *ar*-Tetrahydronaphthyl-2-thiolacetic acid forms a green solution in fuming sulphuric acid; on diluting, boiling, and making alkaline with sodium hydroxide, the *sodium* salt of bis-*ar*-tetrahydrothiophendisulphonic acid,



is precipitated.

When α -naphthol is reduced by means of two molecules of hydrogen at 200° in the presence of nickel, the product consists of about 10% of α -ketotetrahydronaphthalene, 25—30% of *ar*-tetrahydro- α -naphthol and a large quantity of tetrahydronaphthalene. At low temperatures, the ketone is the main product, and it seems probable that it forms an intermediate stage in the production of the hydrocarbon. On reduction by means of sodium and alcohol in moist ether, the ketone yields *ac*-tetrahydro- α -naphthol. *ac*-Tetrahydro- β -naphthol is the chief product of reduction (by the catalytic method) of β -naphthol.

ar-Tetrahydronaphthalene-2-sulphonic acid is therefore a valuable starting point in the preparation of *ar*-tetrahydro- β -naphthol and its derivatives. *ar*-Tetrahydro- β -naphthol forms a *methyl ether*, b. p. 129—131°/11 mm., prepared by the use of methyl sulphate, an *acetate*, b. p. 158°/14 mm., obtained using acetic anhydride, and a crystalline *benzoate*, prisms, m. p. 96°, b. p. 220—222°/10 mm., which is prepared by digesting the phenol with benzoyl chloride and pyridine. On sulphonation, *ar*-tetrahydro- β -naphthol-3-sulphonic acid is produced. It forms needles (2H₂O), m. p. 92°, yields a sparingly soluble *sodium* salt, and a *barium* salt (C₂₀H₂₂S₂O₈Ba), gives strongly coloured *azo-dyes* with the diazonium salts of *p*-nitro-aniline, sulphanilic acid, and naphthionic acid, and when heated with hydrochloric acid generates *ar*-tetrahydro- β -naphthol. 2-Methoxy-*ar*-tetrahydronaphthalene-3-sulphonic acid, m. p. 107°, is obtained by sulphonating the above-mentioned methyl ether. 1-Bromo-*ar*-tetrahydro- β -naphthol, m. p. 74°, may be prepared either by direct bromination of *ar*-tetrahydro- β -naphthol in carbon tetrachloride, or by desulphonation (using hydrochloric acid) of 1-bromo-*ar*-tetrahydro- β -naphthol-3-sulphonic acid (*sodium* salt, crystallises with 3H₂O) which is produced by sulphonation of 1-bromo-*ar*-tetrahydro-

β -naphthol, or, alternatively, by bromination of *ar*-tetrahydro- β -naphthol-3-sulphonic acid. On dibromination, *ar*-tetrahydro- β -naphthol yields 1:3-dibromo-*ar*-tetrahydro- β -naphthol, m. p. 37°, b. p. 198—201°/15 mm., which may also be prepared by the action of bromine on *ar*-tetrahydro- β -naphthol-3-sulphonic acid or on 1-bromo-*ar*-tetrahydro- β -naphthol-3-sulphonic acid, and is characterised by a well-crystallising acetate, m. p. 87°. 1-Bromo-3-nitro-*ar*-tetrahydro- β -naphthol, long, yellow needles, m. p. 129°, is obtained by treating 1-bromo-*ar*-tetrahydro- β -naphthol-3-sulphonic acid with nitric acid, the sulphonic acid group being replaced. The sodium salt forms red leaflets, and the methyl ether, obtained with the aid of methyl sulphate, yellow needles, m. p. 64°. 1-Chloro-3-nitro-*ar*-tetrahydro- β -naphthol, which forms yellow needles, m. p. 96°, is obtained by chlorinating *ar*-tetrahydro- β -naphthol-3-sulphonic acid and treating the crude product with nitric acid. On reduction by stannous chloride, 1-bromo-3-nitro-*ar*-tetrahydro- β -naphthol yields a mixture of 1-bromo-3-amino-*ar*-tetrahydro- β -naphthol, which melts at 127° and yields a hydrochloride, sulphate, and nitrate sparingly soluble in cold water, and 3-amino-*ar*-tetrahydro- β -naphthol, which crystallises in leaflets, m. p. 202°, and gives a hydrochloride and a nitrate easily soluble and a sulphate sparingly soluble in cold water. 1-Bromo-3-amino-2-methoxy-*ar*-tetrahydronaphthalene, the sulphate of which crystallises with 4H₂O, is obtained by reduction of the corresponding nitro-compound. 3-Amino-*ar*-tetrahydro- β -naphthol may also be prepared by hydrolysing its carbonyl derivative, C₁₀H₁₀ $\left\langle \begin{smallmatrix} \text{NH} \\ \text{O} \end{smallmatrix} \right\rangle$ CO (below), m. p. 196°. The piperonyl compound, C₁₀H₁₀ $\left\langle \begin{smallmatrix} \text{NH} \\ \text{O} \end{smallmatrix} \right\rangle$ CH·C₆H₄·O₂CH₂, m. p. 160°, is obtained from the amino-phenol and piperonal, and on methylation with methyl sulphate and alkalis yields 3-piperonylideneamino-2-methoxy-*ar*-tetrahydronaphthalene, OMe·C₁₀H₁₀·N·CH·C₆H₄·O₂CH₂, m. p. 120°, which when hydrolysed gives 3-amino-2-methoxy-*ar*-tetrahydronaphthalene, m. p. 86°. 1-Amino-*ar*-tetrahydro- β -naphthol is obtained by coupling *ar*-tetrahydro- β -naphthol with sulphanilic acid diazide or with benzenediazonium chloride and reducing the azo-compound. 1-Benzeneazo-*ar*-tetrahydro- β -naphthol, m. p. 84°, gives a monobromo-substitution product, m. p. 204°; 1-amino-*ar*-tetrahydro- β -naphthol forms colourless leaflets, m. p. 148°, and yields a crystalline hydrochloride and sulphate. An isomeric benzeneazo-*ar*-tetrahydro- β -naphthol, m. p. 110°, is occasionally also formed; on reduction, it yields ?-amino-*ar*-tetrahydro- β -naphthol, m. p. 173°, the sulphate of which separates from 2N-sulphuric acid. The carbonyl derivative, produced by heating with carbamide, forms small, red needles, m. p. 188°; it lowers the melting point, 189—190°, of the carbonyl derivative of 1-amino-*ar*-tetrahydro- β -naphthol, which is prepared in a similar manner. 1-Amino-2-methoxy-*ar*-tetrahydronaphthalene is produced by reducing 2-methoxy- α -naphthylamine (m. p. 54°, although 84° is the m. p. recorded in the literature) by means of sodium and amyl alcohol. It has m. p. 64°, b. p. 195—200°/20 mm., and on hydrolysis by means of hydro-

chloric acid at 180—190° yields 1-amino-*ar*-tetrahydro- β -naphthol. 1-Nitro-*ar*-tetrahydronaphthalene-3-sulphonic acid, which may be prepared by directly sulphonating 1-nitro-*ar*-tetrahydronaphthalene, and is characterised by a crystalline *amide*, m. p. 189°, gives *ar*-tetrahydro- α -naphthylamine-3-sulphonic acid on reduction by means of stannous chloride or by iron and hydrochloric acid, but the amino-acid is not converted into 4-amino-*ar*-tetrahydro- β -naphthol on fusion with alkalis. The main product is *ar*-tetrahydro- α -naphthylamine, which is also obtained when the amino-sulphonic acid is condensed with *p*-toluenesulphonyl chloride before fusing with alkalis. However, 4-acetyl-amino-*ar*-tetrahydro- β -naphthol, red needles, m. p. 222°, is readily produced by the diazo-reaction applied to 4-acetyl-amino-*ar*-tetrahydro- β -naphthylamine (1-acetyl-derivative of *ar*-tetrahydro-1 : 3-naphthylenediamine, preceding abstract), and on hydrolysis by means of fuming hydrochloric acid gives 4-amino-*ar*-tetrahydro- β -naphthol, leaflets, m. p. 177°, which is characterised by having a sparingly soluble *hydrochloride*. When the unseparated mixture of 1- and 2-nitro-*ar*-tetrahydronaphthalene is sulphonated there is produced, along with nitro-sulphonic acid described above, an isomeride having a much more soluble sodium salt and consisting in all probability of 2-nitro-*ar*-tetrahydronaphthalene-4-sulphonic acid. It forms an *amide*, m. p. 211—212°, and on reduction yields *ar*-tetrahydro- β -naphthylamine-4-sulphonic acid, the *hydrochloride* of which is soluble in 120 parts of hot water. 1 : 3-Dinitro-*ar*-tetrahydro- β -naphthol, yellow needles, m. p. 141°, is produced by adding nitric acid (*d* 1.4) to a solution of *ar*-tetrahydro- β -naphthol in sulphuric acid. Its salts are for the most part sparingly soluble in water, the *sodium*, *potassium*, *ammonium*, *barium*, and *lead* salts being easily precipitated. The dry sodium salt on heating with methyl sulphate in toluene yields 1 : 3-dinitro-2-methoxy-*ar*-tetrahydronaphthalene, which forms colourless needles, m. p. 86.5°. On reduction by means of ethereal stannous chloride, 1 : 3-dinitro-*ar*-tetrahydro- β -naphthol yields 1-nitro-3-amino-*ar*-tetrahydro- β -naphthol, copper-coloured needles, m. p. 127°, and in a similar way the nitro-methoxy-compound gives 1-nitro-3-amino-2-methoxy-*ar*-tetrahydronaphthalene, which has m. p. 117°, and forms a sparingly soluble *hydrochloride*. 1 : 3-Diamino-*ar*-tetrahydro- β -naphthol, leaflets, m. p. 214—216°, is obtained when the dinitro-compound is reduced by alcoholic stannous chloride, and 1 : 3-diamino-2-methoxy-*ar*-tetrahydronaphthalene, prisms, m. p. 89°, when the dinitro-methoxy-derivative is treated similarly or reduced catalytically; its *hydrochloride* is obtained as a colourless, crystalline precipitate with the aid of ethereal hydrogen chloride. When *ar*-tetrahydro- β -naphthol is heated under pressure with carbon dioxide in the presence of alkalis, 2-hydroxy-*ar*-tetrahydronaphthalene-3-carboxylic acid, m. p. 182°, is produced. Its *sodium* salt crystallises without water of crystallisation and its *calcium* salt is sparingly soluble. The *methyl* ester, obtained by direct esterification, has m. p. 42°, b. p. 179°/15 mm., and forms a sparingly soluble *sodium* compound, $\text{ONa} \cdot \text{C}_{10}\text{H}_9 \cdot \text{CO}_2\text{Me}$; the *ethyl* ester is a liquid, b. p. 179°/13 mm. Hydrazine converts

the methyl ester into a *hydrazide*, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{N}_2\text{H}_3$, m. p. 146° , which readily condenses with acetone, forming an *isopropylidene hydrazone*, $\text{HO}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2$, m. p. 235° , and on treatment with nitrous acid yields an *azide*, $\text{HO}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{N}_3$, m. p. $99\text{--}100^\circ$, which on heating eliminates nitrogen and gives the carbonyl derivative of *ar-tetrahydro-2:3-naphthylenediamine* mentioned above. The hydroxy-acid also yields an *anilide*, m. p. $182\text{--}184^\circ$, an *acetyl* derivative, $\text{OAc}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}_2\text{H}$, m. p. $142\text{--}143^\circ$, and a nitro-derivative, *1-nitro-2-hydroxy-ar-tetrahydronaphthalene-3-carboxylic acid*, m. p. $200\text{--}202^\circ$, which on catalytic reduction gives *1-amino-2-hydroxy-ar-tetrahydronaphthalene-3-carboxylic acid*. The latter has m. p. $208\text{--}210^\circ$, and is characterised by a sparingly soluble *hydrochloride*, and by a *diacetyl* derivative, $\text{NHAc}\cdot\text{C}_{10}\text{H}_9(\text{CO}_2\text{H})\cdot\text{OAc}$, m. p. $180\text{--}181^\circ$, which is prepared by acetylating with acetic anhydride in the presence of a trace of sulphuric acid.

4-Amino-ar-tetrahydro- α -naphthol may be obtained by reduction (using stannous chloride) of *4-nitroso-ar-tetrahydro- α -naphthol* (m. p. $161\text{--}163^\circ$) which Green and Rowe (T., 1918, **113**, 955) erroneously supposed to be *4-nitro-ar-tetrahydro- α -naphthol*, or by coupling *ar-tetrahydro- α -naphthol* with sulphanilic acid diazide and reducing the *ar-tetrahydro- β -naphthol-4-azobenzene-p-sulphonic acid* so obtained by means of alkaline hyposulphite. The base has m. p. $146\cdot8^\circ$ and b. p. $208\text{--}210^\circ/10\text{ mm.}$ The ethyl ether ("*p*-amino-*ar-tetrahydronaphthyl* ethyl ether," Jacobsen and Turnbull, A., 1898, i, 441) may be obtained by ethylating *4-benzene-azo-ar-tetrahydro- α -naphthol* with ethyl bromide and alcoholic potassium hydroxide and reducing the product catalytically in the presence of nickel. *2-Amino-ar-tetrahydro- α -naphthol*, m. p. $110\text{--}111^\circ$, is readily obtained by reducing Green and Rowe's *2-nitro-ar-tetrahydro- α -naphthol* (*loc. cit.*); its *hydrochloride*, on heating with carbamide, yields a *carbonyl* derivative, $\text{C}_{10}\text{H}_{10}\langle\text{NH}\rangle\text{CO}$, m. p. 205° , which is also produced when *ar-tetrahydro- α -naphthol-2-carboxylazide* (see below) is heated in toluene. *3-Acetyl-amino-ar-tetrahydro- α -naphthol*, colourless needles, m. p. 211° , is prepared by hydrolysis of the diazonium salt obtained from *3-acetyl-amino-ar-tetrahydro- α -naphthylamine* (*3-acetyl* derivative of *ar-tetrahydro-1:3-naphthylenediamine*, preceding abstract). On hydrolysis with fuming hydrochloric acid, it yields *3-amino-ar-tetrahydro- α -naphthol* which forms leaflets, m. p. 197° , and gives a *hydrochloride* crystallising in colourless needles. *1-Hydroxy-ar-tetrahydronaphthalene-2-carboxylic acid*, m. p. $165\text{--}166^\circ$, is obtained by the action of carbon dioxide under pressure on *ar-tetrahydro- α -naphthol* in the presence of alkalis. The *sodium* salt, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}_2\text{Na}\cdot 3\text{H}_2\text{O}$, crystallises in leaflets. The *acetyl* derivative, $\text{OAc}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}_2\text{H}$, obtained with the aid of acetic anhydride, has m. p. 170° ; the *methyl* ester, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}_2\text{Me}$, m. p. 56° , b. p. $190^\circ/16\text{ mm.}$; the *hydrazide*, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{N}_2\text{H}_3$, m. p. 205° ; the *isopropylidenehydrazone*, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{NH}\cdot\text{N}\cdot\text{CMe}_2$, m. p. 136° ; and the *azide*, $\text{OH}\cdot\text{C}_{10}\text{H}_{10}\cdot\text{CO}\cdot\text{N}_3$, m. p. 84° , are prepared like the isomerides previously mentioned.

C. K. I.

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXIV. The Binary Systems of Anthracene with Nitro-derivatives of Benzene. ROBERT KREMANN and ROBERT MÜLLER II (*Monatsh.*, 1921, **42**, 181—197; cf. following abstract).—In the order of diminishing affinity towards nitro-compounds, the hydrocarbons as yet investigated may be arranged in the following order: naphthalene, acenaphthene, phenanthrene, and benzene, fluorene, triphenylmethane, and diphenylmethane. Examination of the binary systems formed by anthracene with nitro-derivatives of benzene and phenol show that anthracene occupies a position in the above series immediately before tri- and di-phenylmethanes.

The positions and percentages of anthracene corresponding with the eutectics formed by the binary systems of anthracene with nitrobenzenes are: *o*-dinitrobenzene, 110°, 12.5%; *m*-dinitrobenzene, 84°, 8%; *p*-dinitrobenzene, 146°, 35%; 2:4-dinitrotoluene, 66°, 9%; 2:4:6-trinitrotoluene, 75°, 6%. The system anthracene-1:3:5-trinitrobenzene forms a compound (1 mol.: 1 mol.), m. p. 165°, which gives a eutectic with trinitrobenzene at 112° containing 4%, and a eutectic with anthracene at 162° containing 51%, of anthracene.

With *o*-(*p*)-nitrophenol, anthracene gives a eutectic at 44° (106°) containing 2% (6%) of anthracene. With *m*-nitrophenol, a compound (1 mol.: 1 mol.) is formed, m. p. 187°, this giving with anthracene at 186° a eutectic containing 59%, and with *m*-nitrophenol at 93° a eutectic containing 3%, of anthracene. The system anthracene-2:4-dinitrophenol forms a eutectic at 101°, containing 15.5% of anthracene. T. H. P.

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXI. The Binary Systems of Triphenylmethane with Amines and Phenols. ROBERT KREMANN, FRIEDRICH ODELGA, and OTHMAR ZAWODSKY (*Monatsh.*, 1921, **42**, 117—145; cf. Kremann and Wlk, A., 1919, ii, 458).—The binary systems formed by triphenylmethane with *p*-toluidine, α - and β -naphthylamines, and *m*- and *p*-phenylenediamines exhibit only simple eutectics. With *m*-phenylenediamine, two liquid layers are formed in the region corresponding with 20—91% of triphenylmethane, the temperature of the non-variant equilibrium in this region during the crystallisation of triphenylmethane being 81°. Thus, of the amines examined, only aniline gives a compound with triphenylmethane; for this system the authors find the maximum temperature 67.5° and for the eutectic between triphenylmethane and the compound, 67° and 72% of triphenylmethane, whereas Hartley and Thomas (T., 1906, **89**, 1024) found 71.6°, 70°, and 71.5% of triphenylmethane respectively. The total affinity between triphenylmethane and aniline is undoubtedly slight and is annulled by the least alteration in the molecular character of the amine.

Like diphenylmethane, triphenylmethane forms no compounds with phenol, α - and β -naphthols, the three dihydroxybenzenes,

pyrogallol, the three nitrophenols, and picric acid. Somewhat extensive miscibility gaps in the liquid condition occur in the binary systems formed by triphenylmethane with resorcinol, quinol, pyrogallol, and picric acid, and in some cases solid solutions appear to be formed between triphenylmethane and phenols.

The positions of the eutectics in the binary systems formed by triphenylmethane with *p*-toluidine, α - and β -naphthylamines, and *p*- and *m*-phenylenediamines correspond respectively with the following temperatures and percentages of triphenylmethane: 33°, 36%; 37°, 33%; 72°, 75%; 87.5°, 97%; 60°, 3%.

The corresponding results for the binary systems formed by triphenylmethane with phenols are: Phenol, 31°, 26%; β -naphthol, 77°, 80%; α -naphthol, 74°, 70%; catechol, 80°, 82%; resorcinol, 87°, 94%; quinol, 91°, about 100%; pyrogallol, 89°, 97.5%; *o*-nitrophenol, 36°, 30%; *m*-nitrophenol, 80°, 76%; *p*-nitrophenol, 86°, 92.5%. In some cases, it cannot be decided whether the pure components or saturated mixed crystals of the solid solutions of the two components take part in the eutectic. The latter is probable in the systems containing the two naphthols, since mixtures at some distance from the eutectic solidify at temperatures higher than the eutectic temperature. In the systems containing triphenylmethane and *m*-(*p*-)nitrophenol, thermal effects occur below the eutectic temperatures, namely, at 75° (91°); for these no explanation is advanced.

T. H. P.

Preparation of Dihydroxyperylene. ALOIS ZINKE (Brit. Pat. 165771).—One part of 2:2'-dimethoxy-1:1'-dinaphthyl or other alkyl derivative of dihydroxydinaphthyl is heated with 4 parts of aluminium chloride with exclusion of moisture for two hours at 140–150°. The molten mass is treated with hydrochloric acid and the dihydroxyperylene formed is separated and purified by reprecipitation from sodium hydroxide solution or glacial acetic acid, in which reagents it is readily soluble with an intense green fluorescence. 1:12-Dihydroxyperylene is also readily soluble in benzene and toluene, but sparingly so in alcohol. Its solution in aqueous sodium hydroxide is readily oxidisable to the quinone, which, however, is again reduced on treatment with sodium hyposulphite.

G. F. M.

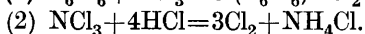
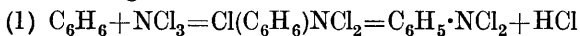
Preparation of Perylene. ALOIS ZINKE (Brit. Pat. 165770).—1:12-Dihydroxyperylene (cf. preceding abstract) is reduced by distilling with or over zinc dust or iron powder. For example, perylene is obtained as a reddish-yellow oil which, after solidification, is purified by crystallisation, by distilling a mixture of 1 part of dihydroxyperylene and 2 parts of zinc dust in a current of hydrogen and passing the vapours over heated pumice stone impregnated with zinc.

G. F. M.

The Reaction between Sulphur Monochloride and Aniline. S. COFFEY (*Rec. trav. chim.*, 1921, **40**, 747–752; cf. Michaelis, A., 1891, **74**, 310 and 715).—In attempting to prepare the sulphur

analogue of nitrobenzene by the action of sulphur monochloride on aniline in dilute ethereal solution, quantitative reaction takes place according to the equation $3\text{NH}_2\text{Ph} + \text{S}_2\text{Cl}_2 \rightarrow \text{NPhS}_2 + 2\text{NH}_3\text{PhCl}$, provided the temperature is sufficiently low. The compound NPhS_2 is a thick, red liquid which cannot be distilled or crystallised. Some of its chemical properties are described. The name dithio-phenylamine is suggested in place of thionitrobenzene, as the substance is analogous to the thionylamines. The nitrogen-sulphur linking is very unstable.
H. J. E.

Chlorination and the Formation of Chloroamines by means of Nitrogen Trichloride. GEORGE H. COLEMAN and WILLIAM ALBERT NOYES (*J. Amer. Chem. Soc.*, 1921, **43**, 2211—2217).—Nitrogen trichloride reacts with ethyl chloride, giving, among other products, ethylene chloride, which is not a normal product of the action of free chlorine on ethyl chloride in the absence of a catalytic agent. With toluene, nitrogen chloride gives benzyl chloride and the monochlorotoluenes, together with more highly chlorinated derivatives. With benzene, the main product is benzene hexachloride. In addition to the above products, toluene, benzene, and benzyl chloride all give with nitrogen trichloride small amounts of *N*-chloroamines, the chloroamine group being located in the nucleus in each case, and not in the side chain. These chloroamines are then further chlorinated by the nitrogen trichloride or free chlorine. Thus with benzene the ultimate product is probably pentachlorophenyldichloroamine, $\text{C}_6\text{Cl}_5\cdot\text{NCl}_2$. These chlorinations take place at the ordinary temperature, and hence are not molecular rearrangements, but similar to the chlorination of aniline hydrochloride by free chlorine. The chlorophenyldichloroamine is decomposed by hydrochloric acid, giving chlorine and chloroaniline. The action of nitrogen chloride on benzene is considered to be



The free chlorine from the second reaction chlorinates the chloroamine. The formation of hydrogen chloride in reaction (1) involves a change of positive chlorine to negative, and this possibly accounts for the formation of considerable quantities of free nitrogen.

W. G.

Hydroxybenzyl dimethylamine. A. MADINAVEITIA (*Anal. Fis. Quím.*, 1921, **19**, 259—264).—Following the method indicated in Bayer's patent (D.R.-P. 92309), *o*-hydroxybenzyl dimethylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NMe}_2$, was prepared by the action of 40% formaldehyde on a mixture of phenol and aqueous dimethylamine. The reaction is incomplete in the cold, but is completed by boiling for three to four hours under a reflux condenser. On cooling, the mixture is acidified with hydrochloric acid and extracted with ether to remove excess of phenol. Excess of aqueous ammonia is added and the amine thus liberated is extracted with ether. The ethereal solution is dried with anhydrous sodium sulphate, and after removal of the ether by evaporation the residue is fractionated.

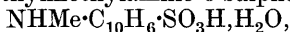
The base thus obtained has b. p. 105—106°/18 mm.; n_D^{15} 1.5273. The *picrate* crystallises in rosettes, m. p. 151°. By treatment of the base with acetic anhydride and saponification of the acetate, saliretin is obtained. By a similar reaction, using guaiacol, a

compound of formula $\text{OH} \begin{array}{c} \text{OMe} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{CH}_2 \end{array} \text{CH}_2 \cdot \text{NMe}_2$ is obtained; it is an oil with b. p. 147—148°/15 mm.; the *picrate* has m. p. 202°. By hydrolysis of the diacetate, vanillyl alcohol is obtained (cf. Tiffeneau, A., 1911, i, 778, 810). G. W. R.

Derivatives of 2:4:6-Trinitrobenzaldehyde. II. ALEXANDER LOWY and WILMER BALDWIN (*J. Amer. Chem. Soc.*, 1921, 43, 1961—1963).—A continuation of previous work (cf. Lowy and Balz, A., 1921, i, 337). The following compounds are described. 2:4:6-Trinitrobenzylidene-*o*-phenetidine, m. p. 178.5°; 2:4:6-trinitrobenzylidene-*p*-phenetidine, m. p. 177°; 2:4:6-trinitrobenzylidene-*o*-anisidine, m. p. 171.5°; 2:4:6-trinitrobenzylidene-*p*-anisidine, m. p. 182°; 2:4:6-trinitrobenzylidene-*o*-chloroaniline, m. p. 187°; 2:4:6-trinitrobenzylidene-*p*-chloroaniline, m. p. 180°; and 2:4:6-trinitrobenzylidene-2:4-dichloroaniline, m. p. 198°.

When the condensations of 2:4:6-trinitrobenzaldehyde with *o*-chloroaniline, *p*-chloroaniline, and 2:4-dichloroaniline were carried out in hot glacial acetic acid solution, products were obtained having m. p. in all cases approximately 100° higher than those of the products prepared in the cold solution. These compounds are probably bimolecular condensation products. W. G.

β -Naphthylmethylamine-6-sulphonic Acid. GILBERT T. MORGAN and HORACE SAMUEL ROOKE (*J. Soc. Chem. Ind.*, 1920, 41, 1—3T).— β -Naphthylmethylamine-6-sulphonic acid,



colourless crystals, m. p. 292°, after becoming changed at 280°, is obtained by the action of methylamine hydrochloride and aqueous sodium hydroxide on Schäffer salt at 180—200°. The following salts are described: *sodium* (+3H₂O and anhydrous), *potassium* (+3H₂O and anhydrous), *calcium* (+6H₂O and anhydrous), *barium* (+10H₂O and anhydrous), *zinc* (+6H₂O and anhydrous), *magnesium* (+6H₂O and anhydrous), *copper*, *silver*, and *lead*. The *dyes* produced by coupling β -naphthylmethylamine-6-sulphonic acid with the diazo-derivatives from aniline, *p*-nitroaniline, picramic acid, diaminstilbenedisulphonic acid, and tolidine are described; *sodium benzeneazo- β -naphthylmethylamine-6-sulphonate* forms bright red crystals. β -Naphthylmethylnitrosoamine-6-sulphonic acid, SO₃H·C₁₀H₆·NMe·NO, yellow needles, is converted by alcoholic hydrogen chloride into 1-nitroso- β -naphthylmethylamine-6-sulphonic acid, orange crystals. The latter substance is converted by evaporation to dryness of its solution in hydrochloric acid or by treatment with acetic acid and zinc chloride into $\alpha\beta$ -naphthiminazole-6-sulphonic acid, SO₃H·C₁₀H₅· $\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \quad \text{C} \\ \diagdown \quad \diagup \\ \text{NH} \end{array}$ CH, pale yellow needles. *Acetyl- β -naphthylmethylamine-6-sulphonyl chloride*, NMeAc·C₁₀H₆·SO₂Cl,

crystallises in prismatic needles, m. p. 142—143°; it is converted by ethyl alcohol into the corresponding *ethyl* ester, colourless needles, m. p. 125—126°, and by ammonia into the *sulphonamide*, colourless, prismatic needles, m. p. 184—185°. *Benzoyl-β-naphthylmethylamine-6-sulphonyl chloride* forms colourless, rhomboidal prisms, m. p. 115—116°, and the corresponding *sulphonamide* crystallises in brownish-white plates, m. p. 225—226°. Sodium β-naphthylmethylamine-6-sulphonate is transformed by methyl sulphate in alkaline solution into the quaternary ammonium salt, $\text{SO}_3\text{Na}\cdot\text{C}_{10}\text{H}_6\cdot\text{NMe}_3\cdot\text{SO}_4\text{Me}\cdot 4\text{H}_2\text{O}$, which is converted by concentrated aqueous potassium hydroxide solution into *potassium β-naphthyl dimethylamine-6-sulphonate*, $\text{SO}_3\text{K}\cdot\text{C}_{10}\text{H}_6\cdot\text{NMe}_2\cdot 3\text{H}_2\text{O}$.

H. W.

Freezing-point Diagram of the System Phenol-Water.

F. H. RHODES and A. L. MARKLEY (*J. Physical Chem.*, 1921, **25**, 527—534).—The complete freezing-point diagram of the system phenol-water has been experimentally determined. It is shown that pure phenol has a melting point of 40·8°, a value which is considerably lower than the usually accepted value of 42—43°. Phenol forms a definite hydrate, $2\text{PhOH}\cdot\text{H}_2\text{O}$, m. p. 15·9°. The system consists of stable equilibria between phenol, phenol hydrate, and water, and metastable equilibria between anhydrous phenol and water. Because of the tendency toward suspended transformation, the solid phase which ordinarily appears when a mixture of phenol and water is cooled is the metastable anhydrous phenol. Hydrated crystals were obtained only by seeding with the hydrate or by cooling to very low temperatures. Phenol hydrate forms a eutectic with water containing 95% water at 0·85° and one with phenol containing 8·25% of water at 15·8°. In the metastable region at 1·7°, two liquid phases appear, a saturated solution of phenol in water and a saturated solution of water in phenol.

J. F. S.

The Action of Nitrous Acid on Phenols. H. A. J. SCHOUTISSEN (*Rec. trav. chim.*, 1921, **40**, 753—762; cf. Nietzki, A., 1890, 156).—By a modification of Liebermann's reaction, indophenols may be prepared from phenols in one operation. The reaction takes place in two stages, first the formation of a nitroso-compound, followed by the condensation of this compound with a second molecule of the phenol. The facility with which the second stage takes place depends on the nature of the intermediate nitroso-phenol. The colouring matters formed in these reactions should be classed among the indophenols as only a small proportion is transformed into oxazine derivatives by the closing of the ring. The author criticises the views put forward by Meyer and Elbers (A., 1921, i, 240).

H. J. E.

Metallic Derivatives of Nitrophenolic Compounds. III. Nitrophenoxides of the Alkali Metals. DOROTHY GODDARD and ARCHIBALD EDWIN GODDARD (T., 1922, **121**, 54—58).

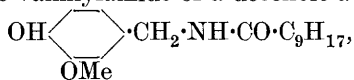
Compound Formation in Phenol-Cresol Mixtures. JAMES KENDALL and J. J. BEAVER (*J. Amer. Chem. Soc.*, 1921, **43**, 1853—1687; cf. this vol., ii, 32, 33).—Phenol and the three cresols have been exhaustively purified by repeated fractionation and absolute purity determined by a minimum specific conductivity. The following data are recorded for the pure substances: Phenol, freezing point $39.70^{\circ} \pm 0.02^{\circ}$, specific conductivity 40° , 11.98×10^{-8} and 50° , 14.07×10^{-8} ; *o*-cresol, f. p. $30.60^{\circ} \pm 0.02^{\circ}$, specific conductivity 0.127×10^{-8} at 25° ; *p*-cresol, f. p. $34.55^{\circ} \pm 0.02^{\circ}$, specific conductivity 1.378×10^{-8} at 25° ; *m*-cresol, f. p. $11.10^{\circ} \pm 0.02$, specific conductivity 1.397×10^{-8} at 25° . These values are compared with the best existing data. The specific conductivity of the six possible binary systems made up from phenol and the cresols has been determined for the whole range of concentrations at 25° . A series of viscosity determinations of these same binary systems is recorded for 25° . A series of molecular weight determinations of the pure substances and certain of the mixtures in solutions in benzene have been made by the freezing-point method. The results indicate that without exception no increase in molecular complexity occurs on mixing these substances. This is in complete accordance with the views correlating additive compound formation with diversity in character of the components, put forward previously (*loc. cit.*). It is apparently in disagreement, however, with the fact that Dawson and Mountford (T., 1918, **113**, 923) succeeded in isolating definite compounds from cresol-phenol mixtures in five out of the six systems. It is, however, shown that the compounds obtained by these authors are to be regarded as substitution rather than as additive compounds. Under this view, no conflict exists between the results of Dawson and Mountford and those of the present work; both fall directly into line with the general theory. J. F. S.

Catalytic Hydrogenation of Polyphenols by the Wet Way. J. B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1921, **173**, 1365—1367).—Quinol, resorcinol, catechol, pyrogallol, phloroglucinol, and hydroxyquinol can be reduced in alcohol by the action of hydrogen under a pressure of 30—50 kilos. in the presence of reduced nickel at 115 — 130° or in aqueous solution at slightly higher temperatures. At higher temperatures, secondary reactions occur. At 130° in alcoholic solution, resorcinol gives cyclohexan-1:3-diol, but at 180° cyclohexanol is the principal product. W. G.

Waage's Phytochemical Synthesis of Phloroglucinol from Dextrose. M. NIERENSTEIN (*Nature*, 1920, **105**, 391).—A series of nearly eighty experiments, performed during fifteen years, failed to confirm statements based on Waage's observations (A., 1891, 605; *Ber. deut. bot. Ges.*, 1890, **8**, 250), that phloroglucinol is formed when leaves floating in solutions of sugar are exposed to sunlight. A. A. E.

Natural and Artificial Pepper-substances and the Relation between Chemical Constitution and Peppery Taste. ERWIN OTT and KURT ZIMMERMANN (*Annalen*, 1921, 425, 314—337).—The elucidation of the constitution of capsaicin by Nelson (A., 1919, i, 543) is made the basis of an examination of the extent to which the various features of the molecule contribute to produce the peppery taste characteristic of that substance.

Capsaicin is the vanillylamide of a decenoic acid,



and it is known that the vanillylamide of Δ^{ω} -undecenoic acid has a similar and about equally sharp taste. Undecenoic acid is, therefore, condensed with a number of bases more or less closely related to vanillylamine, and it is shown that the *p*-hydroxybenzylamide (m. p. 86°) has a taste considerably weaker than that of capsaicin, whilst the taste of the *o*-hydroxybenzylamide (not purified) is weaker still. Hence the presence of the methoxy-group and the particular orientation of the hydroxyl group in capsaicin both contribute to its taste. The presence of a phenolic hydroxyl group appears to be essential, since both the *anisylamide* (white leaflets, m. p. 91°) and the *benzylamide* (m. p. 51 — 52°) are tasteless. So also is the *p*-hydroxyphenylamide (m. p. 107°), which shows that the component amine must be of aliphatic type.

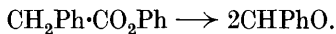
With regard to the conditions governing the character of the acid residue, it is found that the *vanillylamides* of Δ^{α} -nonenoic acid, decenoic acid, and Δ^{ω} -undecenoic acid, have tastes of a comparable strength, whilst those of Δ^{β} -hexenoic acid and crotonic acid possess much less pungent tastes. The taste of the *vanillyl-*amide of *cinnamic acid* (white powder, m. p. 138°) was also only feebly peppery, whilst that of the *vanillylamide* of *oleic acid* was exceedingly pungent but of different quality from the tastes of capsaicin and its closer homologues. On the other hand, the *p*-hydroxybenzylamide of Δ^{α} -nonenoic acid tastes more strongly peppery than the corresponding amide of undecenoic acid (see above). These facts show (a) that the positions of the double bond in the acid residue has comparatively little influence on the peppery taste of the capsaicin-like amides, (b) that, on the other hand, the length of the carbon chain is important, acids with nine, ten, or eleven carbon atoms showing the phenomenon in the most marked and characteristic manner.

One of the most remarkable facts which emerged from the investigation is the necessity for an unsaturated linking in the acid component. The *vanillylamide*, m. p. 86° , of highly purified *stearic acid* is quite without taste, both in the solid state and in concentrated alcoholic solution. Commercially "pure" *palmitic acid*, on the other hand, gives a *vanillylamide* (m. p. 79°) which has a sharp taste, but this is due to the presence of traces of the oleic acid derivative. When the amide is purified by crystallisation from ether, the taste of the solid amide vanishes, but it is still

intense in alcoholic solution. A very delicate test for unsaturated acids may be based on these results.

The *piperidide* of *sorbic acid*, m. p. 77° , has a taste which is very bitter but not at all peppery. C. K. I.

Benzyl Compounds [Benzyl Alcohol]. J. MESSNER (*Pharm. Zentralh.*, 1922, **63**, 1).—The instability of aqueous solutions of benzyl alcohol, even in the absence of air, as, for example, when sealed up in ampoules, is ascribed to autoxidation, catalysed possibly by traces of alkali from the glass, resulting in the formation of 1 mol. of toluene, and 1 mol. of benzaldehyde and water from 2 mols. of the alcohol. A similar change occurs with aqueous solutions of benzyl benzoate, which after a week or so acquire a strong odour of benzaldehyde, remaining, however, neutral in reaction. In this case 2 mols. of benzaldehyde are formed by autoxidation of the ester according to the scheme :



G. F. M.

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXV. The Binary Systems of Triphenylcarbinol with Pyrogallol, Nitrophenols, Polynitrobenzenes, and Phenylenediamines. ROBERT KREMAN, HEINZ HOHL, and ROBERT MÜLLER II (*Monatsh.*, 1921, **42**, 199—220; cf. this vol., i, 131, 159).—Triphenylcarbinol (2 mols.) and pyrogallol (3 mols.) form a compound, m. p. 97° , giving at 65° a eutectic with triphenylcarbinol and at 76° a eutectic with pyrogallol, these containing respectively 70% and 49% of triphenylcarbinol. The latter forms with *o*- and *p*-nitrophenols eutectics at 41° and 97° containing 90% and 63% of the nitrophenol. Triphenylcarbinol and *m*-nitrophenol form a compound which appears to contain 1 molecule of the former and 2 molecules of the latter component, and undergoes considerable dissociation when fused. The system triphenylcarbinol—picric acid forms a compound (1 mol. : 1 mol.), m. p. 138.5° , which gives with picric acid at 110° a eutectic containing 23%, and with triphenylcarbinol at 122° a eutectic containing 67%, of triphenylcarbinol.

The binary systems formed by triphenylcarbinol with *o*-, *m*-, and *p*-dinitrobenzenes, 2 : 4-dinitrotoluene, and 2 : 4 : 6-trinitrotoluene form eutectics at 102° , 82° , 132° , 65° , and 76° , respectively, corresponding with 67%, 82%, 64%, 88%, and 92% of the respective nitro-components. The system triphenylcarbinol—trinitrobenzene forms a compound, m. p. 134.5° , which contains 2 mols. of the alcohol to 3 mols. of the nitro-compound and gives eutectics with the components at 133° and 112° respectively and corresponding with 48% and 15% of triphenylcarbinol.

With the binary systems formed by triphenylcarbinol with *p*- and *m*-phenylenediamines, the fusion curves of the components meet in eutectic points at 118° and 59.5° respectively, these corresponding with 67% and 10% of triphenylcarbinol. T. H. P.

The Interaction of Aromatic Disulphides and Sulphuric Acid. SAMUEL SMILES and ERNEST WILSON McCLELLAND (T., 1922, **121**, 86—90).

Preparation and Properties of the Benzochloroamides. GEORGE ROBERT ELLIOTT (T., 1922, **121**, 202—209).

Steric Hindrance of the Sulpho-acid Group. C. F. VAN DUIN (*Rec. trav. chim.*, 1921, **40**, 724—735).—In preparing the methyl esters of isomeric sulphobenzoic acids, the yield is much greater in the case of the ortho-acid, whilst in the saponification of these esters the SO_3Na -group in the ortho-position considerably retards the reaction. Anomalous results are given by *o*-sulph-amino-benzoic acid. The conclusions drawn are consistent with those of Remsen and Reid (A., 1899, i, 507). H. J. E.

Azomethine Derivatives of the 2- and 4-Hydroxy- α -Naphthaldehydes. GILBERT T. MORGAN and HARRY GORDON REEVES (T., 1922, **121**, 1—7).

Reduction of Naphthalene- and Naphthol-carboxylic Acids. HUGO WEIL and HERMANN OSTERMEIER (*Ber.*, 1921, **54**, [B], 3217—3219).—It has been shown previously that salicylic acid is reduced by sodium amalgam in the presence of boric acid to salicylaldehyde in good yield (A., 1908, i, 800). The observations have now been extended to certain carboxylic acids of naphthalene and the naphthols. Under these conditions, α -naphthoic acid is almost unaffected, whereas β -naphthoic acid is partly converted into β -naphthaldehyde, m. p. $60\cdot5$ — 61° (*phenylhydrazone*, colourless leaflets, m. p. 217 — 218°). 1-Naphthol-2-carboxylic acid gives the corresponding aldehyde, m. p. 59° , the yield being 57%, calculated on the reduced acid. 2-Naphthol-3-carboxylic acid is transformed into an aldehyde, $\text{C}_{11}\text{H}_{12}\text{O}$, b. p. $122^\circ/12$ mm. (*phenylhydrazone*, m. p. 97°). The substance behaves like an aliphatic aldehyde, being resinified by alkali and reducing ammoniacal silver solution, Fehling's solution, and potassium permanganate in cold solution; it appears to be tetrahydro- β -naphthaldehyde, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CH}_2 - \text{CH} \cdot \text{CHO} \\ | \\ \text{CH}_2 - \text{CH}_2 \end{smallmatrix}$. It gives a bisulphite compound which is freely soluble in water. H. W.

Carboxylic Acids of the Semibenzene Group. K. v. AUWERS and K. ZIEGLER (*Annalen*, 1921, **425**, 280—294).—This communication shows that the types of transformation previously discussed (A., 1911, i, 298) have some degree of generality.

Ethyl α -4-hydroxy-1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-propionate, $\text{CO}_2\text{Et} \cdot \text{CHMe} \cdot \text{C}(\text{OH}) \begin{smallmatrix} \text{CH} \cdot \text{CH} \\ | \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{CMe} \cdot \text{CHCl}_2$, is obtained as a viscous, dark oil (impure) by the action of ethyl α -bromopropionate and zinc dust on 1-methyl-1-dichloromethylcyclohexadien-4-one, and on hydrolysis by means of cold alcoholic alkali yields the corresponding acid, which forms stout, white

crystals, m. p. 123° (decomp.). On shaking with formic acid, the ester of the hydroxy-acid is dehydrated, forming *ethyl α-1-methyl-1-dichloromethyl-Δ^{2:5}-cyclohexadien-Δ⁴-propionate* ($d_4^{17.6}$ 1.2033, d_4^{20} 1.201, $n_D^{17.6}$ 1.56017, $n_D^{17.6}$ 1.56682, n_D^{20} 1.5657), which on hydrolysis by means of alcoholic potassium hydroxide yields the free acid, a yellow, crystalline powder, m. p. 101—103°, and can be regenerated from the acid by treating its silver salt with ethyl iodide. On heating, the acid undergoes isomeric change with the formation of *ββ-dichloro-α-p-tolylisobutyric acid*, needles, m. p. 135—136°, which when treated with alkali is converted into *β-chloro-α-p-dimethylstyrene*.

1:3-Dimethyl-1-dichloromethylcyclohexadien-4-one on condensation with ethyl bromoacetate and zinc yields *ethyl α-1:3-dimethyl-1-dichloromethyl-Δ^{2:5}-cyclohexadien-Δ⁴-acetate* ($d_4^{17.6}$ 1.2026, d_4^{20} 1.200, $n_D^{17.6}$ 1.56219, $n_D^{17.6}$ 1.56898, n_D^{20} 1.5679). The free acid, m. p. 125—126°, on heating in petroleum, is converted into *ββ-dichloro-α-m-4-xylylpropionic acid*, m. p. 132—132.5°, which on hydrolysis by means of boiling sodium carbonate solution yields *β-chloro-2:4-dimethylstyrene*. This substance on oxidation in aqueous acetone by permanganate gave 2:4-dimethylbenzaldehyde, which was identified as its semicarbazone.

Ethyl ββ-dichloro-α-m-4-xylylpropionate, b. p. 170—175°/16 mm., is best obtained by the action of heat on ethyl α-1:3-dimethyl-1-dichloromethyl-Δ^{2:5}-cyclohexadien-Δ⁴-acetate. On boiling with alcoholic alkali, it is converted into *β-chloro-2:4-dimethylatropic acid*, $C_6H_3Me_2 \cdot C(CO_2H) \cdot CHCl$, which crystallises in stout tablets, m. p. 111°. C. K. I.

Friedel and Crafts' Reaction. The Preparation of 2-*p*-Toluoylbenzoic Acid. T. C. McMULLEN (*J. Amer. Chem. Soc.*, 1921, **43**, 1965).—In the preparation of 2-*p*-toluoylbenzoic acid from toluene, phthalic anhydride, and aluminium chloride good yields of the acid were obtained using 20 grams of toluene, 5 grams of the anhydride, and 9 grams of the chloride. Increasing the amount of phthalic anhydride or introducing acetic anhydride reduced the yield of acid very considerably or prevented its formation, but resulted in good yields of ditolyl phthalide (cf. Rubidge and Qua, A., 1914, i, 539). W. G.

Friedel and Crafts' Reaction. The Carbomethoxybenzoyl Chlorides with Aromatic Hydrocarbons and Aluminium Chloride. MAURICE E. SMITH (*J. Amer. Chem. Soc.*, 1921, **43**, 1920—1924).—The reaction of each of the carbomethoxybenzoyl chlorides with benzene, toluene, and *m*-xylene, respectively, in the presence of aluminium chloride has been studied. In each case the reaction with toluene takes place in the para-position to the methyl group and with *m*-xylene in the para-position to one of the methyl groups.

o-Carbomethoxybenzoyl chloride gave under these conditions with benzene after hydrolysis of the ester *o*-benzoylbenzoic acid; with toluene *p*-toluoyl-*o*-benzoic acid, and with *m*-xylene 2:4-di-

methylbenzoyl-*o*-benzoic acid. *m*-Carbomethoxybenzoyl chloride gave with benzene *m*-benzoylbenzoic acid; with toluene *p*-toluoyl-*m*-benzoic acid, m. p. 172°, giving a *silver* salt and a *methyl* ester, m. p. 108°; and with *m*-xylene 2 : 4-dimethylbenzoyl-*m*-benzoic acid, m. p. 168°, giving a *silver* salt and a *methyl* ester, m. p. 73°. *p*-Carbomethoxybenzoyl chloride gave with benzene *p*-benzoylbenzoic acid; with toluene *p*-toluoyl-*p*-benzoic acid, and with *m*-xylene 2 : 4-dimethylbenzoyl-*p*-benzoic acid, m. p. 185°, giving a *silver* salt and a *methyl* ester, m. p. 59°.

*iso*Phthalic and terephthalic acids were readily obtained by the oxidation of commercial xylene with potassium permanganate in the presence of sodium hydroxide, the two acids being separated by means of the differing solubilities of their barium salts. W. G.

The Friedel and Crafts' Reaction. Bromophthalic Anhydrides, Benzene, and Aluminium Chloride. H. N. STEPHENS (*J. Amer. Chem. Soc.*, 1921, **43**, 1950—1956).—The various *o*-benzoylbromobenzoic acids and the diphenylbromophthalides have been prepared and identified. 3-Bromophthalic acid was prepared most satisfactorily from 3-aminophthalic acid by the Sandmeyer reaction. Its anhydride when boiled with benzene and aluminium chloride for four hours gave 6-benzoyl-2-bromobenzoic acid, m. p. 231.5°, probably identical with the compound, m. p. 219—221°, described by Pechmann as *o*-bromobenzoylbenzoic acid (cf. *Ber.*, 1879, **12**, 2126). Under similar conditions, 4-bromophthalic anhydride gave 2-benzoyl-4-bromobenzoic acid, m. p. 193°, and 6-benzoyl-3-bromobenzoic acid, m. p. 172.5° (cf. Kohler, *Heritage*, and Burnley, A., 1910, i, 562).

When 3-bromophthalic anhydride is boiled as above with aluminium chloride and benzene and then to the mixture acetic anhydride and more benzene are added and the boiling is continued, a compound, m. p. 148—150°, is obtained which is not, however, a diphenylbromophthalide. Under similar conditions, 4-bromophthalic anhydride gives a mixture of *diphenyl-5-bromophthalide*, m. p. 186°, and *diphenyl-4-bromophthalide*, m. p. 115—116°. *Diphenyl-3-bromophthalide*, m. p. 131°, was obtained from the mixed anhydride, m. p. 168.5°, of 6-benzoyl-2-bromobenzoic acid and acetic acid. The mixed anhydride, m. p. 83—87°, of 2-benzoyl-4-bromobenzoic acid and acetic acid, and the mixed anhydride of 6-benzoyl-3-bromobenzoic acid and acetic acid were also prepared. W. G.

A New Alkylamine and certain of its Derivatives. HANS DERSIN (*Ber.*, 1921, **54**, [B], 3158—3162).—Gabriel and Ohle (A., 1917, i, 565) have described the preparation of amino-alcohols by the action of alkylene oxides on phthalimide and subsequent elimination of the acid group. Since, however, the alkylene oxides are generally prepared with considerable loss from the halogenhydrins, it appears more advantageous to cause the latter to react directly with potassium phthalimide. This method has been used already for the preparation of β -hydroxy-*n*-propylamine (Gabriel

and Ohle, A., 1917, i, 563) and two further examples of its employment are now given.

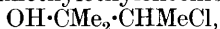
Hydroxyethylphthalimide, $C_8H_4O_2 \cdot N \cdot CH_2 \cdot CH_2 \cdot OH$, m. p. 88—89°, is obtained from potassium phthalimide and ethylene chlorohydrin.

*iso*Butylene chlorohydrin, prepared from chloroacetone or chloroacetic ester and magnesium methyl bromide (but not iodide), is converted by potassium phthalimide into α -phthalimino- β -hydroxy- β -methylpropane, $OH \cdot CMe_2 \cdot CH_2 \cdot N \cdot C_8H_4O_2$, slender, colourless needles or leaflets, m. p. 106—107°. The yield is not very satisfactory. Attempts to prepare the substance from Grignard's reagents and ethyl phthaliminoacetate, acetonylphthalimide, or phthalylglycyl chloride were, however, fruitless. The phthalyl derivative is hydrolysed by sulphuric acid to isobutaldehyde and α -amino- β -hydroxy- β -methylpropane, $OH \cdot CMe_2 \cdot CH_2 \cdot NH_2$; the *hydrochloride*, very hygroscopic, colourless needles, m. p. 70—72°, *platinichloride*, long, very hygroscopic, yellow needles, m. p. 172° (decomp.), *picrate*, large, prismatic crystals, m. p. 165—175°, according to the manner of heating, and *aurichloride*, long, yellow needles or prisms, of the latter are described. The base is converted by phenylthiocarbimide into *N*-phenyl-*N'*-hydroxyisobutylthiocarbamide, $NHPh \cdot CS \cdot NH \cdot C_4H_8 \cdot OH$, colourless needles or prisms, m. p. 136—137°, which is transformed by fuming hydrochloric acid at 100° into the isomeric 2-anilino-5 : 5-dimethylthiazoline, $\begin{matrix} CMe_2 \cdot S \\ | \\ CH_2 - N \end{matrix} \gg C \cdot NHPh$,

colourless prisms, m. p. 153—154°. β -Chloro- α -amino- β -methylpropane hydrochloride, lustrous needles, m. p. 183° (decomp.), is obtained together with the chlorohydrin, $OH \cdot CMe_2 \cdot CH_2Cl$, when the alkylamine hydrochloride is heated with saturated hydrochloric acid at 100°; the oily free base smells like glue, and yields a *picrate*, long needles or plates, m. p. 159°. Potassium thiocyanate converts the chloroalkylamine hydrochloride into 2-amino-5 : 5-dimethylthiazoline (*picrate*, m. p. 103—106°). With benzoyl chloride and sodium hydroxide, the hydrochloride gives β -chloro- α -benzamido- β -methylpropane, $CMe_2Cl \cdot CH_2 \cdot NHBz$, m. p. 97—98°, which is transformed by boiling water into 2-phenyl-5 : 5-dimethylthiazoline, a liquid which gives a *picrate*, needles, m. p. 198—199°. The *platinichloride* of the chloroamine, $CMe_2Cl \cdot CH_2 \cdot NH_2$, crystallises in six-sided prisms, m. p. 200°.

α -Phthalimino- β -hydroxy- β -methylpropane exchanges its hydroxyl-group readily for a halogen atom when warmed with halogen acids. It thus gives β -chloro- α -phthalimino- β -methylpropane, $CMe_2Cl \cdot CH_2 \cdot N \cdot C_8H_4O_2$, needles, m. p. 88—89°, the corresponding *iodo*-compound, prisms, m. p. 100—101°, and *bromo*-derivative, needles or leaflets, m. p. 97°. The latter can be converted by potassium hydroxide, acetic acid, and nitrous acid into the *nitroso*-compound, $C_6H_4 \begin{matrix} \diagup CO \cdot N(NO) \cdot CH_2 \\ \diagdown CO \cdot O - - CMe_2 \end{matrix}$, needles or prisms, m. p. 154° (decomp.).

Attempts to cause trimethylethylenechlorohydrin,



to react with potassium phthalimide were unsuccessful. H. W.

Synthesis of Inactive Para- and Anti-hydroxyaspartic Acids (Aminomalic Acids) [Aminohydroxysuccinic Acids].

H. D. DAKIN (*J. Biol. Chem.*, 1921, **48**, 273—291).—Attempts to obtain *aminohydroxysuccinic acid*, $\text{CO}_2\text{H}\cdot\text{CH}(\text{OH})\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}_2\text{H}$, either synthetically or as a degradation product of proteins have not hitherto been successful, although its isolation has been incorrectly reported (Skraup, A., 1904, i, 539; Neuberg and Silbermann, A., 1905, i, 418; Lossen, A., 1906, 798). In view of its possible occurrence in proteins it was therefore prepared by heating chloromalic acid with 5 parts of concentrated aqueous ammonia for about ten hours in an autoclave immersed in a boiling water-bath. After removal of chlorine, it was isolated from the reaction product by means of its lead salt. The acid so obtained forms a syrup which is difficult to crystallise unless seeded, and consists of a mixture of two optically inactive isomerides. Separation of these was effected by fractional crystallisation from water. The less soluble isomeride, the *para-acid* forms small, opaque cubes, decomposes slowly when heated above 235° , and is converted by nitrous acid into racemic acid. The more soluble form, the *anti-acid*, forms hexagonal plates and thick prisms, and gives mesotartaric acid on similar treatment. With phenylcarbimide, *phenylhydantoin* derivatives are produced, the *para*-compound forming bunches of white needles, m. p. $201.5\text{--}202.5^\circ$, and the *anti*, nacreous plates, m. p. $196\text{--}198^\circ$. The various *salts* produced have the following composition: (Para), $(\text{C}_4\text{H}_6\text{O}_5\text{N})_2\text{Ca}\cdot 5\text{H}_2\text{O}$; $\text{C}_4\text{H}_5\text{O}_5\text{NCa}\cdot \text{Aq}$; $(\text{C}_4\text{H}_6\text{O}_5\text{N})_2\text{Ba}\cdot 3\text{H}_2\text{O}$; $\text{C}_4\text{H}_5\text{O}_5\text{NBa}$; $(\text{C}_4\text{H}_4\text{O}_5\text{N})_2\text{Cu}_3\cdot 8\text{H}_2\text{O}$; $(\text{C}_4\text{H}_4\text{NO}_5)_2\text{Zn}_3\cdot 7\text{H}_2\text{O}$. (Anti), $(\text{C}_4\text{H}_6\text{ON}_5)_2\text{Ca}\cdot 4\text{H}_2\text{O}$; $\text{C}_4\text{H}_5\text{ON}_5\text{Ca}\cdot 2\text{H}_2\text{O}$; $(\text{C}_4\text{H}_6\text{O}_5\text{N})_2\text{Ba}\cdot 3\text{H}_2\text{O}$; $\text{C}_4\text{H}_5\text{O}_5\text{NBa}$; $(\text{C}_4\text{H}_4\text{O}_5\text{N})_2\text{Cu}_3\cdot 8\text{H}_2\text{O}$; $(\text{C}_4\text{H}_4\text{O}_5\text{N})_2\text{Zn}_3\cdot 7\text{H}_2\text{O}$.

By heating chloromalic acid with aniline, the *dianilide of anilino-hydroxysuccinic acid*, $\text{CO}(\text{NHPh})\cdot\text{CH}(\text{NHPh})\cdot\text{CH}(\text{OH})\cdot\text{CO}(\text{NHPh})$, nodular clumps of bright yellow needles softening above 200° and melting at $210\text{--}211^\circ$, and *anilino-hydroxysuccinic acid anil*, $\text{PhN} \begin{array}{l} \diagup \text{CO}\cdot\text{CH}\cdot\text{NHPH} \\ \diagdown \text{CO}\cdot\text{CH}\cdot\text{OH} \end{array}$, bright yellow plates, m. p. $238\text{--}239^\circ$, were obtained.

E. S.

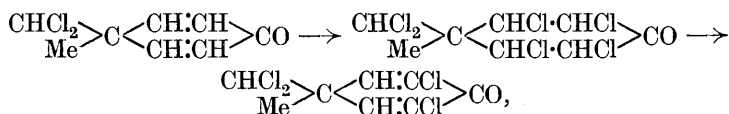
The Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. II. Intra-annular Tautomerism. ERNEST HAROLD FARMER, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE (*T.*, 1922, **121**, 128—159).

The Direct Acetalisation of Aldehydes. ROBERT DOWNS HAWORTH and ARTHUR LAPWORTH (*T.*, 1922, **121**, 76—85).

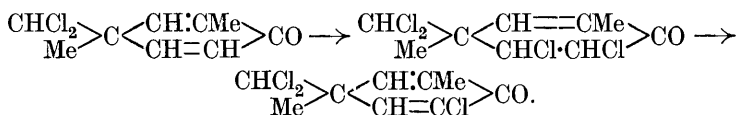
Catalytic Reduction of Nitrones. G. CUSMANO (*Gazzetta*, 1921, **51**, ii, 306—309).—Reduction of an aldonitrone, $\text{CHR}\cdot\text{NR}\cdot\text{O}$, by means of the Grignard reagent yields a β -hydroxylamine, $\text{CH}_2\text{R}\cdot\text{NR}\cdot\text{OH}$ (Angeli, Alessandri, and Ajazzi-Mancini, A., 1911, i, 544), whereas the action of nascent hydrogen results in the formation of the Schiff's base, $\text{CHR}\cdot\text{NR}$. The author finds that catalytic

reduction by means of hydrogen in presence of platinum black converts aldo- and keto-nitrone almost quantitatively into β -substituted hydroxylamines, very small proportions of secondary amines being formed in addition. Thus, phenyl-*N*-phenylnitrone yields phenylbenzylhydroxylamine and benzyaniline, and the catalytic reduction of anisyl-*N*-phenylnitrone and diphenyl-*N*-phenylnitrone proceeds similarly. T. H. P.

Chloro- and Bromo-derivatives of Alkylated *cyclo*Hexadienones. K. VON AUWERS and K. ZIEGLER (*Annalen*, 1921, **425**, 295—313).—It has been shown (A., 1911, i, 383) that the chlorination of 1-methyl-1-dichloromethyl*cyclo*hexadien-4-one takes the following course :



but that the presence of a methyl group in the "ortho"-position to the carbonyl group limits the additive power of the molecule :



In the present communication, it is shown (a) that a methyl group in the meta-position to the carbonyl group does not prevent the addition of the second two atoms of chlorine, but, nevertheless, retards it considerably, (b) that bromination is governed by the same rules as chlorination.

1 : 2-Dimethyl-1-dichloromethyl*cyclo*hexadien-4-one, when treated with chlorine in carbon disulphide, takes up two atoms of chlorine with the formation of 5 : 6-dichloro-1 : 2-dimethyl-1-dichloromethyl- Δ^2 -*cyclohexen*-4-one, which melts at 82—83° with evolution of gas, and, on treatment with potassium acetate in hot acetic acid solution, passes smoothly into 5-chloro-1 : 2-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -*cyclohexadien*-4-one. This substance forms small, stout prisms, m. p. 101—102°, and yields a *p*-nitrophenylhydrazone, m. p. 206—208°. When, however, the original ketone is treated in carbon tetrachloride solution with chlorine in sunlight, four atoms of chlorine are taken up, but the product is too unstable to admit of its being isolated, and passes under the conditions of its production into 3 : 5-dichloro-1 : 2-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -*cyclohexadien*-4-one, which forms glistening crystals, m. p. 87—90°, and shows no tendency to condense with *p*-nitrophenylhydrazine or to combine with chlorine.

Lack of tendency to combine with chlorine and *p*-nitrophenylhydrazine is also exhibited by 5-chloro-1 : 3-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -*cyclohexadien*-4-one, and is to be attributed to the presence of two substituents in positions adjacent to the carbonyl

group. The same is true of 5-chloro-1:3:6-trimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one (m. p. 142—143°), which is obtained by chlorination of 1:3:6-trimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one.

5:6-Dibromo-1-methyl-1-dichloromethyl- Δ^2 -cyclohexen-4-one, which, when freshly prepared, forms colourless needles, m. p. 80—81°, is obtained by allowing equimolecular quantities of 1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one and bromine to combine in carbon disulphide, and, when boiled with potassium acetate and acetic acid, is converted into 5-bromo-1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one, which has m. p. 89—90°, b. p. 183—185°/15 mm. The *p*-nitrophenylhydrazone melts at 154—156°. On treatment with magnesium and methyl iodide, the ketone is converted into 5-bromo-1:4-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol, which forms slender, colourless needles, m. p. 103—104°, and is somewhat less stable than its chlorine analogue.

2:3:5:6-Tetrabromo-1-methyl-1-dichloromethylcyclohexan-4-one is obtained in “*cis*” and “*cis-trans*” modifications by the action of four atoms of bromine on 1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one. The former crystallises in rosettes of colourless needles, m. p. 137° (decomp.), and the latter in needles which immediately after crystallisation melt at 118—119°. This compound does not keep well, however. When either isomeride or the original crude bromine additive product is boiled with potassium acetate and acetic acid, hydrogen bromide is eliminated and 3:5-dibromo-1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one is produced. This substance forms prisms or tablets, m. p. 120—121°, and is stable towards excess of bromine at 100°. It may be prepared in small yield by the action of chloroform and sodium hydroxide on *oo*-dibromo-*p*-cresol, and when treated with magnesium and methyl iodide is converted into 3:5-dibromo-1:4-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-ol, which crystallises in needles, m. p. 91—92°, and eliminates water only at 250°.

The product of addition of two atoms of bromine to 1:3-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one is too unstable to admit of its being isolated, and passes under the conditions of its formation into 5-bromo-1:3-dimethyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadien-4-one, which has m. p. 65—66°, b. p. 180—185°/13 mm., and in agreement with the position assigned to the bromine atom, shows no tendency to react with *p*-nitrophenylhydrazine.

C. K. I.

The Mutual Replacement of Amine Residues by Anils.

G. REDDELIEN (*Ber.*, 1921, 54, [B], 3121—3131).—It has been shown previously (A., 1910, i, 118; 1913, i, 1203) that the formation of ketoneanils can be facilitated greatly by the presence of a suitable catalyst, such as aniline zincchloride or halogen acid, but the procedure gives poor yields with many ketones of high molecular weight and substituted anilines by reason of the slowness of the change. The desired anils may, however, be obtained readily if the simple ketoneanils (in place of the ketones themselves) are

heated with the requisite amine. The process appears to take place in accordance with the scheme: $R_2C:NPh + H_2N \cdot R^1 = R_2C(NHR^1) \cdot NPh = R_2C:NR^1 + NH_2Ph$. The conditions which govern the course of the change are the volatility of the amine, the chemical affinity to the ketonic or aldehydic residue, and the concentration of the amine. If the eliminated amine is not removed (for example, by distillation), an equilibrium governed by the law of mass action becomes established. The replacement of a less by a more volatile amine can, however, be secured if the latter is used in large excess. The amine residue of ketoneanils can be removed by amino-acids in a similar manner; the process does not depend on the activity of the carboxyl groups, since the fission of ketoneanils by carboxylic acids occurs with much less readiness. The new process can be utilised for the production of ketoneanils which, by reason of steric hindrance, are not obtainable directly from the ketones, the starting point being the ketoneimine. The displacements can be catalytically accelerated by aniline zincchloride or halogen acids, but this is not generally necessary. The reaction may also be extended to acid amides, the same catalysts being operative.

Benzophenone- β -naphthil, $CPh_2:N \cdot C_{10}H_7$, short, greenish-yellow prisms, m. p. 96.5° , is prepared by heating a mixture of benzophenoneanil and β -naphthylamine ultimately to 180° in a vacuum. *Fluorenylidene-p-aminodiphenyl*, $C(C_6H_4)_2:N \cdot C_6H_4Ph$, from fluorenoneanil and *p*-aminodiphenyl, crystallises in short, golden-yellow prisms, m. p. 186° . *Di- α -naphthylketoneanil*, from di- α -naphthylketoneimide, m. p. 87° , and aniline, forms pale yellow prisms, m. p. 155° . *Di- α -naphthylketone- α -naphthil*, short, yellow prisms, has m. p. 211° . *Benzophenone-p-anilinoanil*, $CPh_2:N \cdot C_6H_4 \cdot NPh$, from benzophenoneanil and *p*-aminodiphenylamine, forms dark yellow, oblique, four-sided rods, m. p. 111° . Benzophenoneanil-*p*-carboxylic acid, $CPh_2:N \cdot C_6H_4 \cdot CO_2H$, short, pale yellow prisms, m. p. 240° , is obtained readily from *p*-aminobenzoic acid and benzophenoneanil or benzophenoneimide; the sodium salt, an intensely yellow, crystalline powder, and the potassium salt are described. *Fluorenoneanil-p'-carboxylic acid*, from fluorenoneanil and *p*-aminobenzoic acid, crystallises in yellow leaflets, m. p. 253° . Benzophenoneimide is prepared conveniently by heating benzophenoneanil at 200° in the presence of a little aniline hydrobromide in a current of dry ammonia. Fluorenoneimide, pale yellow, slender needles, m. p. 124° , is prepared in a similar manner. *Benzophenone-methylimide*, $CPh_2:NMe$, a colourless liquid, b. p. $158-159^\circ/13\text{ mm.}$, is obtained by heating benzophenoneanil and aniline hydrobromide at $200-210^\circ$ in a current of dry methylamine. *Fluorenonemethylimide* crystallises in pale yellow leaflets, m. p. $110-111^\circ$. *Benzophenonebenzoylhydrazone*, $CPh_2:N \cdot NHBz$, from benzophenoneanil and benzoylhydrazine at 100° , forms small, colourless rods, m. p. 115.5° ; it can also be prepared in almost quantitative yield by protracted ebullition of a solution of its components in alcohol. *Fluorenonebenzoylhydrazone* forms pale yellow needles, m. p. 171° .

H. W.

Fission of Anils. G. REDDELIEN and HILDEGARD DANILOF (*Ber.*, 1921, **54**, [B], 3132—3142; cf. A., 1910, i, 118; 1913, i, 1203, and preceding abstract).—Anils are hydrolysed by aqueous solutions of mineral acids with a readiness which depends to an unusual extent on the presence of substituents. Steric hindrance is shown when the latter are present in the ortho-position, but hydrolysis is also facilitated greatly by positive and retarded by negative groups in the para-position. The stability of substances such as benzophenoneanil-*p*'-carboxylic acid is probably due to a subsidiary valency linking as indicated by the formula $\text{CPh}_2\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, which also renders possible an explanation of the ready fission of the corresponding esters. The anils are much more stable towards alkali than towards acid. The aldehydeanils, however, are hydrolysed more or less completely by protracted heating with sodium hydroxide, whereas certain ketoanils are completely stable even towards the 30% solution. The similarity of the behaviour of the C:NPh group in anils with the keto-group has been emphasised previously by Miller and Plöchl (A., 1896, i, 609) and by Reddelien (*loc. cit.*). This, however, does not extend to the behaviour of the substances towards alkali, since the ketones undergo fission with much greater readiness than do the ketoanils. The remarkable stability of the latter towards alkali has caused the authors to investigate the possibility of esterifying hydroxyanils and anil-carboxylic acids and of acylating hydroxyanils and ketoneimides in alkaline solution. Esterification with methyl sulphate proceeds smoothly. Benzoylation according to the Schotten-Baumann method is more complex, since the hydroxyanils suffer fission when the solution is warmed, whereas in cold solution this action is less marked (but never completely suppressed) and the desired benzoates are produced. Acetylation of hydroxyanils with acetic anhydride and sodium acetate occurs invariably with great smoothness.

Benzoylation of the ketoneimines cannot be effected by the Schotten-Baumann method, since benzamide is always produced owing to fission of the imine. The benzoylated products can, however, be prepared in pyridine solution or by the use of benzoic anhydride dissolved in benzene. In contrast to the ketoneimines, they are very stable substances, which are hydrolysed only by boiling acid or alkali.

The anils are also decomposed by hydrogen sulphide in accordance with the equation $\text{CR}_2\text{:NPh} + \text{H}_2\text{S} = \text{CR}_2\text{:S} + \text{NH}_2\text{Ph}$. Reaction occurs with some difficulty, and not invariably in warm alcoholic solution, and is effected preferably by passing hydrogen sulphide through a suspension of the anil salt in benzene.

The following individual substances are described. Benzophenone-*p*-dimethylaminoanil, $\text{CPh}_2\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, yellow crystals, m. p. 86—87°, which is obtained conveniently from benzophenone, dimethyl-*p*-phenylenediamine, and hydrobromic acid at 160—180° (cf. Reddelien, A., 1910, i, 118; Moore, A., 1910, i, 281). *Ethyl benzophenoneanil-p*'-carboxylate, $\text{CPh}_2\text{:N}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$ (from benzophenoneanil and ethyl *p*-aminobenzoate in a vacuum at 180—200°),

small, yellow needles, m. p. 93—94°. *Methyl benzophenoneanil-p'-carboxylate* (from the acid, methyl sulphate, and sodium hydroxide), pale yellow leaflets, m. p. 133°. *Methyl fluorenoneanil-p'-carboxylate*, $C_{13}H_8 \cdot N \cdot C_6H_4 \cdot CO_2Me$, yellow leaflets, m. p. 170°. *Ethyl benzylidene-p-aminobenzoate*, $CHPh \cdot N \cdot C_6H_4 \cdot CO_2Et$, pale yellow needles, m. p. 47°. *Benzylidene-p-anisidine*, m. p. 72°. *Benzophenonebenzoylimide*, $CPh_2 \cdot N \cdot Bz$, colourless prisms, m. p. 117—118°. *Fluorenonebenzoylimide*, pale yellow leaflets, m. p. 130°. *Benzylidene-p-aminophenyl benzoate*, $CHPh \cdot N \cdot C_6H_4 \cdot OBz$, colourless needles, m. p. 144°. The benzoate, pale yellow leaflets, m. p. 105°, and acetate, pale yellow prisms, m. p. 93—94°, of benzophenone-p-hydroxyanil.

Benzilmonoanil is converted by potassium hydroxide at 170—180° into benzilic and anilindiphenylacetic acids.

Benzophenoneanil hydrochloride is transformed by hydrogen sulphide into thiobenzophenone, a dark blue liquid, b. p. 176—178°/18 mm. In a similar manner, p-dimethylaminobenzophenoneanil hydrochloride, red needles, m. p. 178° (decomp.), is converted into p-dimethylaminothiobenzophenone, $C_{15}H_{15}NS$, bluish-red, rhombic leaflets, m. p. 91°.

Thiobenzophenone is also produced when hydrogen sulphide is passed through molten benzophenoneanil, but the action proceeds further to the formation of diphenylmethane, $CPh_2 \cdot S + H_2S = CH_2Ph_2 + S_2$. Under similar conditions, fluorenoneanil gives a red sulphide which could not be isolated in a homogeneous condition

and dithiodifluorenone $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix} > C < \begin{matrix} S \\ | \\ S \end{matrix} < C < \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}$ (cf. Smedley, T., 1905, 87, 1253).

H. W.

Dibenzylideneacetone [Distyryl Ketone] and Triphenylmethane. X. Ionogenically Linked Halogen Atoms. FRITZ STRAUS and AMADÄUS DÜTZMANN (*J. pr. Chem.*, 1921, [ii], 103, 1—68; cf. A., 1912, i, 989).—The unsaturated chlorides obtained by the action of phosphorus pentachloride on distyryl ketone and other ketones of similar structure contain the group $CHCl$, and are derived from diphenylchloromethane by the separation of one of the benzene nuclei from the methane carbon atom by a more or less long, conjugated chain of ethylene linkings. In the reactions of these unsaturated chloro-compounds, the secondary chlorine atom exhibits a highly developed "ionogenic" linking closely resembling that observed with triphenylchloromethane. Thus, the chlorine atom is readily replaceable by hydroxyl, methoxyl, another halogen, etc., and also induces in the compounds ability to unite with compounds of different character, forming intensely coloured complexes. Among the latter, a special position is occupied by the additive compounds formed with sulphur dioxide, the coloured solutions of these compounds in excess of the liquefied gas exhibiting electrical conductivity; in a few instances, such compounds may be isolated and analysed.

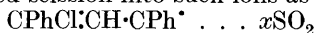
The authors have measured the conductivities of a considerable number of these solutions with the object of determining the manner in which the conductivity varies with constitutive altera-

tion in the molecular structure of the unsaturated chloro-compounds (cf. Straus and Hüssy, A., 1909, i, 490). Benzyl chloride and diphenylchloromethane, which may be regarded as the parent substances of the whole series, show no measurable conductivity even in concentrated solution. Conductivity makes its appearance when an ethylene linking is introduced between the methyl carbon atom and the one nucleus, and increases with the number of such linkings in the molecule until it assumes considerable magnitude. As regards the influence of nuclear substituents on the conductivity of these unsaturated chloro-compounds, the only data available refer to compounds in which either chlorine or methoxyl is introduced in the para-position in both nuclei; such data show that the conductivity is diminished by chlorine, but is increased by methoxyl to the order of magnitude of the conductivities exhibited by the best-conducting true salts. Thus, the influence of nuclear methoxyl suppresses all other constitutive influences.

Of the effects on the conductivity of change of the anion little is known. Replacement of the secondary chlorine by bromine results in considerable augmentation of the conductivity. The carbinols obtained by treating the chloro- or bromo-compounds with water also dissolve in liquid sulphur dioxide, giving coloured complex compounds, the conductivities of which are approximately 10% of those of the corresponding chloro-compounds. The methyl ethers of the carbinols give coloured and conducting solutions in sulphur dioxide only when they correspond with highly conducting chlorides; the molecular conductivities of such ethers are about one-half as great as those of the corresponding carbinols, but persistently increase, instead of remaining constant, for any definite dilution.

The magnitudes of the conductivities of these coloured solutions exhibit parallelism with the intensities of their colour, these varying, for solutions of the different compounds of similar concentrations, to the same degree as the molecular conductivities. Indeed, in all the cases investigated, gradual diminution of the conductivity is accompanied by fading of the colour; further, with the carbinols examined and with triphenylcarbinol, which give solutions at first colourless, the subsequent change into coloured solutions corresponds with measurable increases in the conductivity. It is therefore assumed that, even in solutions of the chlorides in liquid sulphur dioxide, an equilibrium exists between a colourless, non-conducting form, which may be regarded as formed by heterogeneous association between molecules of the chloride and of the solvent, and represents simple solution such as occurs with organic solvents, and a second, coloured, conducting form, arising by transformation of the solvate originally formed, $:\text{CHCl} \dots x\text{SO}_2$ (colourless) \rightleftharpoons $:\text{CHCl} \dots x\text{SO}_2$ (coloured). With the chlorides themselves, the establishment of this equilibrium proceeds too rapidly to permit of direct observation. In considering the observed variation of the conductivity, it must be borne in mind that dilution causes, not only the normal increase in the dissociation, but also a simultaneous displacement of the equilibrium between colourless and coloured forms.

The results of Hantzsch's investigations (A., 1918, ii, 2, 4) show that the process of ionisation does not, of itself, condition alteration of the light absorption, and that with a coloured ion there must correspond a coloured non-dissociated parent form. Hence, in the coloured solutions of these chlorides in sulphur dioxide, the presence of a second, coloured, ionisable compound must be assumed. As yet it has not been found possible to prove experimentally the assumed scission into such ions as



and $\text{Cl}' \dots x\text{SO}_2$, by electrolysis of one of these chlorides (cf. Schlenk, A., 1910, i, 236).

The investigation of the velocities with which these halogen compounds are decomposed by water (A., 1909, i, 490; 1910, i, 593; 1912, i, 989) yielded results which, together with those now obtained, indicate that similar alterations in the molecules of the halogen compounds or, in other words, similar alterations in the affinity demands of the methyl carbon atom, influence the velocity of the decomposition by water and the electrical conductivity qualitatively in the same direction.

The conclusions drawn by Straus, Lutz, and Hüsey (A., 1910, i, 563) regarding the dependence of the stability of the coloured complex compounds formed by various chlorides on the number of unsaturated linkings and on the nature of the substitution in the nucleus are confirmed.

According to Werner's hypothesis, the hydrolysis of the complex chlorides results first in a loose union of the water molecule with the chlorine atom, this proceeding to varying extents with the different chlorides; the affinities are then brought into equilibrium by the formation of the carbinol rather than by displacement of an electron: $\text{R}_1\text{R}_2\text{H:C:Cl} \dots \text{HOH} \longrightarrow \text{R}_1\text{R}_2\text{H:C} \overset{\curvearrowright}{\text{Cl}\cdot\text{H OH}}$.

The phenomena observed with the unsaturated chlorides in solution in sulphur dioxide are discussed in relation to the halochromy of the unsaturated ketones, and it is found that the conductivities of sulphur dioxide solutions of these chlorides are extremely small and bear no relationship to those of the corresponding chlorides.

Walden (A., 1902, i, 536) drew the conclusion that the capacity of these chlorides to undergo electrolytic dissociation is determined principally by the number of radicles united to the carbon atom, and that only tertiary compounds exhibit appreciable electrical conductivity. The authors' results show, however, that secondary halogen compounds also may display the properties of strong electrolytes.

A full description is given of the methods employed in the conductivity measurements which have been applied to: (I) Derivatives of benzophenone and fluorenone: diphenylchloromethane; the chloride of 4:4'-diphenylbenzophenone, $\text{CCl}_2(\text{C}_6\text{H}_4\text{Ph})_2$; *p*:*p'*-dimethoxybenzophenone and the corresponding dichloro-compound, $\text{CCl}_2(\text{C}_6\text{H}_4\cdot\text{OMe})_2$, and monochloro-compound, $\text{CHCl}(\text{C}_6\text{H}_4\cdot\text{OMe})_2$; the chloride of fluorenone. (II) Derivatives of phenyl styryl

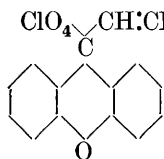
ketone: $\alpha\gamma$ -dichloro- $\alpha\gamma$ -diphenylpropylene; $\alpha\gamma$ -dichloro- $\alpha\gamma$ -di-*p*-chlorophenylpropylene; α -chloro- γ -bromo- $\alpha\gamma$ -di-*p*-chlorophenylpropylene; *p*-anisyl *p*-methoxystyryl ketone; $\alpha\gamma$ -dichloro- $\alpha\gamma$ -di-*p*-anisylpropylene; α -chloro- γ -bromo- $\alpha\gamma$ -di-*p*-anisylpropylene; $\alpha\gamma$ -dibromo- $\alpha\gamma$ -di-*p*-anisylpropylene. (III) Derivatives of distyryl ketone and of phenyl cinnamylidenemethyl ketone: $\gamma\epsilon$ -dichloro- $\alpha\epsilon$ -diphenyl- $\Delta^{\alpha\gamma}$ -pentadiene; γ -chloro- $\alpha\epsilon$ -diphenyl- $\Delta^{\alpha\gamma}$ -pentadiene- ϵ -ol, $\text{OH}\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CHPh}$, and its methyl ether; $\gamma\epsilon$ -dichloro- $\alpha\epsilon$ -di-*p*-chlorophenyl- $\Delta^{\alpha\gamma}$ -pentadiene; γ -chloro- $\alpha\epsilon$ -di-*p*-chlorophenyl- $\Delta^{\alpha\gamma}$ -pentadiene- ϵ -ol, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CCl}\cdot\text{CH}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\text{Cl}$, and its methyl ether; ϵ -chloro- $\alpha\epsilon$ -di-*p*-chlorophenyl- $\Delta^{\alpha\gamma}$ -pentadiene; dianisylidenemethyl ketone; $\gamma\epsilon$ -dichloro- $\alpha\epsilon$ -di-*p*-anisyl- $\Delta^{\alpha\gamma}$ -pentadiene; γ -chloro- ϵ -methoxy- $\alpha\epsilon$ -di-*p*-anisyl- $\Delta^{\alpha\gamma}$ -pentadiene. (IV) Derivatives of dicinnamylidenemethyl ketone: $\alpha\epsilon$ -dichloro- $\alpha\epsilon$ -diphenyl- $\Delta^{\alpha\gamma}$ -pentadiene; $\epsilon\iota$ -dichloro- $\alpha\iota$ -diphenyl- $\alpha\gamma\epsilon\eta$ -nonatetrene; ϵ -chloro- $\alpha\iota$ -diphenyl- $\alpha\gamma\epsilon\eta$ -nonatetrene- ι -ol, and its methyl ether. (V) Tridiphenylchloromethane. T. H. P.

Halochromic Phenomena with Diarylstyrylcarbinols.

KARL ZIEGLER (*Ber.*, 1921, **54**, [B], 3003—3009).—The recent publication of Hess and Weltzien (this vol., i, 35) has induced the author to put forward an account of his work in this field. It is based on the hypothesis that the halochromy of the triarylcarbinols is connected with the possibility of existence of the triarylmethyls, and that the cause is to be found in the unsaturated nature of the benzene nucleus. If this is the case, it should be possible to replace the latter by unsaturated groups without disturbance of the typical properties of the substances. This has been achieved in a number of instances by the aid of the styryl complex.

Benzophenone gives with the magnesium compound of β -bromostyrene a compound which becomes intensely red and then green when treated with concentrated sulphuric acid, the colour disappearing on addition of water. A similar substance is derived from phenyl *p*-tolyl ketone, but not from acetophenone, thus conforming to theory. The compounds have not been isolated in the homogeneous condition.

[With KURT OCHS.]—The Grignard reagent from β -bromostyrene gives with 4:4'-dimethoxybenzophenone in ethereal solution *di-p-anisylstyrylcarbinol*, $\text{OH}\cdot\text{C}(\text{C}_6\text{H}_4\cdot\text{OMe})_2\cdot\text{CH}\cdot\text{CHPh}$, which is isolated in the form of its *perchlorate*, a stable, dark red powder, m. p. about 90°. The salt gives a magenta-red solution in acetone or chloroform, which is stable in the cold but rapidly becomes discoloured when warmed. The similar compounds from other diaryl ketones all give magenta-red solutions, but the isolation of other crystalline perchlorates has not been effected. 9-*Styrylxanthanyl perchlorate* (annexed formula) is obtained similarly from xanthone; it forms red prisms or thin, orange-yellow leaflets, decomp. 187—189°. The substance is remarkably stable. When boiled with alcohol, it is converted into *ms*-styrylxanthene, m. p. 215°. 9-*Styryl-1-meth-*



oxyxanthanyl perchlorate is a stable, dark red powder which softens at 160° and becomes black, without melting, at 250° . 9-*Styryldi- $\beta\beta'$ -naphthoxanthanyl perchlorate* is somewhat less stable. H. W.

The Beckmann Transformation. JAKOB MEISENHEIMER (*Ber.*, 1921, 54, [B], 3206—3213).—Two stereoisomeric forms of benzilmonoxime are known and, in accordance with the results of the Beckmann transformation, the formulæ $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{HO}\cdot\text{N}}{\underset{|}{\text{C}}}}\cdot\text{Bz}$ and $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{OH}}{\underset{|}{\text{C}}}}\cdot\text{Bz}$

have been assigned to the β - and α -forms. It has been assumed that intramolecular reactions take place with greater readiness when the reacting groups are disposed near to one another in space, but this has never been proved strictly to be the case. The incidental observation that 3 : 4 : 5-triphenylisooxazole is converted by chromic acid in glacial acetic acid solution or by ozone into benzoyl- β -benzilmonoxime, $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{O}\cdot\text{C}\cdot\text{Ph}}{\underset{|}{\text{C}}}}\cdot\text{Ph} \rightarrow \text{Ph}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{OBz}}{\underset{|}{\text{C}}}}\cdot\text{Ph}$

(Meisenheimer, this vol., i, 176), proves, however, that the configurations assigned previously to the benzilmonoximes are incorrect, and that, during the Beckmann change, the transformation occurs, not between vicinal groups, but between those placed in the *anti*-position to one another. It is hereby assumed that in the opening of a ring only one form can be produced, which must contain the developed groups in the vicinal position to one another; the necessary precautions have been taken to prove that the benzoyl-benzilmonoxime is actually the primary product of the fission of 3 : 4 : 5-triphenylisooxazole.

The new view of the course of the Beckmann change necessitates a redistribution of the formulæ among the benzildioximes, the α -, β -, and γ -forms now receiving the configurations $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{HO}\cdot\text{N}}{\underset{|}{\text{C}}}}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{OH}}{\underset{|}{\text{C}}}}\cdot\text{Ph}$,

$\text{Ph}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{OH}}{\underset{|}{\text{C}}}}\cdot\text{Ph}$, $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{HO}\cdot\text{N}}{\underset{|}{\text{C}}}}\cdot\text{Ph}$, $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{N}\cdot\text{OH}}{\underset{|}{\text{C}}}}\cdot\text{Ph}$, respectively, thus involving

the transpositions of the formulæ assigned previously to the α - and β -forms, whilst leaving that of the γ -variety unchanged. A review of the literature on the subject shows that the chemical behaviour of the dioximes is in much better accord with the new than with the older formulæ.

The mechanism of the Beckmann transformation is now explained in the following manner. In the oximes, the radicles attached to the vicinal carbon atom, for example, the phenyl group of α -benzilmonoxime, exert an attraction on the hydroxyl group, and thus displace it from its normal position. The residual or partial valency of the nitrogen atom on the side remote from the hydroxy-group is thereby strengthened. In certain circumstances (the best conditions for the Beckmann change), the residual valency becomes so powerful that it attracts the vicinal group attached to the carbon atom to itself. Momentarily, therefore, a compound, $\text{Ph}\cdot\overset{\text{O}}{\underset{\text{X}\cdot\text{N}\cdot\text{Bz}}{\underset{|}{\text{C}}}}\cdot\text{Ph}$, with trivalent carbon and quadrivalent nitrogen is pro-

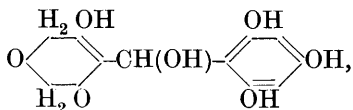
duced. In the latter, the radicle X attached to the nitrogen by oxygen has but little relationship to the nitrogen, and is therefore eliminated and naturally becomes attached to the tervalent carbon atom.

Triphenylisooxazole, dissolved in carbon tetrachloride, is converted by successive treatment with ozone and water into benzoyl- β -benzilmonoxime, m. p. 137·5—138·5°, in addition to a little oxalic and benzoic acids. The oxime and benzoic acids are also produced when the isooxazole is oxidised with chromic acid in glacial acetic acid solution, but the yields are very small. Benzoyl- β -benzilmonoxime is obtained conveniently by the action of benzoyl chloride on the oxime in the presence of pyridine. Under similar conditions, α -benzilmonoxime gives a compound of the expected composition, which, however, is probably ON-dibenzoylsobenzamide, OBz·CPh·NBz, m. p. 95—96° (cf. Werner and Piguet, A., 1905, i, 66). Benzoyl- β -benzilmonoxime is converted by sodium hydroxide in aqueous alcoholic solution almost quantitatively into the β -oxime and benzoic acid. Under similar conditions, the benzoyl compound obtained from the α -oxime gives benzonitrile and benzoic acid.

H. W.

Condensation Reactions of Formic Acid. ERW. SCHWENK (*J. pr. Chem.*, 1921, [ii], **103**, 103—105).—That the condensation reaction of formic acid with 2-methylindole (Scholtz, A., 1913, i, 893) is not confined to such pyrrole derivatives is shown by the behaviour of formic acid in presence of concentrated sulphuric acid towards 3-oxythionaphthen and towards phloroglucinol. In the first case, the product of the reaction is the 3-oxythionaphthen-1-aldehydethioindogenide, m. p. about 270°, obtained by Friedländer and Kielbasinski (A., 1911, i, 1021) from 3-oxythionaphthen-1-aldehyde and acids, and by Friedländer and Risse (A., 1914, i, 876) by the action of chloroform and an alkali on 3-oxythionaphthen; this compound forms an *acetyl* derivative, C₁₇H₁₀O₂S₂, m. p. 211°.

The action of formic acid on phloroglucinol in presence of sulphuric acid yields an orange, pulverulent compound, C₁₃H₁₂O₇, possibly



which does not melt at 300°, and at 150° is converted into the compound, C₁₃H₁₀O₆.

T. H. P.

Preparation of Hydroxyanthraquinones from Nitroanthraquinones. ERW. SCHWENK (*J. pr. Chem.*, 1921, [ii], **103**, 106—108).—The methods which have been suggested for replacing the nitro-groups of nitroanthraquinones by hydroxyl groups give either poor yields or impure products, or are tedious to execute. The author finds, however, that this replacement may be readily effected by prolonged heating of the nitro-compound with potassium

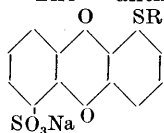
acetate and acetic acid in an oil-bath at 170—180°. The nitro-group is doubtless replaced first by acetyl, but in no instance could the acetyl compound be isolated; the readiness with which the acetyl group is replaced is doubtless related to the difficulty experienced in acetylating the α -hydroxyanthraquinones (Dimroth, Friedmann, and Kämmerer, A., 1920, i, 443). Replacement of nitro-groups by hydroxyls by the action of potassium acetate does not take place in the naphthalene or benzene series; with 3-nitrophthalic acid, a reaction occurs, but this has not been investigated.

T. H. P.

Derivatives of Anthraquinone. Aliphatic Thioethers, Dithioethers, and Thioether Sulphonic Acids. E. EMMET REID, COLIN M. MACKALL, and GEORGE E. MILLER (*J. Amer. Chem. Soc.*, 1921, **43**, 2104—2117).—Anthraquinone- α -sulphonic acid and the 1:5- and 1:8-disulphonic acids when heated with aliphatic mercaptans in alkaline solution reacted readily to form thioethers, thioether sulphonic acids, and dithioethers. The reaction takes place rapidly at 100°. The corresponding sulphones were prepared from the thioethers and dithioethers by oxidation with nitric acid. The following compounds are described:

Thioethers, $C_{14}H_7O_2SR$: Anthraquinone methyl thioether, m. p. 221°; anthraquinone ethyl thioether, m. p. 184°; *anthraquinone propyl thioether*, m. p. 151°; *anthraquinone butyl thioether*, m. p. 112·5°; *anthraquinone isobutyl thioether*, m. p. 144°; *anthraquinone isoamyl thioether*, m. p. 86°. The corresponding sulphones, $C_{14}H_7O_2SO_2R$, are: methyl, m. p. 254°; ethyl, m. p. 211·5°; *propyl*, m. p. 204·5°; *butyl*, 150°; *isobutyl*, m. p. 190°; *isoamyl*, m. p. 133°.

The anthraquinone-5-sulphonic acid 1-alkyl thioethers,



, were isolated in the form of various salts as follows:

Anthraquinone-5-sulphonic acid 1-methyl thioether as its *sodium, barium, aniline*, m. p. 290—299° (decomp.), *o-toluidine*, m. p. 285—290° (decomp.), and *p-toluidine*, m. p. 298—304° (decomp.), salts. *Anthraquinone-5-sulphonic acid 1-ethyl thioether* as its *sodium, barium, aniline*, m. p. 276—285° (decomp.), *o-toluidine*, m. p. 264—274° (decomp.), and *p-toluidine*, m. p. 276—285° (decomp.), salts. *Anthraquinone-5-sulphonic acid 1-propyl thioether* as its *sodium, barium, aniline*, m. p. 270—277° (decomp.), *o-toluidine*, m. p. 255—257° (decomp.), and *p-toluidine* salts. *Anthraquinone-5-sulphonic acid 1-butyl thioether* as its *sodium, barium, strontium, calcium, aniline*, m. p. 257—259° (decomp.), *o-toluidine*, m. p. 234—237° (decomp.), and *p-toluidine*, m. p. 256—260° (decomp.), salts. *Anthraquinone-5-sulphonic acid 1-isoamyl thioether* as its *sodium, barium, aniline*, m. p. 263—265° (decomp.), *o-toluidine*, m. p. 250—254° (decomp.), and *p-toluidine*, m. p. 267—277° (decomp.), salts.

1:5-Anthraquinone dialkyl dithioethers: *dimethyl*; *methyl ethyl*,

m. p. 229°; *methyl propyl*, m. p. 209°; *methyl butyl*, m. p. 173·5°; *methyl isoamyl*, m. p. 175°; *diethyl*, m. p. 226·5°; *ethyl propyl*, m. p. 188·5°; *ethyl butyl*, m. p. 156°; *ethyl isoamyl*, m. p. 152°; *dipropyl*, m. p. 227°; *propyl butyl*, m. p. 175°; *dibutyl*, m. p. 159·5°; *butyl isoamyl*, m. p. 134°, and *di-isoamyl*, m. p. 158·5°. The corresponding disulphones are *dimethyl*; *methyl ethyl*, m. p. > 300°; *methyl propyl*, m. p. 291°; *methyl butyl*, m. p. 264°; *methyl isoamyl*, m. p. 266°; *diethyl*, m. p. 269·5°; *ethyl propyl*, m. p. 243·5°; *ethyl butyl*, m. p. 194°; *ethyl isoamyl*, m. p. 198°; *dipropyl*, m. p. 265°; *propyl butyl*, m. p. 220°; *dibutyl*, m. p. 184·5°; *butyl isoamyl*, m. p. 203·5°, and *diisoamyl*, m. p. 202°.

The anthraquinone-8-sulphonic acid 1-alkyl thioethers prepared are as follows: 1-*methyl* as its *sodium*, *barium*, *aniline*, m. p. 260° (decomp.), *o-toluidine*, m. p. 255° (decomp.), and *p-toluidine*, m. p. 260° (decomp.), salts; 1-*ethyl* as its *sodium*, *barium*, *aniline*, m. p. 250° (decomp.), *o-toluidine*, m. p. 260° (decomp.), and *p-toluidine*, m. p. 255°, salts; 1-*propyl* as its *sodium*, *barium*, *aniline*, m. p. 242° (decomp.), *o-toluidine*, m. p. 260° (decomp.), and *p-toluidine*, m. p. 260° (decomp.), salts; 1-*butyl* as its *sodium*, *barium*, *strontium*, *calcium*, *lead*, *nickel*, *cobalt*, *copper*, *aniline*, m. p. 260° (decomp.), *o-toluidine*, m. p. 260° (decomp.), and *p-toluidine*, m. p. 255° (decomp.), salts; and 1-*isoamyl* as its *sodium* and *barium* salts.

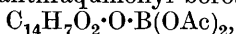
The 1:8-anthraquinone dialkyl dithioethers are: *dimethyl*, m. p. 222°; *methyl ethyl*, m. p. 210°; *methyl propyl*, m. p. 173·5°; *methyl butyl*, m. p. 134°; *methyl isoamyl*, m. p. 114°; *diethyl*, m. p. 167·5°; *ethyl butyl*, m. p. 95°; *dipropyl*, m. p. 142°; *propyl butyl*, m. p. 119·5°; *propyl isoamyl*, m. p. 104°; *dibutyl*, m. p. 131°; *butyl isobutyl*, m. p. 103·5°; *butyl isoamyl*, m. p. 116·5°, and *di-isoamyl*, m. p. 133°. The corresponding disulphones are: *dimethyl*, m. p. 310°; *methyl ethyl*, m. p. 220°; *methyl propyl*, m. p. 211°; *methyl butyl*, m. p. 169°; *methyl isoamyl*, m. p. 172°; *diethyl*, m. p. 228°; *ethyl butyl*, 128°; *dipropyl*, m. p. 210°; *propyl butyl*, m. p. 200·5°; *propyl isoamyl*, m. p. 147·5°; *dibutyl*, m. p. 138°; *butyl isobutyl*, m. p. 168·5°; *butyl isoamyl*, m. p. 154° and *diisoamyl*, m. p. 176°.

Attempts were made to prepare similar derivatives from sodium naphthalene- α -sulphonate, but no reaction took place. Preliminary experiments showed that when sodium anthraquinone- α -sulphonate was replaced by the β -sulphonate replacement by the mercaptan residue took place with much greater difficulty, if at all.

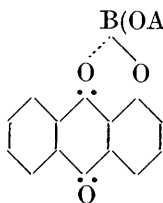
W. G.

Boric Esters of Hydroxyanthraquinones. OTTO DIMROTH and THEO FAUST (*Ber.*, 1921, **54**, [B], 3020—3034).—Boric acid is used extensively in the chemistry of the hydroxyanthraquinones as a protective agent in oxidations and as accelerator in condensations and nitrations. Its action has been attributed frequently to the formation of boric esters, but the question does not appear to have been investigated systematically. It is now shown that boric esters of the hydroxyanthraquinones can be obtained conveniently from the latter by the action of a solution of boric acid

in acetic anhydride. Thus, 1-hydroxyanthraquinone is transformed into 1-hydroxyanthraquinonyl boroacetate,



which loses a molecule of acetic anhydride when heated in a vacuum, and forms 1-hydroxyanthraquinonyl metaborate, $\text{C}_{14}\text{H}_7\text{O}_2\cdot\text{O}\cdot\text{B}\cdot\text{O}$. 2-Hydroxyanthraquinone, on the other hand, does not react with boric acid. This difference between the behaviour of hydroxy-groups in positions 1 and 2 is characteristic and general. The unusual greater reactivity of the 1-hydroxy-group is explained by the hypothesis that a subsidiary valency union occurs between the boron atom and the ketonic oxygen atom, thus giving rise to compounds of the type indicated by the annexed



formula, which are thus analogous to the compounds with tin tetrachloride described by Pfeiffer (A., 1913, i, 879). The correctness of this supposition is supported by the observations that anthraquinone itself reacts with boroacetic anhydride (the compound formed could not be isolated), that 1:5-dihydroxyanthraquinone reacts with two molecules of boroacetic anhydride, whereas the 1:8-compound reacts with only one molecule, and that 1:4:5-trihydroxyanthraquinone unites with two molecules of boric acid, whilst the third hydroxy-group becomes acetylated.

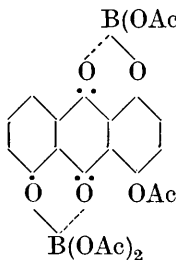
The formation of boric esters of hydroxyanthraquinones in acetic acid solution is accompanied by characteristic changes in colour and spectrum. Investigation of the latter is not yet complete, but it is established that all diborates are distinguished by very sharp and characteristic absorption bands.

It is remarkable that an α -hydroxy-group in 1:8-dihydroxyanthraquinone is acetylated readily by warming for a short time with boric acid-acetic anhydride solution, whereas such groups are generally difficult to acetylate. In acetic anhydride solution, it is found that 1:8-dihydroxyanthraquinone is more readily mono-acetylated than the 1:5-compound. In general, the author is inclined to attribute the difficulty of acetylating and alkylating *o*-hydroxyketones to chemical rather than to steric effects, and suggests the possibility of an unstable, subsidiary valency bond between the hydrogen of the hydroxyl group and the ketonic oxygen atom.

The analysis of the hydroxyanthraquinonyl boroacetates is effected by decomposing them with water and weighing the precipitated hydroxyanthraquinone. Acetic acid is estimated in the filtrate by titration with alkali until neutral red becomes yellow, after which mannitol and phenolphthalein are added and the titration is continued until the solution becomes pink.

1-Hydroxyanthraquinonyl boroacetate, orange-red plates, which decomposes when heated without showing a definite melting point, is prepared by gently warming 1-hydroxyanthraquinone with a solution of boroacetic anhydride in an excess of acetic anhydride; it is very readily hydrolysed by water and is unstable towards moist air. It loses acetic anhydride when preserved in a desiccator, rapidly when heated in a vacuum, and passes into 1-hydroxyanthra-

quinonyl metaborate, brown crystals which are much more stable towards water than is the boroacetate. 1:4-*Dihydroxyanthraquinonyl diboroacetate* forms coarse, ruby-red crystals, whilst the corresponding *di-metaborate* is rust-brown. *Alizarin 1-boroacetate* forms dark red crystals which are extremely sensitive to moisture. 2-*Acetylalizarin-1-boroacetate*, orange-red crystals, is decomposed by water into 2-acetylalizarin, m. p. 198°, acetic acid, and boric acid. *Purpuren-1:4-diboroacetate*, purple-red crystals, and 2-*acetyl-purpuren 1:4-diboroacetate*, dark red to violet-red crystals, are also described. *Anthrarufindiboroacetate* crystallises in golden-yellow,



iridescent leaflets. *Chrysazin-monoboroacetate*, pale red crystals with a dull golden glance, and δ -*acetylchrysazin-1-boroacetate*, red crystals, are described; the latter, when hydrolysed, gives 1-*hydroxy- δ -acetoxyanthraquinone*, orange-yellow prisms, m. p. 178°, or lemon-yellow needles, m. p. 179° (the two modifications are interconvertible). 4-*Acetoxy-1:5-dihydroxyanthraquinonyl diboroacetate* (annexed formula), rust-brown crystals with golden glance, is hydrolysed by water to 1:5-*dihydroxy-4-acetoxyanthraquinone*, yellow needles, m. p. 165°; the position of the hydroxy-groups in the latter follows from its inability to be oxidised by lead tetra-acetate to a di-quinone.

H. W.

Researches on Residual Affinity and Co-ordination. VII. Cobaltic Lakes of the Alizarin Series. GILBERT T. MORGAN and J. D. MAIN SMITH (T., 1922, 121, 160—169).

The Action of Bromine on Quinizarin and Alizarin. OTTO DIMROTH, ERNST SCHULTZE, and FRITZ HEINZE (*Ber.*, 1921, 54, 3035—3050; cf. A., 1916, i, 563; 1920, i, 443).—Quinizarin is unaffected by bromine water at the ordinary temperature, but it is rapidly oxidised by a concentrated solution of bromine in potassium bromide to quinizarinquinone, which is a much more powerful oxidising agent than benzoquinone. Bromine water in presence of free bromine, however, converts quinizarin into *quinizarinquinone dibromide*, slender, pink needles, m. p. 210—215° (decomp.); this is also formed by boiling quinizarinquinone with an excess of bromine and glacial acetic acid. It is reduced by sulphurous acid to monobromoquinizarin, red needles, m. p. 228—230° (Liebermann and Riiber, A., 1900, i, 451), which forms a *diacetyl* derivative, pale yellow needles, m. p. 216—218°, whereas treatment with acetic anhydride-sulphuric acid yields *dibromodiacetylquinizarin*, pale yellow needles, m. p. 270—271°, which is hydrolysed by sulphuric acid to dibromoquinizarin, m. p. 252—253° (Liebermann and Riiber, *loc. cit.*).

Quinizarin in methyl alcoholic suspension readily reacts with bromine with ice cooling, forming *quinizarinquinone methoxybromide*, yellow crystals, m. p. 96°, which is converted by acetic anhydride in the cold into 3-*bromodiacetylpurpurin 2-methyl ether*,

pale yellow crystals, m. p. 145°, hydrolysed by sulphuric acid to 3-bromopurpurin-2-methyl ether, red needles, m. p. 260°.

Alizarin reacts with bromine more readily than does quinizarin and forms 3-bromoalizarin, yellow plates, m. p. 260—261°, when boiled with an acetic acid solution of bromine, but treatment with bromine water, or a potassium bromide solution of bromine, or bromine water and free bromine yields in each case 3-bromoalizarin-quinone, very sparingly soluble, yellow needles which readily decompose. Alizarinquinone methoxybromide, obtained in a similar manner to the corresponding quinizarin derivative, forms lanceolate, yellow needles, m. p. 230°, after decomposing and sintering at 200°. A methyl-alcoholic suspension of alizarin, on the other hand, when treated with bromine without cooling, yields 3:4-dibromoalizarin, yellow needles, m. p. 251—252°; diacetyl derivative, pale yellow rosettes of needles, m. p. 199—200°; 3:4-dibromoalizarinquinone, yellow crystals.

Alizarin in ethyl alcoholic suspension reacts with bromine with cooling, with formation of alizarinquinone ethoxybromide, yellow tables, m. p. 205° with decomp. after sintering at 180°.

F. M. R.

Anthradiquinones and Anthratriquinones. OTTO DIMROTH and VALENTIN HILCKEN (*Ber.*, 1921, **54**, 3050—3063; cf. A., 1916, i, 563; 1920, i, 443).—Quinizarinquinone in glacial acetic acid suspension reacts with hydrogen fluoride with formation of 2-fluoroquinizarin, red prisms; diacetyl derivative, slender, yellow needles, m. p. 189°. With benzenesulphonic acid, quinizarinquinone yields quinizarin-2-phenylsulphone, slender, red needles, m. p. 250°; diacetyl derivative, yellow crystals, m. p. 210°. When quinizarinquinone is suspended in acetaldehyde and exposed to sunlight in a closed vessel, monoacetylquinizarin, yellowish-orange needles, m. p. 186°, is formed.

In order to determine the effect of hydroxyl groups on the properties, mono- and di-hydroxyanthradiquinones have been prepared by the oxidation of tri- and tetra-hydroxyanthraquinones respectively with lead tetra-acetate. 6-Hydroxyquinizarinquinone forms small, brownish-yellow crystals, m. p. 215—220° after decomposing and sintering at 200°, and when treated with acetic anhydride-sulphuric acid yields a mixture of hydroxyanthrapurpurin and hydroxyflavopurpurin. 5-Hydroxyquinizarinquinone forms brown needles, m. p. 220° after darkening at 210°. 5:8-Dihydroxyquinizarinquinone could not be isolated from its deep bluish-violet solution in nitrobenzene.

The acetyl derivative of 1:4:5:6:8-pentahydroxyanthraquinone is obtained by oxidising a glacial acetic acid solution of alizarin-bordeaux with lead tetra-acetate and adding an excess of acetic anhydride and sulphuric acid, and, similarly, the diquinones derived from β -monoacetyl-alizarin-bordeaux and anthrapurpurin were only obtained in acetic acid solution.

When 1:2:4:5:8-pentahydroxyanthraquinone and 1:2:4:5:6:8-hexahydroxyanthraquinone are oxidised by air in alkaline solution,

the *tri*- and *tetra*-hydroxyanthradiquinones respectively are obtained, and crystallise from aqueous pyridine in dark violet needles. The hydroxy-derivatives of quinizarinquinone are weaker oxidising agents than the parent substance, and the oxidising power varies with the position of the hydroxyl group in the molecule, for 5-hydroxyquinizarinquinone is a weaker oxidising agent than its 6-hydroxy-isomeride. With regard to the rate of oxidation of a hydroxyanthraquinone to a diquinone, the oxidation to an *o*-quinone proceeds more rapidly than the oxidation to a *p*-quinone. When an acetic acid or nitrobenzene solution of a polyhydroxy-anthraquinone, which contains hydroxyl groups in an ortho- or para-position in both benzene rings, is oxidised with lead tetra-acetate, the blue to bluish-violet diquinone is first formed, but on further oxidation yellow or yellowish-brown solutions of the triquinone are obtained. Solutions of the triquinones derived from 1 : 4 : 5 : 8-tetrahydroxy-, 1 : 2 : 5 : 8-tetrahydroxy-, pentahydroxy-, and hexahydroxy-anthraquinones were obtained in this manner, but the triquinones were not isolated. F. M. R.

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXII. The Binary Systems of Camphor with Phenols. ROBERT KREMANN and FRIEDRICH ODELGA (*Monatsh.*, 1921, **42**, 147—165; cf. this vol., i, 131).—The fusion diagrams of the binary systems formed by camphor with *p*- and *m*-nitrophenols are completely analogous to that of the system camphor-phenol (Kremann, Wischo, and Paul, A., 1916, i, 217), the curves for the two components falling so steeply that meeting in a simple eutectic is not to be expected; in the region corresponding with 59—69% (for *p*-nitrophenol) or 60—69% (for *m*-nitrophenol) of camphor, no crystallisation is induced by inoculation either with one of the components or with the resorcinol-camphor compound. In almost all cases in which *m*- and *p*-nitrophenols form compounds with a second component, *o*-nitrophenol fails to do so owing to steric hindrance. Hence, if the inability of the camphor-*m*-(or *p*-)nitrophenol system to exhibit crystallisation over the ranges mentioned is due to the existence of a compound seeding with which is impossible, the system camphor-*o*-nitrophenol should form no compound and its fusion diagram should be realisable completely; this is actually the case, the eutectic corresponding with 15° and 54% of camphor. The binary systems formed by camphor with 2 : 4-dinitrophenol and picric acid show similar behaviour, the eutectics corresponding respectively with 67° and 61% of camphor, and 71° and 60% of camphor; the 2 : 4-dinitrophenol and picric acid branches exhibit points of inflexion. Here, then, unlike what is observed in other analogous cases, introduction of electronegative nitro-groups into a compound removes the tendency to combine with camphor.

For the systems formed by camphor with pyrogallol and catechol, the fusion curves for the two components descend rapidly and do not meet in a eutectic point on extrapolation. If, however, the intermediate critical viscous melt is seeded with the camphor-

resorcinol compound, a new branch of the diagram of state is realised, this corresponding with the primary crystallisation of a compound of the two components. Contrary to the statements of Efremov (A., 1913, i, 635), the compounds formed are composed of 1 mol. of catechol + 2 mols. of camphor and, apparently, 1 mol. of pyrogallol + 3 mols. of camphor. That the number of molecules of camphor combined should agree with the number of hydroxyl groups in the molecule of the other component is conceivable, but with other compounds, such as amines, steric hindrance to the valency relations results from the ortho-positions of the hydroxyl groups of catechol and pyrogallol, so that the number of molecules of the second component combined is usually less than the number of hydroxyl groups in the hydroxybenzene; in such cases, the two hydroxyl groups act only when they occur in the meta- or para-position. In their behaviour towards camphor, however, the valency activities of the hydroxyls of the dihydroxybenzenes appear to support one another when near and to weaken one another when distant. The fusion curve for the system camphor-quinol exhibits no indication of the formation of the equimolecular compound mentioned by Efremov (*loc. cit.*).

T. H. P.

Saponins. V. Hederin and its Hederagenin. A. W. VAN DER HAAR (*Ber.*, 1921, 54, [B], 3142—3148; cf. A., 1916, i, 41).—It has been shown previously that the crystalline α -hederin is hydrolysed to α -hederagenin, *l*-arabinose, and rhamnose according to the scheme, $C_{42}H_{66}O_{11} + 3H_2O = C_{31}H_{50}O_4 + C_5H_{10}O_5 + C_6H_{12}O_5$. The previous conclusion that it contains five hydroxyl-groups is somewhat modified, since four of these are found to be capable of acetylation, whereas the fifth is present in the carboxyl group. Since α -hederagenin does not dissolve in aqueous carbonate or bicarbonate solutions, whilst it can be titrated with alkali hydroxide in alcoholic solution, it was considered to be a lactone; this view is now abandoned, since the methyl and ethyl esters are found to contain the two hydroxyl groups present in the original substance, which is now regarded as a dihydroxy-carboxylic acid,

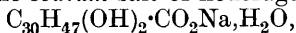


α -Hederin is converted by diazomethane into the corresponding methyl ester, colourless crystals, m. p. 198—200°, which is transformed by acetic anhydride and anhydrous sodium acetate into the tetra-acetyl ester. The sodium salt of α -hederin, $C_{42}H_{65}O_{11}Na \cdot 5H_2O$, and the potassium salt are described.

H. W.

Saponins. VI. Hederagenin. A. W. VAN DER HAAR and A. TAMBURELLO (*Ber.*, 1921, 54, [B], 3148—3158; cf. van der Haar, A., 1916, i, 41, and preceding abstract; Palazzo and Tamburello, *Arch. Farm. Sci. affi.*, 1913, 5, 15).—New analyses of hederagenin have confirmed the formula, $C_{31}H_{50}O_4$, proposed by van der Haar. Diacetylhederagenin loses one of its acetyl groups when heated at 100° or when crystallised from aqueous alcohol, and passes into monoacetylhederagenin, m. p. 156°. The labile

acetyl group appears to be vicinal to the carboxyl-group and to be influenced by its proximity, since the di-acetates of the corresponding methyl and ethyl esters are completely stable towards aqueous alcohol. The *sodium* salt of hederagenin,



is described. *Hederagenin methyl ester*, $\text{C}_{32}\text{H}_{52}\text{O}_4$ (from the sodium salt and methyl iodide, by the successive action of thionyl chloride and boiling methyl alcohol on the sodium salt, by means of methyl sulphate or by diazomethane), has m. p. 240° , $[\alpha]_D^{18} + 70.9^\circ$ in chloroform solution. Diacetylhederagenin methyl ester, $\text{C}_{36}\text{H}_{56}\text{O}_6 \cdot \text{H}_2\text{O}$, has m. p. 193° , $[\alpha]_D^{18} + 61.8^\circ$, when dissolved in absolute alcohol. Hederagenin ethyl ester crystallises in small, colourless needles, m. p. $218\text{--}219^\circ$, $[\alpha]_D^{18} + 72.5^\circ$, in absolute alcoholic solution; the corresponding di-acetate has m. p. 150° , $[\alpha]_D^{18} + 76.47^\circ$, when dissolved in chloroform. Hederagenin methyl ester is converted by fuming nitric acid into a nitro-compound, decomp. 165° , which has not been analysed. The gradual addition of a solution of bromine in chloroform to hederagenin methyl ester dissolved in the same solvent leads to the formation of the dibromo-compound, $\text{C}_{32}\text{H}_{50}\text{O}_4\text{Br}_2$, small, colourless needles, decomp. $215\text{--}217^\circ$. Bromination of hederagenin under similar conditions appears to proceed somewhat irregularly, giving on the one hand a bromo-derivative, colourless needles, decomp. $157\text{--}158^\circ$, which was not analysed but is probably a dibromo-compound (Tamburello), and, on the other, a mixture of two bromo-derivatives, lustrous, hexagonal leaflets, m. p. 242° , and pale yellow needles, $\text{C}_{31}\text{H}_{48}\text{O}_4\text{Br}_2$, m. p. 262° (van der Haar); attempts to repeat the latter preparations led, however, to somewhat different results, giving products of m. p. $268\text{--}270^\circ$ and 255° , respectively.

Hederagenin acid amide, $\text{C}_{31}\text{H}_{51}\text{O}_3\text{N} \cdot \text{H}_2\text{O}$, colourless needles, m. p. 285° , is prepared by the action of ammonia on an ethereal solution of the corresponding chloride obtained by the action of thionyl chloride on hederagenin or its sodium salt. H. W.

Picrotoxin. XII. Picrotin Ketone, $\text{C}_{14}\text{H}_{16}\text{O}_3$. PAUL HORMANN and FRIEDRICH BISCHOF (*Arch. Pharm.*, 1921, 259, 165—176).—The ketone, $\text{C}_{14}\text{H}_{16}\text{O}_3$, first noticed among the reduction products of picrotoxin by phosphorus and hydriodic acid by Angelico (A., 1910, i, 577) was obtained in better yield by first converting the picrotoxin into α -picrotinic acid and picrotoxinic acid by boiling with mineral acid, and then reducing these acids in the same way as picrotoxin itself. It was isolated by means of its oxime, m. p. 212° , and purified by distillation in a vacuum, b. p. $190^\circ/8$ mm. It forms a thick, colourless syrup which crystallises after long keeping. Its *semicarbazone* has m. p. 216° . By the action of methyl alcoholic potassium hydroxide it is hydrolysed into acetic acid and the substance $\text{C}_{12}\text{H}_{14}\text{O}_2$. An attempted degradation of the ketone by converting it into an unsaturated compound through the corresponding tertiary alcohol obtained by the action of magnesium methyl iodide was not successful. *Oximinopicrotin ketone*, $\text{C}_{11}\text{H}_{11}\text{O}_2 \cdot \text{C}(\text{NOH}) \cdot \text{COMe}$ is obtained by the

action of amyl nitrite and sodium ethoxide on the ketone. It is a white substance, m. p. 215° , and forms a *semicarbazone*, m. p. 249° (decomp.), a *phenylhydrazone*, m. p. 220° , an *oxime*, m. p. 192° , and a benzoyl derivative, m. p. $178-182^{\circ}$. It did not yield the diketone on treatment with sodium nitrite or mineral acids, but on oxidation with nitric acid or ammoniacal silver oxide it was converted into acetic acid and a *monobasic acid*, $C_{11}H_{11}O_2 \cdot CO_2H$, which could not be obtained in a crystalline condition. By the action of sodium hypobromite, the ketone was converted into α -*bromopicrotin ketone*, $C_{14}H_{15}O_3Br$, coarse needles, m. p. 145° .

G. F. M.

Physiology of Anthocyanin and Chemistry of Chlorophyll.

J. COSTANTIN (*Ann. Sci. Nat. Bot.*, 1919, [x], **1**, 38—52).—A discussion of the present state of knowledge with regard to anthocyanin and chlorophyll. Reduction with nascent hydrogen of a yellow flavone pigment from *Vitis* is known to yield anthocyanin, and the production of a yellow flavone by oxidation of anthocyanin is affirmed. Chlorophyll is now considered to have the formula $CO_2H \cdot C_{31}H_{29}N_4Mg(CO_2Me)(CO_2 \cdot C_{20}H_{39})$. Treatment with ethyl alcohol produces substitution of an ethyl group for the phytol group, $C_{20}H_{39}$, yielding Willstätter's crystallisable chlorophyll.

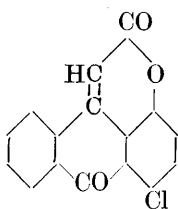
CHEMICAL ABSTRACTS.

Catechutannins. I. Paullinia Tannin. MAXIMILIAN NIERENSTEIN (*T.*, 1922, **121**, 23—28).

Anthracoumarin Derivatives. I. W. J. MINAEFF and KURT RIPPER (*Monatsh.*, 1921, **42**, 73—81).—The only derivatives of anthracoumarin (Kostanecki, A., 1888, 291) as yet known are styrogallol (Jakobson and Julius, A., 1888, 56; Kostanecki, A., 1888, 292) and a hydroxystyrogallol (Slama, A., 1900, i, 177), which are both mordant dyestuffs. In order to obtain compounds with structures similar to those of the vat dyestuffs derived from anthraquinone, the authors have synthesised 6-chloroanthracoumarin, which has been converted into 1-anilinoanthracoumarin. Preliminary experiments on the preparation of di-anthracoumarin have also been carried out.

The 6-chloro-3-hydroxybenzoic acid required was prepared (1) by Mazzara and Bertozzi's method (A., 1900, i, 596), (2) by Peratoner and Condorelli's method (A., 1898, i, 642), with the difference that the hydroxyl of the 6-chloro-3-hydroxytoluene was protected during the oxidation by formation of the mono-phosphoric ester (Heymann and Koenigs, A., 1887, 241), and (3) by reduction of 6-chloro-3-nitrobenzoic acid (Holleman and de Bruyn, A., 1901, i, 591), followed by replacement of the resulting amino-group by hydroxyl.

Condensation of cinnamic and 6-chloro-3-hydroxybenzoic acids in presence of sulphuric acid yields 1-chloroanthracoumarin, which resembles 1-chloroanthraquinone in chemical behaviour, except that its chlorine is more mobile, probably owing to the influence of the negative radicle in the para-position.



6-Chloroanthracoumarin (annexed formula) sublimes in long, golden needles and crystallises in a felted mass of golden needles, m. p. 274°.

6-Anilinoanthracoumarin, $C_{22}H_{13}O_3N$, prepared from 1-chloroanthracoumarin and aniline in presence of fused potassium acetate and copper acetate, crystallises in reddish-violet leaflets, m. p. 184—186°.

The interaction of 6-chloroanthracoumarin and nitrobenzene in presence of "Naturkupfer C" appears to yield di-anthracoumaryl, but no pure product was isolated. T. H. P.

Phenylthioxanthyl. M. GOMBERG and WESLEY MINNIS (*J. Amer. Chem. Soc.*, 1921, **43**, 1940—1944).—The work of Gomberg and Schoepfle (cf. A., 1917, i, 551) on the molecular weight of phenylxanthyl checked by parallel oxygen absorptions has been extended to phenylthioxanthyl. Pure phenylthioxanthanol chloride was prepared by bubbling dry air through a solution of phenylquinothioxanthanol chloride hydrochloride in dry benzene at 90°. This material was used for the oxygen absorption and for the attempts to prepare the free radicle. The free radicle was prepared in solution, but found to be very unstable, and it could not be isolated in the solid state. The values obtained by Schlenck and Renning (cf. A., 1913, i, 34) for the molecular weight of this substance were made on material which was, in all probability, not the free radicle. W. G.

2 : 2'-Sulphonidotriphenylmethyl. M. GOMBERG and E. C. BRITTON (*J. Amer. Chem. Soc.*, 1921, **43**, 1945—1950).—2 : 2'-*Sulphonidotriphenylcarbinol*, $HO \cdot CPh < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > SO_2$, m. p. 224—225°, was obtained by the oxidation of phenylthioxanthanol or by the action of magnesium phenyl bromide on benzophenone sulphone. When heated with phosphorus pentachloride at 110—120°, it yielded 2 : 2'-*sulphonidotriphenylcarbiny chloride*, m. p. 160—161°, which, when reduced with stannous chloride and hydrochloric acid, gave 2 : 2'-*sulphonidotriphenylmethane*, m. p. 193—194°. The carbiny chloride when shaken in benzene solution with molecular silver gave the free radicle, 2 : 2'-*sulphonidotriphenylmethyl*, m. p. 180° (decomp.), which when exposed in benzene solution to air yielded a crystalline *peroxide*, m. p. 238—239° (decomp.).

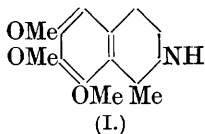
The oxygen and iodine absorptions of the free radicle were determined, and molecular-weight determinations in benzene and in *p*-bromotoluene as solvents indicate little change in molecular weight with rise in temperature from 6° to 27°. The free radicle in solution is unimolecular to the extent of 30% to 38%. W. G.

The Anhalonium Alkaloids. II. Constitution of Pellotine, Anhalonidine, and Anhalamine. ERNST SPÄTH (*Monatsh.*, 1921, **42**, 97—115).—If pellotine actually possesses the constitution suggested (A., 1919, i, 548), protection of its phenolic hydroxyl

group by introduction of a carbethoxyl or an ethyl radicle and cautious oxidation of the resulting compound by means of permanganate should yield substituted gallic acids. No trace of the latter could, however, be obtained and similar failure to detect trimethylgallic acid was experienced on oxidising a methylated anhalamine. The view that pellotine and anhalonidine are derivatives of mezcaline containing a phenolic hydroxyl group cannot be maintained, as it is found that dimethylmezcaline methiodide is identical with neither methylpellotine methiodide nor dimethyl-anhalonidine methiodide.

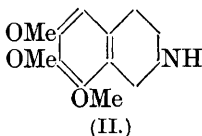
These results suggest that the nitrogen in the two bases forms part of a closed ring, and this view is confirmed by the observation that, when heated with alkali hydroxide, the quaternary, completely methylated pellotine methiodide gives an amine which, when again combined with methyl iodide and subsequently boiled with alkali hydroxide, is converted into a nitrogen-free compound. On the assumptions that the ring in question is the *isoquinoline* ring, that Heffter's formula, $C_{13}H_{19}O_3N$, for pellotine is correct, and that the base contains a phenolic hydroxyl group, a methyl group united to nitrogen, and a gallic acid residue, various constitutions are suggested for pellotine methyl ether; the most probable of these is 6:7:8-trimethoxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline, which best expresses the relationship of pellotine to mezcaline and explains the optical inactivity of pellotine, the formation of the latter from mezcaline being brought about by ring closure by means of acetaldehyde, so that assumption of enzyme action is unnecessary. The methiodide of 6:7:8-trimethoxy-1:2-dimethyl-1:2:3:4-tetrahydroisoquinoline, prepared synthetically from mezcaline, is identical with methylpellotine methiodide, and since pellotine contains a hydroxyl group in place of a methoxyl group of the synthetic base, Heffter's formula, $C_{13}H_{19}O_3N$, for pellotine is confirmed.

The identity of the methiodides of the completely methylated derivatives of pellotine and anhalonidine shows that these two bases have the same ring system. Further, the formation of *N*-acyl derivatives of anhalonidine demonstrates the latter to be a secondary base, so that *O*-methylanhalonidine should have the annexed constitution (I), which accords with the observation that the *N*-*m*-nitrobenzoyl derivative of the synthetic base (I) is identical with methyl-*N*-*m*-nitrobenzoyl-anhalonidine; the formula for anhalonidine is, therefore, $C_{12}H_{17}O_3N$, and not, as Heffter thought, $C_{12}H_{15}O_3N$. Thus, pellotine and anhalonidine are derivatives of 6:7:8-trimethoxy-1-methyltetrahydroisoquinoline, but which of the three methoxy-groups exists as hydroxyl in the original bases remains undecided.



As regards anhalamine, it appeared possible that this represents *N*-methylmezcaline with a hydroxyl in place of one of the methoxy-groups. The non-identity of the methiodides of dimethylmezcaline and dimethylanhalamine shows, however, that anhalamine is not

of the mezcaline type, and the further observation that O-methylanhalamine fails to yield the trimethyl ether of gallic acid when oxidised proves that the nitrogen atom does not occur in an open side-chain and indicates that this compound may be an *isoquinoline* derivative of the structure (II). The accuracy of the latter is proved by the facts that this compound is readily synthesised from mezcaline and formaldehyde and that it gives an *N-m-nitrobenzoyl* derivative identical with *N-m-nitrobenzoyl-O-methylanhalamine*; further, the quaternary iodides of the base (II) and O-methylanhalamine are identical. Anhalamine is therefore the dimethyl-ether of 6 : 7 : 8-trihydroxytetrahydroisoquinoline, but here also the position of the non-methylated phenolic hydroxyl is unknown. Heffter's formula, $C_{11}H_{15}O_3N$, for anhalamine is thus confirmed.



Of the anhalonium alkaloids, anhaline and mezcaline belong to the β -phenylethylamines occurring in various plant families, and are almost certainly decomposition products of substituted phenylalanines resulting from the degradation of proteins. The presence in the same plants as anhaline and mezcaline of the tetrahydroisoquinoline derivatives, pellotine, anhalonidine, and anhalamine, indicates that the latter are formed from the former by condensation with acetaldehyde or formaldehyde.

6 : 7 : 8-Trimethoxy-1-methyl-3 : 4-dihydroisoquinoline, obtained by the action of phosphoric oxide on the *N*-acetyl derivative of synthetic mezcaline, yields a *picrate*, $C_{13}H_{17}O_3N, C_6H_3O_7N_3$, m. p. 181—182°; a *platinichloride*, $(C_{13}H_{17}O_3N)_2 \cdot H_2PtCl_6$, which forms orange crystals darkening at 199°, m. p. 200—201° (frothing), and an *aurichloride*, $C_{13}H_{17}O_3N, HAuCl_4$, which forms straw-yellow crystals, m. p. 154—156°.

6 : 7 : 8-Trimethoxy-1-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, formed from the preceding compound by catalytic hydrogenation in presence of platinum and palladium, yields a *picrate*, $C_{13}H_{19}O_3N, C_6H_3O_7N_3$, m. p. 172—173°, a *platinichloride*, $(C_{13}H_{19}O_3N)_2 \cdot H_2PtCl_6$, m. p. on slow heating 204—206° (decomp.), on rapid heating 210—212°; and an *aurichloride*, m. p. 147—148° (frothing). The action of methyl sulphate on this base gives

6 : 7 : 8-Trimethoxy-1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydroisoquinoline, which is identical with methylpellotine and forms a *picrate*, $C_{15}H_{23}O_3N, C_6H_3O_7N_3$, m. p. 167—168°, an *aurichloride*, m. p. 135—136°, and a *platinichloride*, m. p. 216—217° (decomp.).

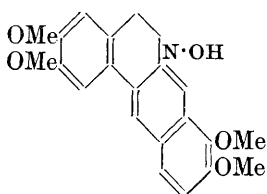
Dimethylanhalamine methiodide, $C_{14}H_{22}O_3NI$, forms crystals, m. p. 211.5—212.5°.

6 : 7 : 8-Trimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline, prepared from mezcaline and formaldehyde according to Decker and Becker's process (A., 1913, i, 291), forms a *hydrochloride*, $C_{12}H_{17}O_3N, HCl$, m. p. 242—243°, an *aurichloride*, m. p. 139—140° (frothing), a *platinichloride*, m. p. 207—208° (frothing and blackening), and a *picrate*, m. p. 184—185°; the quaternary iodide, obtained by treating the hydrochloride with methyl sulphate and sodium

hydroxide and subsequently with sodium iodide, is identical with dimethylanhalamine methiodide (*vide supra*).

N-m-Nitrobenzoylanhalamine, $C_{16}H_{12}O_4N_2(OMe)_2$, has m. p. 175—176°, and its methyl ether, $C_{16}H_{11}O_3N_2(OMe)_3$, m. p. 147—148°. T. H. P.

Conversion of Berberine into Palmatine. ERNST SPÄTH and NORBERT LANG (*Ber.*, 1921, **54**, [B], 3064—3074).—Palmatine



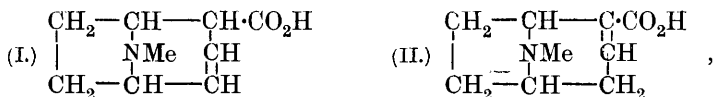
has been isolated from calumba root by Feist (A., 1908, i, 101) and, subsequently, the annexed formula has been assigned to it by Feist and Sandstedt (*Arch. Pharm.*, 1918, **256**, 1). The close similarity of this formula to that of berberine has induced the authors to attempt to confirm it by direct synthesis. For this purpose, bromopapaverine was reduced by granulated tin and hydrochloric acid to tetrahydrobromopapaverine, m. p. 111° (+xH₂O), m. p. 71—73°, which was treated with a mixture of glacial acetic acid, hydrochloric acid, water, and methylal. A small amount of a product, m. p. 151—153°, was thus obtained which was possibly bromotetrahydropalmatine. Debromination of this substance by hydrogen in the presence of palladised barium sulphate did not yield tetrahydropalmatine but norcoralydine (cf. Pictet and Tsau Quo Chou, A., 1916, i, 418).

The possibility of removing the hydroxymethylene group of berberine and replacing it by two methoxyl groups (thus giving palmatine) has been examined. Orientating experiments with piperonal and tetrahydroberberine showed that the hydroxymethylene group can be removed with some difficulty by dilute hydrochloric acid under suitable conditions, but, simultaneously, the phenol produced is very extensively resinified by the liberated formaldehyde. Better results were obtained with tetrahydroberberine and methyl alcoholic potassium hydroxide solution in an evacuated tube at 180°; it is remarkable that, under suitably chosen conditions, the hydroxymethylene group can be removed, whereas the two methoxyl groups remain intact. Nuclear condensation by the liberated formaldehyde appears to occur to only a slight extent, probably owing to the rapid transformation of the aldehyde into potassium formate and methyl alcohol. Methylation of the product of the change by diazomethane gave a poor yield of tetrahydropalmatine. Better results were obtained by its complete methylation by treatment with a large excess of methyl sulphate and alkali in the absence of oxygen and isolation of the completely methylated quaternary iodide by addition of potassium iodide and potassium hydroxide. The salt was found to be identical with tetrahydropalmatine methiodide. When distilled in a vacuum, it gave tetrahydropalmatine, identical with the product derived from natural sources. It was oxidised by a solution of iodine in alcohol to palmatine.

H. W.

A New Base from the Residues of the Hydrolytic Products of Cocaine, Isomeric with Tropine and ψ -Tropine. J. TRÖGER and K. SCHWARZENBERG (*Arch. Pharm.*, 1921, **259**, 207—226).—By fractional crystallisation from alcohol of the hydrochlorides of the basic residues left after the removal of the ecgonine from the product of the hydrolysis of the coca alkaloids, the hydrochloride of a new base, isomeric with tropine and ψ -tropine, was isolated from the more soluble fractions. The new base, $C_8H_{15}ON$, is a very hygroscopic, crystalline substance, m. p. 53° , b. p. $225\text{--}230^\circ$, and distinctly volatile at the ordinary temperature. The *hydrochloride*, *hydrobromide*, and *hydriodide* are crystalline salts, very soluble in water and alcohol, and melt at $157\text{--}160^\circ$, 175° , and 186° , respectively. The *picrate*, $C_8H_{15}ON \cdot C_6H_2(NO_2)_3 \cdot OH$, forms hygroscopic, yellow needles, which sinter at 225° , and decompose at 237° . The *platinichloride*, $(C_8H_{15}ON)_2 \cdot H_2PtCl_6$, is also very soluble in water, and was obtained in long, yellow needles, m. p. 184° , by evaporating the aqueous solution to dryness and crystallising from absolute alcohol and ether. The preparation of the aurichloride in an analytically pure state presented difficulties owing apparently to partial reduction and varying gold content of the salt. The *benzoyl* derivative, crystallised from a mixture of alcohol and ether, formed glistening, white prisms, m. p. $139\text{--}140^\circ$. The *methiodide* of the base crystallises from alcohol in well characterised, white needles, m. p. $238\text{--}240^\circ$. It was converted into the corresponding ammonium base by means of silver oxide, and this on distillation gave trimethylamine and a residue giving no solid derivatives and otherwise not further examined. Attempts to oxidise the original base with chromic acid, permanganate, ferricyanide, and hydrogen peroxide were either without result or gave oily products from which solid derivatives could only in one or two instances be obtained, and then not in an analytically pure condition. G. F. M.

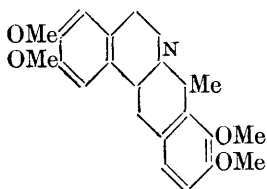
Ecgonine. LXIX. J. GADAMER and CARL JOHN (*Arch. Pharm.*, 1921, **259**, 227—240).—Of the two possible formulæ for anhydroecgonine,



Willstätter decided in favour of I (A., 1899, i, 178), but it is now shown that formula II must be correct, since on reduction to hydroecgonidine at least two different optical isomerides are produced, which could only be the case by the creation of a third asymmetric carbon atom, and on the basis of formula I this is not possible without assuming the occurrence of isomerisation during the reduction. Such isomerisation is conceivable if the reduction is carried out by Willstätter's method with sodium and amyl alcohol, but the hydrogenation was also carried out by the Paal and Skita method, in which an isomerisation is extremely unlikely, and two

hydroecgonidines were again obtained. In each case, the optical isomerides were separated through their aurichlorides. For further confirmation, the ethyl esters of the various aurichlorides were also prepared. Hydroecgonidine, prepared by the reduction of the hydrogen bromide additive product of anhydroecgonine, was an individual substance identical with one of the isomerides obtained by Paal and Skita's method. As, according to formula II, anhydroecgonine contains a conjugated system of double bonds, an exaltation of the molecular refraction was expected, as compared with hydroecgonidine. Determination of the molecular refractions of the ethyl esters in each case showed this expected exaltation, although anhydroecgonine ethyl ester considered by itself actually showed a depression, which must be attributed, however, to the pyrrolidine ring. The following were prepared during the investigation: Hydroecgonidine hydrochloride by Willstätter's method, m. p. 233—234°, $[\alpha]_D -3.0^\circ$, giving two aurichlorides, m. p. 210° and 230°, respectively, which on reconversion into *hydroecgonidine hydrochloride* yielded two corresponding isomerides, both melting at 233—234°, but having $[\alpha]_D -2.77^\circ$ and -4.4° , respectively. Reduction by the Paal-Skita method gave a product which was also resolvable into two aurichlorides, m. p. 210° and 220°, respectively, and these on reconversion gave two hydroecgonine hydrochlorides having $[\alpha]_D -2.30^\circ$ and -1.24° respectively. The hydroecgonine hydrochloride prepared by the reduction of the hydrogen bromide additive product of anhydroecgonine with zinc and sulphuric acid gave only one aurichloride, m. p. 210°, $[\alpha]_D +2.78^\circ$. The aurichloride, m. p. 210°, gave an ethyl ester melting at 173—174°, and the aurichloride, m. p. 220°, an ethyl ester, m. p. 123°. The ethyl ester obtained from the dextrorotatory aurichloride melted at 173—174° and gave an ester hydrochloride having $[\alpha]_D +5.1$. G. F. M.

The Constitution of Corydaline. ERNST SPÄTH and NORBERT LANG (*Ber.*, 1921, **54**, [B], 3074—3078).—The annexed formula



has been assigned to corydaline by Dobbie and Lauder (P., 1902, **17**, 252), and, after consideration of several alternative expressions, has been adopted by Gadamer. The positions of the methyl group and of the two methoxyl groups attached to the benzene nucleus have not, however, been placed beyond doubt, and, for this reason, the authors have attempted the synthesis of a number of these compounds. If the above formula be correct, corydaline is to be regarded as methyltetrahydropalmatine (cf. Späth and Lang, this vol., i, 166). The latter substance, however, is found not to be identical with *r*-corydaline or *mesocorydaline*. Dobbie and Lauder's formula, therefore, appears to be inexact.

Palmatine iodide is converted by magnesium methyl iodide in ethereal solution into α -methyl*dihydropalmatine*, yellow needles, m. p. 128—130°, which is reduced by platinised zinc and dilute

sulphuric acid to a mixture of α -methyltetrahydropalmatines, greenish-yellow leaflets, m. p. 165° and m. p. 67—69°, respectively.

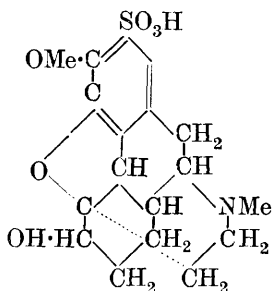
H. W.

Codeineoxidesulphonic Acids and their Derivatives.

EDMUND SPEYER and HERMANN WIETERS (*Ber.*, 1921, **54**, [B], 2976—2987).—The action of acetic anhydride and sulphuric acid on codeine-*N*-oxide has been shown by Freund and Speyer (*A.*, 1911, i, 809) to lead to the formation of α -codeine-*N*-oxidesulphonic acid, $C_{18}H_{20}O_3 \leq \begin{smallmatrix} SO_2 \\ N(OH) \end{smallmatrix} > O$, and codeine-*N*-oxidesulphonic

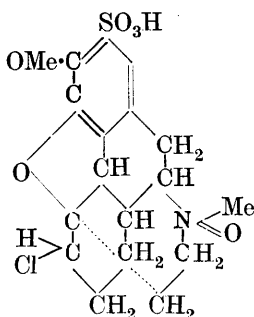
acid, $C_{18}H_{20}O_3 \leq \begin{smallmatrix} SO_3H \\ N:O \end{smallmatrix} >$, which are reduced by sulphurous acid to the same codeinesulphonic acid. The behaviour of the isomeric sulphonic acids when catalytically hydrogenated is now described.

Codeine-*N*-oxidesulphonic acid is reduced by hydrogen in the presence of colloidal palladium to *dihydrocodeinesulphonic acid* (annexed formula), six-sided leaflets or well-defined prisms, decomp. 330—340° after darkening at 30°, $[\alpha]_D^{20} -76.7^\circ$ in faintly alkaline solution. The same acid is obtained by catalytic hydrogenation of codeinesulphonic acid. The acid is reconverted by water at 150° or by stannous chloride and concentrated hydrochloric acid at 100° into dihydrocodeine. It is transformed by nitric acid (*d* 1.36) into nitrodihydrocodeine, yellow double pyramids, m. p. 221°, identical with the substance described by Freund and Melber (*A.*, 1920, i, 717). Similarly, α -codeineoxidesulphonic acid yields α -*dihydrocodeinesulphonic acid*, a colourless, crystalline powder, decomp. 315—320°, $[\alpha]_D^{20} -88^\circ$ in aqueous solution; the corresponding *monohydrate* is also described. It is converted by water at 150—160° into dihydrocodeine and by cold nitric acid (*d* 1.36) into α -nitrodihydrocodeine, slender, yellow needles, m. p. 180°.



Attempts were also made to prepare the isomeric dihydrocodeine-sulphonic acid from dihydrocodeine. For this purpose, the latter was transformed by hydrogen peroxide into *dihydrocodeine-N-oxide*, pale yellow, rhombic crystals, decomp. 225° after softening at 215° (*hydrochloride*, hexagonal plates, m. p. 217° after previous softening; *picrate*, four-sided prisms, m. p. 161—162°). Under the action of sulphuric acid and acetic anhydride, the latter yields a single *dihydrocodeine-N-oxidesulphonic acid*, $C_{18}H_{23}O_7NS$, prisms, decomp. 273—275°, which is reduced by sulphurous acid to dihydrocodeine-sulphonic acid.

The applicability of sulphoacetic acid for the sulphonation of derivatives of codeine has been tested further in the case of chlorodihydrocodide-*N*-oxide (cf. Freund and Melber, *loc. cit.*). It has been found possible to isolate a *chlorodihydrocodide-N-oxidesulphonic*



acid (annexed formula), feathery crystals, decomp. 290—295°, but the occurrence of an isomeride could not be observed. The acid is reduced by sulphurous acid to *chlorodihydrocodidesulphonic acid*, prisms, decomp. about 300°.

Dihydrocodeinesulphonic acid, after neutralisation by sodium hydroxide, is converted by an excess of methyl iodide into *dihydrocodeinesulphonic acid methylhydroxide*, $C_{19}H_{27}O_7NS$, rectangular plates, decomp. 280—285°; the latter is very stable towards water, but is decomposed by sodium hydroxide solution (4%) at 140° into tetramethylethylenediamine and a nitrogen-free substance which could not be isolated.

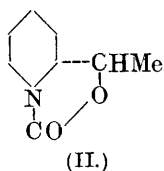
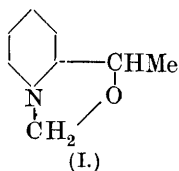
In view of the mutability of the codeine molecule, it is possible that the formation of isomeric sulphonic acids is due to preliminary isomerisation of the codeine itself. In this case, it must be possible to derive one of the sulphonic acids from an isomeric codeine. In this connexion, ψ -codeine has been transformed by hydrogen peroxide into ψ -codeine-*N*-oxides, prisms, m. p. 226—228° (*picrate*, needles, m. p. 166—168°), which is transformed by a mixture of acetic anhydride and sulphuric acid into ψ -codeine-*N*-oxidesulphonic acid, long, glassy prisms, decomp. about 300°, which is not identical with α -codeineoxidesulphonic acid, although resembling it in being soluble in water.

H. W.

1- α -*N*-Methylpiperidylethane-1-one. KURT HESS and WILHELM CORLEIS (*Ber.*, 1921, **54**, [B], 3010—3020).—The synthesis of 1- α -*N*-methylpiperidylethane-1-one is described, the method adopted being similar to that used in the preparation of the corresponding propane derivative, which the new substance resembles closely. Unexpectedly, its transformation into hygrine could not be realised on account of the failure to effect demethylation to the secondary amine.

α -Pyridyl methyl ketone is catalytically hydrogenated in the presence of platinum to a mixture of the diastereoisomeric forms of 1- α -piperidylethane-1-ol, b. p. 106—110°/18 mm., which is converted by formaldehyde and formic acid into a mixture of 1- α -*N*-methylpiperidylethane- α -ols, b. p. 94—105°/22 mm. The latter is oxidised by chromic acid in acetic acid solution to 1- α -*N*-methylpiperidylethane- α -one, $C_5NH_9Me \cdot COMe$, a mobile, hygroscopic liquid, b. p. 78—80°/14 mm., which decomposes somewhat rapidly when preserved. The *picrate*, short prisms, m. p. 119—120°, *semicarbazone*, m. p. 175—177°, *methiodide*, small plates, m. p. 144°, and a non-homogeneous *hydrazone*, b. p. 115—117°/15 mm. [*picrate* of latter, m. p. 189° (decomp.)], are described. The *hydrazone* is converted by a solution of sodium ethoxide in alcohol at 160—170° into 1- α -*N*-methylpiperidylethane (*picrate*, m. p. 170—171°). The ketone does not react with ethyl azidodicarboxylate. It reacts

with cyanogen bromide to form the expected methobromide (*aurechloride* of the corresponding *methochloride*, $C_9H_{18}ONCl, AuCl_3$, ochre-yellow crystals, m. p. 142°) and cyanamide derivative, but the hydrolysis of the latter leads to the production of a non-basic substance (which was not obtained in the pure state, but is probably an imidazolone derivative) in place of the desired secondary ketone.



The action of formaldehyde and hydrochloric acid on 1- α -piperidylethane-1-ol at $120-130^\circ$ leads to the production of the *oxazolidine* derivative (annexed formula I), b. p. $79-81^\circ/18$ mm. (*picrate*, slender needles, m. p. 163°), whereas the corresponding *oxazol- idone* (annexed formula II), b. p. $164^\circ/14$ mm., is obtained when the urethane of 1- α -piperidylethane- α -ol is distilled under diminished pressure.

H. W.

The Preparation of Pyridine and of certain of its Homologues in a State of Purity. JOSEPH GREENWOOD HEAP, WILLIAM JACOB JONES, and JOHN BAMBER SPEAKMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 1936—1940).—Pyridine, 2-methylpyridine, and 3-methylpyridine were separated from the crude coal tar bases from a light oil by repeated fractional distillation and subsequently purified through their additive compounds with zinc chloride. 2:6- and 2:4-Dimethylpyridines were similarly obtained from the crude bases of middle oil, but purified through their mercurichlorides. The following physical constants, using special precautions, were obtained: pyridine, b. p. 115.3° ; d_4^{25} 0.9776; 2-methylpyridine, b. p. $128-129^\circ$; d_4^{25} 0.9404; 3-methylpyridine, b. p. 143.8° ; d_4^{25} 0.9515; 2:6-dimethylpyridine, b. p. 137.5° ; d_4^{25} 0.9200; 2:4-dimethylpyridine, b. p. 157.1° ; d_4^{25} 0.9273.

W. G.

Some Physical Properties of Aqueous Solutions of certain Pyridine Bases. WILLIAM JACOB JONES and JOHN BAMBER SPEAKMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 1867—1870; compare preceding abstract).—The densities of aqueous solutions of pyridine, 2-methylpyridine, and 3-methylpyridine have been determined at 25° . In the case of pyridine, the density rises with increasing concentration of water, to a maximum (1.0032) at 50% water; in the other cases the density rises regularly with increasing concentration of water. The composition of the constant boiling mixture of each of the three bases is determined at various pressures, and it is shown that at ordinary pressures the constant boiling mixture with pyridine contains 42% of water, with 2-methylpyridine 48% of water, and with 3-methylpyridine 61% of water. The boiling points of the mixtures are respectively, 93.0° , 93.5° , and 96.2° . The miscibility of 2:4-dimethylpyridine with water has been investigated. It is shown that the minimum critical solution temperature is 22.5° ,

and the boiling point of the constant boiling mixture is 96.5° . The distillate condensed into two layers, but on cooling below 23.2° it became homogeneous and contained 66% of water.

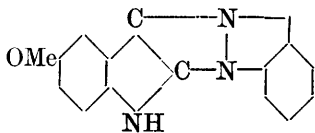
J. F. S.

5-Methoxydioxindole and 5-Methoxyisatin. J. HALBERKANN (*Ber.*, 1921, **54**, [B], 3079—3090; cf. this vol., i, 174).—The experiments described were undertaken in the hope of discovering a convenient method for the preparation of quinic acid in quantity; they were not completely successful.

Ethyl mesoxalate condenses with *p*-anisidine in hot glacial acetic acid solution to give *ethyl 3-hydroxy-5-methoxy-2-ketodihydroindole-3-carboxylate*, $\text{NH}\cdot\text{C}_6\text{H}_3\cdot\text{OMe}$
 $\text{CO}\cdot\text{C}(\text{OH})\cdot\text{CO}_2\text{Et}$, coarse, colourless needles or plates, m. p. $193\text{--}194^{\circ}$. The yield is 33—37% of that theoretically possible, and is not improved by the addition of anhydrous sodium acetate or of acetic anhydride. A *by-product*, brownish-yellow, rectangular platelets or needles, m. p. 256° , is also formed. The ester is not produced when its components are melted together. It is converted by acetic anhydride and sodium acetate into the corresponding *diacetyl* compound, colourless rhombohedra, m. p. $122\text{--}123^{\circ}$, and by a large excess of phenylhydrazine or hydroxylamine into 5-methoxyisatin-3-phenylhydrazone, m. p. $216\text{--}217^{\circ}$ (Bauer, A., 1909, i, 467, gives m. p. 219°), and 5-methoxyisatin-3-oxime, brownish-red, intertwined, prismatic needles, m. p. $234\text{--}235^{\circ}$. Hydrolysis of the ester with potassium hydroxide, and subsequent acidification with hydrochloric acid leads to the separation of 5-methoxydioxindole, long, colourless to pale brown, four-sided needles, m. p. $204\text{--}205^{\circ}$ [*diacetyl* compound, colourless, rhombohedric prisms, m. p. $225\text{--}226^{\circ}$ (decomp.).] When an ice-cold solution of the dioxindole in alkali is acidified with acetic acid, 2-amino-5-methoxymandelic acid, colourless plates or rhombohedra ($+1\text{H}_2\text{O}$) separates. It has m. p. $160\text{--}161^{\circ}$ (evolution of steam) when heated rapidly, after which it resolidifies and melts again at $203\text{--}204^{\circ}$ (m. p. of 5-methoxydioxindole). An aqueous suspension of the acid is coloured brown, green, bluish-violet, and ultimately dark red by ferric chloride; the action does not depend on complex salt formation, since a similar effect is produced by bromine water. A diazotised solution of the acid couples with an alkaline solution of β -naphthol to give a dark reddish-violet dye. The stability of the acid is remarkable, since *o*-aminomandelic acid appears to be incapable of existence.

5-Methoxydioxindole is only converted with difficulty by air or oxygen into 5-methoxyisatin; as a rule, the action only proceeds to the formation of the *methoxylated isatyde*, m. p. 246° (decomp.) after softening at 135° (? water of crystallisation). 5-Methoxyisatin, almost black, prismatic needles, is, however, readily produced from the dioxindole by the action of very dilute ferric chloride solution. When boiled with an alcoholic solution of aniline, 5-methoxyisatin yields the corresponding 3-anilide, lustrous, orange-red needles, m. p. 223° , which dissolves to a dark green solution in concentrated

sulphuric acid. The *acetyl* derivative of 5-methoxyisatin forms red, prismatic needles or coarse prisms, m. p. 144—145°. When the isatin is melted with *o*-phenylenediamine, it gives 10-methoxyindophenazine (annexed formula), m. p. 247°, which sublimes in long, orange-yellow needles when heated cautiously. H. W.



Bromo-2-methylquinolines. K. L. MOUDGILL (*J. Amer. Chem. Soc.*, 1921, **43**, 2257—2258).—6-Bromo-2-methylquinoline is prepared by the condensation of *p*-bromoaniline and paracetaldehyde in hydrochloric acid (cf. Bastow and MacCollum, *A.*, 1904, i, 686). It gives a *methiodide*, m. p. 237° (decomp.), and an *ethiodide*, m. p. 218°. *m*-Bromoaniline condenses with paracetaldehyde to give (?)*-bromo-2-methylquinoline*, m. p. 77°, giving an *ethiodide*, m. p. 217°; a *nitrate*, m. p. 102°; a *zincchloride*, m. p. 268°; a *stannichloride*; a *mercurichloride*, m. p. 245°; and a *picrate*, m. p. 207°. Whether the bromine atom is in position 5 or 7 has not been settled. W. G.

Constitution of Kynurenic Acid. ERNST SPÄTH (*Monatsh.*, 1921, **42**, 89—95).—Kynurenic acid, regarded by Camps (*A.*, 1901, i, 751) as 4-hydroxyquinoline-3-carboxylic acid, was shown by Homer (*A.*, 1914, i, 730) to have m. p. 289°, which is that of the 4-hydroxyquinoline-2-carboxylic acid obtained by Camps. Neither Camps nor Homer, however, compared derivatives of natural kynurenic acid with those of the synthetic hydroxyquinolinecarboxylic acid, and Ellinger and Matsuoka's work (*A.*, 1920, i, 696) on the conversion of tryptophan into kynurenic acid in the animal body appears to indicate the accuracy of Camps's constitution for the acid.

The author finds that kynurenic acid may be rapidly freed from protein compounds by conversion into its methyl ester, the hydrochloride of which is sparingly soluble in methyl alcohol. Treatment of the pure kynurenic acid with phosphorus pentachloride yields a 4-chloroquinolinecarboxylic acid and catalytic replacement of the chlorine by hydrogen in presence of palladium and barium sulphate yields quinoline-2-carboxylic acid, which was identified by means of its methyl ester and amide. Further, the methyl ester, the methyl ester of the methyl ether, and the benzoyl-methyl ester of synthetic 4-hydroxyquinoline-2-carboxylic acid agree in properties with the corresponding derivatives of natural kynurenic acid. The contradictory results of Camps and Homer appear to be due to the fact that the melting point of kynurenic acid varies from 255° to 289°, according to the rapidity of the heating.

Methyl kynurenate methyl ether (methyl 4-methoxyquinoline-2-carboxylate), $C_{12}H_{11}O_3N$, has m. p. 148—149°, and *methyl benzoyl-kynurenate*, $C_{18}H_{13}O_4N$, forms white crystals, m. p. 143°.

T. H. P.

*g**

Derivatives of Quinic Acid. J. HALBERKANN (*Ber.*, 1921, 54, [B], 3090—3107).—A record of the preparation of derivatives of quinic acid from 5-methoxyisatin (cf. Halberkann, this vol., i, 172).

5-Methoxyisatin condenses with pyruvic acid in alkaline solution to form 6-methoxyquinoline-2 : 4-dicarboxylic acid, almost colourless, prismatic rods or prisms, m. p. 239—240° (evolution of carbon dioxide). The lead, copper, silver, and ferric salts were prepared. When heated with concentrated hydrochloric acid under pressure, the acid is converted into 6-hydroxyquinoline-2 : 4-dicarboxylic acid, small needles or plates (+1H₂O), m. p. 318°, which couples with diazonium salts in the usual manner. [The ammonium hydrogen salt, needles (+1H₂O), has m. p. 318° (decomp.) after becoming discoloured at 285°.] 5-Methoxyquinoline-2 : 4-dicarboxylic acid loses carbon dioxide when heated slightly above its melting point and passes into 6-methoxyquinoline-4-carboxylic acid (quinic acid) which is identical with the substance derived from quinine. The direct production of quinic acid from 5-methoxyisatin and acetaldehyde is impossible, since the latter becomes resinified by the alkali, whilst, if acetoxime is used it is difficult to remove the methoxy-β-isatoxime formed simultaneously. Attempts to prepare the acid directly from *p*-anisidine (cf. Pictet and Mesner, A., 1912, i, 650) by replacing the pyruvic ester by the free acid and methylal by ethyl orthoformate, gave only small yields of the desired substance.

6-Methoxyquinoline-2 : 3 : 4-tricarboxylic acid, aggregates of needles (+1H₂O), m. p. 224—225° (decomp.) after previous darkening, is prepared by the condensation of 5-methoxyisatin and ethyl oxalacetate in concentrated alkaline solution. 5-Methoxyisatin and acetophenone in hot alcoholic alkaline solution give 6-methoxy-2-phenylquinoline-4-carboxylic acid, pale yellow needles (+1H₂O), m. p. 236°, which, however, is prepared more conveniently from *p*-anisidine, benzaldehyde, and pyruvic acid. When triturated with hydrochloric acid (*d* 1.125), the acid gives an intensely yellow hydrochloride which is decomposed readily by water. When heated with concentrated hydrochloric acid under pressure, the methoxy-acid is converted into 6-hydroxy-2-phenylquinoline-4-carboxylic acid, yellow needles, m. p. 330° (decomp.). The latter couples with diazotised sulphanilic acid, giving 5-*p*-sulphobenzenazo-6-hydroxy-2-phenylquinoline-4-carboxylic acid, a red, structureless powder which darkens above 200° and gradually becomes carbonised, without melting, at a higher temperature. The corresponding aniline salt, dark red prisms, behaves similarly when heated. The azo-dye is reduced by sodium hyposulphite to 5-amino-6-hydroxy-2-phenylquinoline-4-carboxylic acid, an unstable substance which passes readily into the corresponding quinone.

6-Methoxy-2-phenylquinoline-4-carboxylic acid is smoothly converted by the calculated quantity of potassium nitrate in the presence of concentrated sulphuric acid into 5-nitro-6-methoxy-2-phenylquinoline-4-carboxylic acid, long, pale-yellow, rectangular platelets, m. p. 262° (decomp.), when rapidly heated, after darkening

above 250°. It is reduced by ferrous hydroxide in alkaline solution to 5-amino-6-methoxy-2-phenylquinoline-4-carboxylic acid, rosettes of violet-red needles or platelets, m. p. 255—256° (decomp.). After being diazotised, it couples with β -naphthol in alkaline solution to yield 5-hydroxynaphthaleneazo-6-methoxy-2-phenylquinoline-4-carboxylic acid, almost black, granular aggregates which do not melt below 300°. When the amino-compound reacts in sodium carbonate solution with diazotised sulphanilic acid, it yields 8-p-sulphobenzenediazo-5-hydroxy-6-methoxy-2-phenylquinoline-4-carboxylic acid, a violet powder, m. p. 205° (decomp.) after softening at 190°. According to the author's unpublished observations, a similar replacement of the amino- by the hydroxy-group during coupling is shown by 5-aminohydroquinine.

Deoxybenzoin and 5-methoxyisatin give 6-methoxy-2 : 3-diphenylquinoline-4-carboxylic acid, colourless needles, m. p. 306° (decomp.). With acetone, 5-methoxyisatin yields 6-methoxy-2-methylquinoline-4-carboxylic acid, bluish-yellow needles, m. p. 286°, which is obtained more conveniently from *p*-anisidine, pyruvic acid, and acetaldehyde. It is converted by concentrated hydrochloric acid at 145° into 6-hydroxy-2-methylquinoline-4-carboxylic acid, slender needles, which begins to decompose above 300° with evolution of a brownish-yellow oil (? 6-hydroxy-2-methylquinoline), but is not completely melted at 340°. The methoxy-acid is converted by chloral into 6-methoxy-2- γ -trichloro- Δ^{α} -propenylquinoline-4-carboxylic acid, colourless, prismatic rods, m. p. 216° (decomp.) after darkening above 190°, which is transformed by alkali into 4-carboxy-6-methoxyquinoline-2- β -acrylic acid, $\text{OMe}\cdot\text{C}_6\text{H}_3\text{N} < \begin{smallmatrix} \text{C}(\text{CO}_2\text{H})\cdot\text{CH} \\ \text{N} \end{smallmatrix} \text{C}\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, pale yellow, slender needles, m. p. 249° (decomp.) after darkening at about 220°. The latter is oxidised by potassium permanganate to 6-methoxyquinoline-2 : 4-dicarboxylic acid.

6-Methoxy-2-(2')-furylquinoline-4-carboxylic acid, prepared from 2-acetylfuran and 5-methoxyisatin or from *p*-anisidine, furfuraldehyde, and pyruvic acid, crystallises in yellow needles, m. p. 241° (decomp.) after previous darkening.

1-Acetyl-5-methoxyisatin is quantitatively transformed (apart from the regenerated isatin) when heated with aqueous sodium hydroxide solution into 6-methoxy-2-keto-1 : 2-dihydroquinoline-4-carboxylic acid, dark yellow, prismatic rods, m. p. 326° (decomp.). When precipitated from its alkaline solution by mineral acids, it forms an almost colourless gel (? 2-hydroxy-6-methoxyquinoline-4-carboxylic acid), which subsequently passes into the yellow variety. The latter does not couple with diazotised sulphanilic acid in sodium carbonate solution. Boiling glacial acetic acid converts that portion of it which remains undissolved into intensely yellow, woolly needles, m. p. 326° (decomp.). The corresponding ethyl ester, small, orange-yellow needles, m. p. 231° after softening at 205°, can be obtained directly in small amount from *p*-anisidine and ethyl oxalacetate in glacial acetic, but not in alcoholic solution.

H. W.

*g** 2

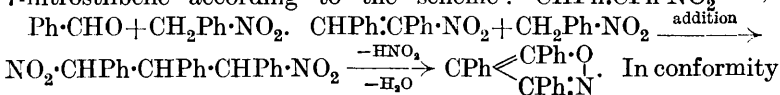
Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXIII. The Binary Systems of Carbazole or Acenaphthene with Polynitro-derivatives of Benzene and Toluene. ROBERT KREMANN and HUBERT STRZELBA (*Monatsh.*, 1921, **42**, 167—180; cf. this vol., i, 159).—The results obtained by Kremann and Slovák (A., 1920, i, 564) show that the ability of picric acid to combine with carbazole depends on its nitro-groups, the hydroxyls being inert.

The authors find that no compound is formed in the solid state by carbazole with any one of the three dinitrobenzenes or with 2:4-dinitrotoluene, simple eutectics being obtained in all cases. For *o*-, *m*-, and *p*-dinitrobenzenes and 2:4-dinitrotoluene, these eutectics correspond respectively with 107° and 15%; 72° and 13%; 143° and 34%, and 62° and 11% of carbazole. With *s*-trinitrobenzene (1 mol.), carbazole (1 mol.) forms a compound which melts homogeneously (m. p. 203°) with little dissociation and gives a eutectic with carbazole at 195° containing 44% of trinitrobenzene and a eutectic with trinitrobenzene at 120° containing about 97·5% of trinitrobenzene. With 2:4:6-trinitrotoluene, carbazole also forms a compound (1 mol. : 1 mol.) which, however, exhibits considerable dissociation in the fused condition, so that introduction of the electropositive methyl group appears to weaken the activity of the nitro-groups.

Towards nitro-derivatives of benzene, acenaphthene behaves similarly to naphthalene (Kremann and Haas, A., 1919, ii, 457). With 1:3:5-trinitrobenzene, acenaphthene forms a compound (1 mol. : 1 mol.), m. p. 161°, which with acenaphthene gives a eutectic corresponding with 87° and 8%, and with 1:3:5-trinitrobenzene a eutectic corresponding with 115° and 94% of the trinitrobenzene. With 2:4:6-trinitrotoluene, acenaphthene forms a compound (1 mol. : 1 mol.), m. p. 112° (compare Buguet, A., 1910, i, 105), which gives a eutectic with acenaphthene at 81° containing 18%, and a eutectic with trinitrotoluene at 72° containing 92% of trinitrotoluene. T. H. P.

Triarylisooxazoles. JAKOB MEISENHEIMER and KARL WEIBEZAHN (*Ber.*, 1921, **54**, [B], 3195—3206).—By the action of potassium hydroxide solution on β -nitro- α -methoxy- α - β -diphenylethane or on 7-nitrostilbene and as by-product of the condensation of phenylnitromethane with benzaldehyde according to the method of Knoevenagel and Walter (A., 1905, i, 65), Heim (A., 1911, i, 717) has isolated a substance which is regarded as 3:4:5-triphenylisooxazole, $\text{CPh} \begin{smallmatrix} \diagup \text{CPh} \cdot \text{O} \\ \diagdown \text{CPh} \cdot \text{N} \end{smallmatrix}$. The proof of the correctness of this formula is now given by the observation that the substance is oxidised by ozone to benzoylbenziloxime, $\text{CPh}(\text{:N} \cdot \text{OBz})\text{Bz}$; it is remarkable, however, that the benzoyl derivative of benzil β -oxime is produced in place of the expected α -compound (cf. Meisenheimer, this vol., i, 152). The constitution is confirmed further by synthesis of the compound from dibenzoylphenylmethane or tri-benzoylphenylmethane and hydroxylamine. Heim (*loc. cit.*) has

advanced the theory that 3 : 4 : 5-triphenylisooxazole is formed from 7-nitrostilbene according to the scheme: $\text{CHPh}:\text{CPh}\cdot\text{NO}_2 \longrightarrow$



In conformity with this conception, it is shown that the yields of 3 : 4 : 5-triphenylisooxazole are increased very considerably when an equivalent amount of phenylnitromethane is added to the α -nitrostilbene before it is heated with potassium hydroxide. Further, it is found that α -nitro-4'-methoxystilbene is convertible in good yield into 3 : 5-diphenyl-4-anisylisooxazole, which can only be explained if it is assumed that the nitromethoxystilbene suffers partial fission to anisaldehyde and phenylnitromethane followed by condensation of the latter with unchanged nitromethoxystilbene. Several other substituted isooxazoles have been synthesised in a similar manner. Reaction proceeds smoothly if all three substituents or the two in the 3 and 5 positions are similar. If, however, the two latter are dissimilar, two structural isomerides are generally produced simultaneously. In the latter case, a further complication ensues, owing to the fact that the nitrostilbene suffers fission to the aldehyde and arylnitromethane, the latter not being identical with the arylnitromethane employed. This also condenses with unchanged nitrostilbene, and a complex mixture thus results from which it is impossible to isolate the desired isooxazole.

* 3 : 4 : 5-Triphenylisooxazole, slender, colourless needles, m. p. 212—213°, is stable towards boiling alkaline permanganate and does not absorb bromine. It is converted by boiling nitric acid (*d* 1·4) into *tri-p-nitrotriphenylisooxazole*, m. p. 298—300°; the simultaneous production of *p*-nitrobenzoic acid shows that the nitro-groups have entered into the *p*-position in the isooxazole compound. α -Nitro-4'-methoxystilbene is converted by boiling sodium hydroxide solution (15%) into 3 : 5-diphenyl-4-anisylisooxazole, colourless, slender needles, m. p. 188—189°.

p-Methoxyphenylacetonitrile, b. p. 152°/16 mm., is obtained in almost quantitative yield by the action of methyl sulphate and sodium hydroxide on *p*-hydroxyphenylacetonitrile, and is converted by ethyl nitrate and potassium ethoxide according to the method of Wislicenus and Endres (A., 1903, i, 472) into the *potassium salt of p-anisylisonitroacetonitrile*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{C}(\text{NO}\cdot\text{OK})\cdot\text{CN}$ (the *sodium salt* was analysed), which is transformed by boiling sodium hydroxide solution into *p-anisylnitromethane*, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NO}_2$, b. p. 158—160°/11 mm. (the corresponding *enolic form*, m. p. 65—70°, is unstable). *p*-Anisylnitromethane condenses with benzaldehyde in the presence of a little methylamine to give α -nitro-4-methoxystilbene, $\text{CHPh}:\text{C}(\text{NO}_2)\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$, pale yellow crystals, m. p. 95°, and with anisaldehyde to yield α -nitro-4 : 4'-dimethoxystilbene, pale yellow crystals, m. p. 140—141°, b. p. 240—245°/16 mm. α -Nitro-4-methoxystilbene and *p*-anisylnitromethane yield 4-phenyl-3 : 5-di-*p*-anisylisooxazole, colourless needles, m. p. 170—172°. 3 : 4 : 5-Tri-*p*-anisylisooxazole, small, colourless needles,

m. p. 146—147°, is obtained from α -nitro-4 : 4'-dimethoxystilbene and *p*-anisylnitromethane. Phenylnitromethane and α -nitro-4 : 4'-dimethoxystilbene give 3(? 5)-*phenyl*-4 : 5(? 3 : 4)-*di-p-anisylisooxazole*, colourless needles, m. p. 156—157°. α -Nitrostilbene and α -nitro-4'-methoxystilbene yield with *p*-anisylnitromethane mixtures of isooxazoles from which only the most sparingly soluble components, namely, triphenylisooxazole and 3 : 5-diphenyl-4-*p*-anisylisooxazole, can be isolated in an approximately homogeneous condition.

An ethereal solution of the sodium compound of deoxybenzoin (prepared by means of sodamide) is converted by benzoyl chloride mainly into *tribenzoylphenylmethane*, colourless crystals, m. p. 152°. The course of the action is explained by the assumption of the initial formation of dibenzoylphenylmethane which, as a relatively strong acid, displaces the deoxybenzoin from its metallic derivative and forms the sodium compound of the diketone which reacts with a further portion of benzoyl chloride, giving tribenzoylphenylmethane. The latter is converted by hydroxylamine hydrochloride in glacial acetic acid solution in the presence of a little concentrated hydrochloric acid at 200° into 3 : 4 : 5-triphenylisooxazole. If the alcoholic solution of the triketone is treated with sodium ethoxide or sodium hydroxide solution at the atmospheric temperature, it passes into *dibenzoylphenylmethane*, lustrous, pale yellow needles, m. p. (indefinite), 148—151°, after previous softening; the latter can also be prepared, under certain conditions, from sodiodeoxybenzoin and benzoyl chloride. When boiled for a considerable time with a quantity of alcohol insufficient for solution, it is transformed into tribenzoylphenylmethane. It does not appear to be identical with the substance described by Japp and Lander (T., 1896, 69, 742).

H. W.

Preparation of Anthraquinone Derivatives [1 : 2-Anthraquinonylisooxazoles]. FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 147001; 160433).—By the action of fuming sulphuric acid on 1-nitro-2-alkyl-anthraquinones or their substitution derivatives, products insoluble in alkalis and of great reactive power are formed, which constitute valuable intermediates for the manufacture of anthraquinone dyes. The substances are produced by the elimination of 1 mol. of water from the nitro-alkylanthraquinone, and they are probably isooxazole derivatives of the constitution $C_6H_4 \begin{smallmatrix} <CO> \\ <CO> \end{smallmatrix} C_6H_2 \begin{smallmatrix} <N> \\ C-R \end{smallmatrix} O$; $\alpha\beta$ -*Anthraquinonyl-*

isooxazole, prepared by mixing 1 part of 1-nitro-2-methylantraquinone and 20 parts of sand into a paste with 60% fuming sulphuric acid and pouring on to ice, crystallises from xylene as a brownish-yellow powder, sparingly soluble in the usual organic solvents, and melting at 250° (decomp.). 7-Nitro- $\alpha\beta$ -*anthraquinonylisooxazole*, prepared by introducing 1 part of 1 : 5-dinitro-2-methylantraquinone into 15 parts of 40% fuming sulphuric acid with cooling, and pouring the mixture on to ice, crystallises from chlorobenzene as a greenish-yellow, crystalline powder, which decomposes without

previous melting. **3-Methyl- $\alpha\beta$ -anthraquinonylisooxazole**, prepared in a similar way, forms coarse, dark brown crystals, m. p. 210° . **5:6:7:8-Tetrachloro-2-methylantraquinone** prepared in the usual manner from *o*-benzoyltetrachloro-*p*-methylbenzoic acid, forms a pale greenish-yellow powder, m. p. 192° . On nitration, it yields **5:6:7:8-tetrachloro-1-nitro-2-methylantraquinone**, pale yellow crystals, m. p. 262° (decomp.). On treatment with fuming sulphuric acid at $5-10^{\circ}$, the nitro-compound is converted into **7:8:9:10-tetrachloro- $\alpha\beta$ -anthraquinonylisooxazole**, forming yellow, crystalline needles, m. p. 242° (decomp.).

According to the second patent (160433), the anthraquinonyl-isooxazoles are obtained in much greater purity if the reaction is conducted with exclusion of air, for example, in an atmosphere of carbon dioxide. G. F. M.

NN' -Di(*p*-allyloxyphenyl)acetamidine. J. SCHULER (U.S. Pat. 1384637). NN' -Di(*p*-allyloxyphenyl)acetamidine, colourless crystals, m. p. $85-86^{\circ}$, readily soluble in alcohol and ether and insoluble in water, forming a hydrochloride, m. p. $152-153^{\circ}$, which dissolves easily in alcohol, is less soluble in water, and insoluble in ether, is adapted for use as a local anæsthetic in ophthalmological practice. It is prepared by condensing allyloxylaniline with *p*-allyloxyacetanilide in the presence of phosphorus pentoxide or similar condensing agent. CHEMICAL ABSTRACTS.

Action of Iodine on NN' -Dialkyltetrahydro-4:4'-dipyridyls. BRUNO EMMERT and PAUL PARR (*Ber.*, 1921, **54**, [B], 3168—3176; cf. A., 1909, i, 602; 1917, i, 221; 1919, i, 455; 1920, i, 331).—The action of iodine on the blue solutions of dimethyl-, diethyl-, and dibenzyl-tetrahydrodipyridyls has been shown to lead to the production of the corresponding alkylpyridinium iodides and of amorphous, yellow substances containing iodine which have not been investigated more closely. The corresponding *diisobutyl* and *diisoamyl* compounds are now shown to react in a similar manner, but, in addition, to give small amounts of the 4:4'-dipyridyldialkyl iodides
$$\begin{array}{c} R > N < \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} > C \cdot C < \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} > N < R \\ I \end{array}$$
; the mode of removal of the two hydrogen atoms in position "4" has not been elucidated fully.

Diisoamyltetrahydrodipyridyl is converted by iodine in alcoholic solution into a yellow, amorphous product, *isoamylpyridinium iodide* (*platinichloride*, $C_{20}H_{32}N_2Cl_6Pt$, pale yellow, rhombic leaflets) and **4:4'-dipyridyl diisoamyl iodide**; the latter substance is obtained readily from its components. It crystallises in long, thin, red prisms, m. p. $270-280^{\circ}$ (decomp.). When the cold aqueous solution of the salt is agitated with silver oxide, it gives a colourless solution of the *base*, which becomes blue when warmed, but again colourless when cooled or treated with air. The corresponding *bromide*, green plates, colourless *chloride*, and *platini-chloride*, long, orange-yellow needles, m. p. $260-270^{\circ}$ (decomp.), are described.

4 : 4'-*Dipyridyl diisobutiodide*, red, rhombic leaflets, is prepared by the same methods as the *isoamyl* compound; the corresponding *platinichloride* has m. p. above 300° (decomp.).

The communication includes an exhaustive reply to the recent criticism of Weitz and Nelken (A., 1921, i, 804). H. W.

A Comparison of Three Isomeric Carbocyanines. WALTER THEODORE KARL BRAUNHOLTZ (T., 1922, 121, 169—173).

spiroPyrimidines. III. Condensation of cycloPropane-1 : 1-dicarboxylic Ester with Carbamides. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1921, 43, 2097—2101; cf. A., 1921, i, 360, 740).—The yield of ethyl *cyclopropane-1 : 1-dicarboxylate* from ethylene bromide and ethyl malonate by the action of sodium ethoxide (cf. Perkin, T., 1885, 47, 808; 1887, 51, 849) was increased by modifying the conditions. The ester has b. p. 214—216°/748 mm. (corr.), the *monoamide*, m. p. 195°, and the *diamide*, m. p. 198°.

The ester condensed with carbamide, guanidine, and thiocarbamide to give stable amorphous compounds, which were apparently not *spiropyrimidines*, but *polymerides*. Hydrolysis of the polymeride from carbamide, followed by elimination of carbon dioxide, gave a crystalline *acid*, $C_8H_{12}O_4$, m. p. 152°. The probable course of the condensation of the ester and carbamide is that *cyclopropane-1 : 5-spirobarbituric acid* is first formed and this undergoes rearrangement to *vinylbarbituric acid*, which then polymerises, giving a *cyclobutanedibarbituric acid*. The latter acid on hydrolysis and loss of carbon dioxide should yield *cyclobutane-1 : 2-* or *1 : 3-diacetic acid*, which could exist in *cis* and *trans* forms, but such acids are not yet known. W. G.

The Halogenated Indigotins. E. GRANDMOUGIN (*Compt. rend.*, 1921, 173, 1363—1365).—It is not possible to foretell with certainty the shade of colour of new indigotin derivatives. The marked influence of the positions 6 and 6' which prevent the tendency towards green of neighbouring groups, as shown in the case of octabromoindigotin (cf. this vol., i, 55), is further verified in the chloro-series, where octachloroindigotin is more violet than the 5 : 7 : 5' : 7'-tetrachloro-derivative. The absorption rays of certain di- and tetra-halogenated indigotins in solution in xylene or methyl benzoate are given. W. G.

Constitution of the Dipeptides of Aspartic Acid. C. RAVENNA (*Gazzetta*, 1921, 51, ii, 281—284).—Both the dipeptide of aspartic acid obtained by Fischer and Koenigs from diketopiperazinediacetic anhydride (A., 1907, i, 486) and that prepared by Ravenna and Bosinelli (A., 1920, i, 150, 151) from asparagine yield voluminous precipitates with lead acetate, but in the former case the precipitate is sparingly, and in the latter case readily, soluble in excess of the reagent. Further, the former dipeptide gives only a distinct blue coloration with copper sulphate and potassium hydroxide, whereas the latter gives the characteristic biuret reaction.

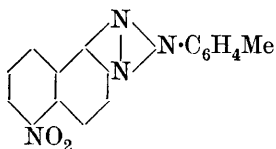
Diketopiperazinediacetic anhydride has been prepared from

each of the two dipeptides and from ammonium hydrogen malate; the three preparations yield the β -dipeptide, unmixed with α -isomeride, when treated with barium hydroxide solution. It is possible also that the α -dipeptide may be obtainable directly from α -asparagine by boiling its aqueous solution.

These results confirm the constitutions previously ascribed to the two dipeptides (A., 1920, i, 600). T. H. P.

6-Amino-2-*p*-tolyl- $\alpha\beta$ -naphthatriazole. GILBERT T. MORGAN and SYDNEY CHAZAN (*J. Soc. Chem. Ind.*, 1922, **41**, 1T).—The investigation was undertaken with the object of securing a series of substituted α -naphthylamines capable of acting as middle components in the production of poly-azo-dyes. The difficulty with which they react with diazonium compounds, however, renders the 6-amino-2-aryl- $\alpha\beta$ -naphthatriazoles unsuitable for this purpose. On the other hand, these aminotriazoles yield stable, sparingly soluble diazo-derivatives which couple readily to form azo-compounds with the phenols and the more reactive aromatic bases.

5-Nitro- β -naphthylamine, m. p. 140—142°, is prepared by the action of concentrated sulphuric acid below -5° on β -naphthylamine nitrate and is converted by a diazotised solution of *p*-toluidine into *p*-toluene-1-azo-5-nitro- β -naphthylamine, red, nodular crystals, m. p. 197—199° after softening at 190°. The latter substance is oxidised by chromic acid in acetic acid solution to 6-nitro-2-*p*-tolyl- $\alpha\beta$ -naphthatriazole (annexed formula), yellow, flaky crystals, m. p. 207—208°. 6-Amino-2-*p*-tolyl- $\alpha\beta$ -naphthatriazole has m. p. 178—180°; the corresponding *hydrochloride*, m. p. 263—267° (decomp.) after softening at 240°, and *acetyl* derivative, light brown needles, m. p. 305—307°, are described. A diazotised solution of the aminotriazole couples with β -naphthol in alkaline solution, giving *p*-tolyl- $\alpha\beta$ -naphthtriazoleazo- β -naphthol, m. p. (indefinite) 250—260°. With *p*-nitrobenzenediazonium chloride, the aminotriazole gives 7-*p*-nitrobenzenediazo-6-amino-2-*p*-tolyl- $\alpha\beta$ -naphthtriazole, a sparingly soluble, brownish-red compound, m. p. 195—197° (decomp.), which is oxidised by chromium trioxide in hot glacial acetic acid to a brown, *bistriazole* derivative, m. p. 220—240° (decomp.) after softening at 210°. H. W.



The Velocity of Reaction of Diazotisation in its Bearing on the Problem of Substitution in the Benzene Ring. II. The Character of the Diazonium Group. H. A. J. SCHOUTISSEN (*Rec. trav. chim.*, 1921, **40**, 763—774; cf. Martinsen, A., 1907, ii, 609).—As a result of failure in attempts to nitrate benzenediazonium sulphate, it is inferred that the diazonium group is very strongly negative, more so than the nitro-group, and its directing influence on entering groups is towards the meta-position. Para-substituted-amino-diazonium compounds have also been dealt with and similar results obtained, except in the case of the *p*-aminophenoldiazonium compound. The author puts forward an

alternative explanation to that of Cain (T., 1907, **91**, 1049) with regard to certain phenomena in diazo-compounds. H. J. E.

Method for the Separation of Amino-acids from the Products of Hydrolysis of Proteins and Other Sources. HAROLD W. BUSTON and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1921, **15**, 636—642).—A preliminary indication of a method whereby dicarboxylic amino-acids are precipitated by alcohol as barium salts, after saturating their aqueous solution with baryta. If then, without removing the alcohol, carbon dioxide is passed into the solution, other amino-acids are precipitated as barium carbamates (cf. Siegfried, A., 1906, i, 324). No individual amino-acid was isolated. G. B.

Estimation of the Monoamino-acids in the Hydrolytic Cleavage Products of Lactalbumin. D. BREESE JONES and CARL O. JOHNS (*J. Biol. Chem.*, 1921, **48**, 347—360).—The following results were obtained: Glycine 0.37%, alanine 2.41%, valine 3.30%, leucine 14.03%, proline 3.76%, phenylalanine 1.25%, aspartic acid 9.30%, glutamic acid 12.89%, hydroxyglutamic acid 10.00%, serine 1.76%, tyrosine 1.95%. E. S.

Swelling of Fibrin by Acids. R. SOMOGYI (*Biochem. Z.*, 1921, **120**, 103—105).—The swelling of fibrin by acids resembles the effect of acids on gelatin, the acids following the same order of activity. The biologically important acids, hydrochloric, lactic, and formic, produce pronounced swelling. H. K.

Alkaline Hydrolysis of Casein. MARY A. GRIGGS (*J. Ind. Eng. Chem.*, 1921, **13**, 1027—1028).—The maximum yield of amino-nitrogen (60% of the total nitrogen) is obtained when casein is heated at 150° under pressure for five hours with 10% sodium hydroxide solution. W. P. S.

The Influence of Electrolytes on the Solution and Precipitation of Casein and Gelatin. JACQUES LOEB and ROBERT F. LOEB (*J. Gen. Physiol.*, 1921, **4**, 187—211).—Two types of colloidal solution exist. The first type is easily precipitated by small quantities of neutral salts, the second requires much larger quantities. In the first type, the particles go into solution as the result of swelling in consequence of the Donnan equilibrium, and remain in solution as a result of the osmotic and electrical forces which the Donnan equilibrium necessitates. The second type is of the nature of true solution and there exist primarily only ions and molecules, although aggregates may be formed secondarily. Measurements of the rate of solution of casein chloride in varying concentrations of acids and neutral salts indicate that the process of solution is regulated by the Donnan equilibrium and that it is of the first type. Here the effect of small quantities of neutral salts as precipitants is to reduce the osmotic forces and also the electric charges, according to the theory of the Donnan equilibrium. Casein dissolves in sodium hydroxide solutions essentially like a crystalline substance, and the solution is of the second type. Solutions of gelatin are also of this type, although aggregates of

the dissolved particles tend to form on keeping (cf. A., 1921, i, 822). Experiments on the solubility and viscosity of gelatin solutions as influenced by neutral salts give evidence of the existence of these aggregates.

W. O. K.

Swelling of Gelatin in Aqueous Solutions of Organic Acids.

ALFRED KUHN (*Koll. Chem. Beihefte*, 1921, **14**, 147—208).—The swelling of gelatin in aqueous solutions of various concentrations of a large number of organic acids has been determined by the so-called volume method at 20°, and from the results the increase in the swelling is ascertained in each case. A few experiments are described at 0°, 16°, and 22°, which were made to ascertain the influence of temperature on the swelling. The following acids were investigated: Formic, acetic, propionic, *n*-butyric, *isobutyric*, *n*-valeric, *isovaleric*, *isooctic*, glycolic, lactic, chloroacetic, dichloroacetic, trichloroacetic, bromoacetic, cyanoacetic, oxalic, malonic, succinic, malic, *d*-tartaric, citric, maleic, fumaric, aminoacetic, benzoic, *m*-toluic, phenylacetic, salicylic, *m*-hydroxybenzoic, mandelic, benzenesulphonic, sulphanilic, cinnamic, phthalic, protocatechuic, gallic, tannic, and picric, also hydrochloric, sulphuric, and nitric acids, phenol, quinol, resorcinol, catechol, and naphthalene-1-sulphonic acid. It is shown that, with the exception of the sparingly soluble acids, all acids show a swelling maximum at a medium concentration. Swelling is the result of four simultaneous processes of which at least two operate in opposite directions. The first process is the actual swelling, *A* (hydration) and is the chief process at low concentrations; opposed to this are sol formation and hydrolysis, *B*; the fourth process is dehydration and coagulation. The swelling maximum is defined as that point at which the amount of swelling (*A*) with increasing concentration is exceeded by the sol formation (peptisation) and the decreasing hydrolysis (*B*). No relationship between the maximum swelling and the degree of dissociation of the acids could be found, but an approximate connexion between the concentrations at which the maximum occurs and the strength of the acid was found. With strong acids, the maximum swelling concentrations lie at lower concentrations and with weaker acids at higher concentrations, whilst with acids of medium strength the curve only shows a bend. The swelling maximum as the resultant of the hydration, sol formation, and hydrolysis shows no linear relationship, rather, especially in the case of acids of medium strength, does the sol formation appear to play the greater rôle. The actual swelling in the region of small concentrations is well represented by the equation $h=qC^n$, in which *h* is the swelling height, *C* the concentration of the acid, and *q* and *n* are constants. The principal part of the swelling can be quantitatively represented by the constants *q* and *n*. Neither *q* nor *n* has any connexion with the strength of the acid, and, further, the swelling maximum is not determined by either *q* or *n*. Hence it is shown that acids operate in the swelling of gelatin in the sense that at lower concentrations a specific increase in the power of binding water is

brought about. Whether thereby a chemical or adsorption compound is formed has not been settled. At higher concentrations, sol formation and hydrolysis commence and at the same time dehydration and precipitation, which are opposed to the actual swelling process.

J. F. S.

A New Function of the Tryptic Ferment (Anhydrase) and the Preparation of *d*-Tyrosine-anhydride and *d*-Tryptophan-anhydride from the Products of Tryptic Digestion. SIGMUND FRÄNKEL and EMIL FELDSBERG (*Biochem. Z.*, 1921, **120**, 218—229).—Casein, when digested with trypsin until the bromine test for tryptophan is negative, yields a dextrorotatory tyrosine-anhydride and a dextrorotatory tryptophan-anhydride. The amino-groups are free, but the carboxyl groups are combined as in acetic anhydride. *d*-Tyrosine-anhydride has m. p. 273° and $[\alpha]_D + 37.59^\circ$ in alkaline solution, $[\alpha]_D + 93.87^\circ$ in acid solution. *d*-Tryptophan-anhydride decomposes at 230—245° and has $[\alpha]_D + 20.59^\circ$ in water.

H. K.

The Activity of Adsorbed Invertase. J. M. NELSON and DAVID I. HITCHCOCK (*J. Amer. Chem. Soc.*, 1921, **43**, 1956—1961).—The result obtained by Nelson and Griffin that a given quantity of invertase exhibited the same activity when adsorbed on a solid in the bottom of the reaction vessel as when uniformly distributed throughout the solution (cf. A., 1916, i, 516) is not general, but represents only a special case. It is now shown that, other conditions being equal and the velocity of hydrolysis relatively large, the amount of sucrose hydrolysed in a given time is less in the presence of an adsorbent. The decrease in rate is apparently due largely to the uneven distribution of the invertase in the reaction mixture, and the extent of the retardation may be considerably diminished by stirring the mixture and thus preventing the settling of the adsorbent. Results comparable with those of Nelson and Griffin (*loc. cit.*), are obtained only when the velocity of hydrolysis is relatively small, and it is suggested that, under these conditions, the rate of diffusion of the sucrose to, and of the invert-sugar from, the enzyme combined with the adsorbent is probably greater than the rate of hydrolysis of the sucrose.

W. G.

The Distinctive Properties of Amylases from Different Sources. JEAN EFFRONT (*Compt. rend.*, 1922, **174**, 18—21).—Amylases from different sources may be distinguished from one another by the ratio of their liquefying power to their saccharifying power, by the intensity of their saccharifying power, by their optimum temperatures, by their resistance to temperatures of 70—100°, and by their action at 20°. Some amylases in juices or extracts when heated at 60° and filtered recover after filtration their activity lost during heating, whilst other amylases lose their activity altogether.

W. G.

A Study of the Catalase of Flour. T. MERL and J. DAIMER (*Z. Unters. Nahr. Genussm.*, 1921, **42**, 273—290).—A catalase was prepared from the wheat embryo having five times the activity

of ordinary flour. The optimum hydrogen-ion concentration for the catalase corresponds with $p_H=6.2-7.1$; and the optimum temperature is $30-40^\circ$ with a temperature coefficient of approximately 1.5. The catalase is relatively resistant to dry heat, but extremely sensitive to moist heat. It is less affected by toluene than by alcohol, benzene, or hydrocyanic acid. [Cf. *J. Soc. Chem. Ind.*, 1922, 114 A.] A. G. P.

Decomposition of Amygdalin from the Point of View of Conjugated Fermentation. J. GIAJA (*J. Chim. Physique*, 1921, 19, 77—99).—The decomposition of amygdalin by emulsin from *Helix pomatia* and by emulsin from almonds at $37-40^\circ$ takes place in two stages with intermediate products which are different in the two cases. The fermentation decomposition of amygdalin is not a simple process; the decomposition is a conjugated or coupled fermentation made up at least of two reactions, a primary and a secondary fermentation. The decomposition of amygdalin by the above-named emulsins is probably an unique case in which it is possible to follow exactly the progress of both the primary and secondary fermentations. The two actions constituting the couple are within certain limits independent of one another, for it is shown that changes in the concentration of amygdalin, ferment, dextrose, hydrocyanic acid, and benzaldehyde, as well as ultra-violet light affect the two reactions differently. The ratio in which the dextrose and hydrocyanic acid appear in the course of the reaction with emulsin from *Helix pomatia* varies with the speed of the reaction, that is to say, with the concentration of the ferment. The more rapid the reaction the more nearly does the ratio approach that in which the dextrose and hydrocyanic acid exist in amygdalin. The influence of the initial concentration of amygdalin on the secondary reaction with both ferments is that the secondary reaction proceeds more rapidly when the initial concentration is small. The influence of an addition of dextrose is different in the case of the two ferments, but in both cases it only affects the reaction which produces dextrose. The addition of benzaldehyde and hydrocyanic acid retards the reaction in which these substances respectively are produced. Thus whilst dextrose and hydrocyanic acid affect the fermentation reaction itself, benzaldehyde acts on the ferment and destroys it. Ultra-violet rays affect the reaction with emulsin from *Helix pomatia* in the sense that the formation of dextrose is more rapid than that of hydrocyanic acid. If the reaction with emulsin from *Helix pomatia* is stopped before completion by heating, and emulsin from almonds is added, it is found that the reaction does not go so far as either ferment alone would have taken it. Thus emulsin from almonds cannot complete the reaction started by emulsin from *Helix pomatia*, but emulsin from *Helix pomatia* can complete the reaction started by emulsin from almonds. J. F. S.

Urease. STURE LÖVGREN (*Biochem. Z.*, 1921, 119, 215—293).—This paper contains a valuable bibliography of 212 papers, and is illustrated throughout with quotations from original papers.

The author has carried out experiments covering a wide range of properties of urease, but the main portion deals with an attempt to find the time equation which covers the reaction adequately. Van Slyke and Cullen's equation was found not to hold, but a simple, apparently empirical, modification of the unimolecular equation gave excellent results provided that at each concentration of urea the solution was kept at the particular optimum P_H .

H. K.

Additive Reactions of Phosphorus Haloids. IV. The Action of the Trichloride on Saturated Aldehydes and Ketones.

J. B. CONANT, A. D. MACDONALD, and A. MCB. KINNEY (*J. Amer. Chem. Soc.*, 1921, **43**, 1928—1935).—It has previously been shown that benzaldehyde reacts with phosphorus trichloride in acetic acid to give good yields of an α -hydroxyphosphinic acid (cf. A., 1921, i, 69). It is now shown that the reaction can be extended to other aldehydes and ketones, although with ketones it is of somewhat limited scope and in certain cases it was found desirable to replace the acetic acid by benzoic acid as the medium and work at 150° instead of below 30°.

The hydroxyphosphinic acids were difficult to isolate in the crystalline state and in some cases could only be obtained as their lead salts. With acetophenone and acetone, an unsaturated phosphinic acid was also, in each case, produced, but only isolated from acetophenone. The following new compounds are described: α -Phenylvinylphosphinic acid, $\text{CH}_2\text{:CPh}\cdot\text{PO}_3\text{H}_2$, m. p. 112°; α -hydroxy- α -methylpropylphosphinic acid isolated as its lead salt; α -hydroxy- α -ethylbutylphosphinic acid as its lead salt; α -hydroxy- $\alpha\beta\beta$ -trimethylpropylphosphinic acid as its lead salt; α -hydroxy- β -phenyl- α -benzylethylphosphinic acid, m. p. 181—182°; α -hydroxy- $\alpha\gamma$ -diphenylpropylphosphinic acid, m. p. 165—168°; α -hydroxy- γ -phenyl- α -(β -phenylethyl)propylphosphinic acid, m. p. 173—174°; α -hydroxydiphenylmethylphosphinic acid, m. p. 171—172°. Additive products could not be obtained with benzil or anthraquinone.

W. G.

The Relation between the Mode of Synthesis and Toxicity of Arsphenamine [Salvarsan] and Related Compounds.

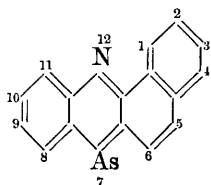
WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1921, **43**, 2202—2210).—The variation in toxicity of different samples of salvarsan prepared by reduction of 3-nitro-4-hydroxyphenylarsinic acid by hyposulphite is due to variations in the experimental conditions during the reduction of the nitro-group. To obtain a sample of low toxicity a cold solution of the nitro-compound should be added to a cold solution of magnesium chloride and sodium hyposulphite with vigorous stirring. The mixture is then rapidly heated at 40° after the addition of vegetable charcoal and filtered, the filtrate being rapidly heated at 55°. If the solutions are mixed warm with slow stirring and the mixture only slowly raised to 55° a salvarsan of high toxicity is obtained. For the consistent production of salvarsan of the lowest toxicity it is advisable to use pure 3-amino-4-hydroxyphenylarsinic acid as the starting material, in

which case there is no need to adhere strictly to the conditions at the beginning. This variation in toxicity is apparently general to the aminoarylsenso-compounds. It has been found with 3-amino-4 : 4'-dihydroxyarsenobenzene hydrochloride, 3 : 5 : 3'-tri-amino-4 : 4'-dihydroxyarsenobenzene trihydrochloride, and 3 : 5 : 3' : 5'-tetra-amino-4 : 4'-dihydroxyarsenobenzene tetrahydrochloride. The variation in toxicity is due to the formation of by-products, during the reduction of the nitro-group, which unite with the amino-acid in the subsequent reduction of the arsinic acid group, giving unsymmetrical arseno-compounds. W. G.

Arsenated Benzophenone and its Derivatives. W. LEE LEWIS and H. C. CHEETHAM (*J. Amer. Chem. Soc.*, 1921, **43**, 2117—2121).—Dichloro-*p*-arsinobenzoyl chloride condenses quite readily with aromatic hydrocarbons and phenyl ethers in the presence of anhydrous aluminium chloride, using carbon disulphide as a solvent. Thus with benzene, after warming the product with aqueous sodium hydroxide, *benzophenone-p*-arsenious oxide, $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}$, was obtained, which on boiling with water gave *benzophenone-p*-arsenious acid, $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{As}(\text{OH})_2$, and on oxidation with hydrogen peroxide yielded *benzophenone-p*-arsinic acid, $\text{COPh}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$, giving an *oxime*. On nitration, the arsinic acid gave *nitrobenzophenone-p*-arsinic acid, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{AsO}_3\text{H}_2$. Other compounds, similarly prepared, are 4-methylbenzophenone-4'-arsenious oxide; 4-methylbenzophenone-4'-arsinic acid; 4-methoxybenzophenone-4'-arsinic acid; 4-ethoxybenzophenone-4'-arsinic acid, and 4-phenoxybenzophenone-4'-arsinic acid. *p*-Carboxyphenylarsinic acid is best obtained for these preparations from *p*-aminobenzoic acid by Bart's method (Ger. Pat. 250264 and 254345) and subsequently converted into dichloro-*p*-arsinobenzoyl chloride by Poulenc's method (French Pat. 441215). W. G.

4-Carboxy-2-phenylquinoline-6-arsinic acid. J. R. JOHNSON and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1921, **43**, 2255—2257).—When pyruvic acid is added to a boiling solution of arsanilic acid and benzaldehyde in absolute alcohol and the mixture boiled for four hours 4-carboxy-2-phenylquinoline-6-arsinic acid, m. p. 186—187° (corr.) (decomp.), is obtained. It gives a neutral *disodium* and a slightly alkaline *trisodium* salt, a green *copper* salt, yellow *silver*, *lead*, *mercurous*, *mercuric*, and *cadmium* salts, and reddish-brown *cobalt* and *ferric* salts. W. G.

7-Chloro-7 : 12-dihydro- γ -benzophenarsazine and some of its Derivatives. W. LEE LEWIS and C. S. HAMILTON (*J. Amer. Chem. Soc.*, 1921, **43**, 2218—2223).—The annexed constitution is considered as probably that of γ -benzophenarsazine.



Phenyl- α -naphthylamine readily reacts with arsenic trichloride to give 7-chloro-7 : 12-dihydro- γ -benzophenarsazine, m. p. 219°, which is physiologically much less irritant than the corresponding diphenylchloroarsine. It readily reacts with sodium alkyl oxides or aryloxides

to give stable alkyloxy- or aryloxy-derivatives of the type $\text{NH} \langle \text{C}_{10}\text{H}_6 \rangle \text{As} \cdot \text{OR}$. The following are described: 7-Methoxy-7:12-dihydro- γ -benzophenarsazine, m. p. 209° ; 7-ethoxy-7:12-dihydro- γ -benzophenarsazine, m. p. 165° ; 7-n-propoxy-7:12-dihydro- γ -benzophenarsazine, m. p. 152° ; 7-n-butoxy-7:12-dihydro- γ -benzophenarsazine; 7-phenoxy-7:12-dihydro- γ -benzophenarsazine, m. p. 179° ; 7-benzyloxy-7:12-dihydro- γ -benzophenarsazine, m. p. 154° . When oxidised in acetic acid solution by hydrogen peroxide, 7-chloro-7:12-dihydro- γ -benzophenarsazine gives γ -benzophenarsazinic acid, $\text{NH} \langle \text{C}_{10}\text{H}_6 \rangle \text{As}(\text{OH})_3$, giving a sodium salt. Freshly precipitated silver oxide reacts in ammoniacal solution with 7-chloro-7:12-dihydro- γ -benzophenarsazine to give 7:12-dihydro- γ -benzophenarsazine oxide, $(\text{NH} \langle \text{C}_{10}\text{H}_6 \rangle \text{As})_2\text{O}$. The corresponding sulphide, 7:12-dihydro- γ -benzophenarsazine sulphide, m. p. $204\text{--}205^\circ$, was obtained by bubbling hydrogen sulphide through an alcoholic solution of the chloro-compound. When boiled with an excess of hydrobromic acid 7-phenoxy-7:12-dihydro- γ -benzophenarsazine gave 7-bromo-7:12-dihydro- γ -benzophenarsazine, m. p. 227° . 7-Iodo-7:12-dihydro- γ -benzophenarsazine, m. p. 205° , was similarly prepared. Diphenylhydrazine when warmed with arsenic trichloride gives 6-chlorophenarsazine.

W. G.

Organo-derivatives of Bismuth. V. The Stability of Halogen, Cyano-, and Thiocyano-derivatives of Tertiary Aromatic Bismuthines. FREDERICK CHALLENGER and JOHN FREDERICK WILKINSON (T., 1922, 121, 91—104).

Organo-derivatives of Bismuth. VI. The Preparation and Properties of Tertiary Aromatic Bismuthines and their Interaction with Organic and Inorganic Halogen Compounds. FREDERICK CHALLENGER and LESLIE RANDAL RIDGWAY (T., 1922, 121, 104—120).

Aromatic Mercuri-organic Derivatives. The Hofmann Rearrangement and the Nature of Valencies of Mercury in Mercuri-organic Derivatives. MORRIS S. KHARASCH (*J. Amer. Chem. Soc.*, 1921, 43, 1888—1894).—Mercury diphenyl reacts with various acyl halogen amides in dry benzene, giving phenyl mercury haloid and the alkylcarbimide, the mercury diphenyl thus playing the same part as sodium hydroxide in aqueous solution or sodium ethoxide in absolute alcohol, and the amide undergoes the Hofmann rearrangement. Thus with *N*-bromoacetamide, the products are mercury phenyl bromide and methylcarbimide, similar changes occurring with *N*-bromobenzamide and with *m*-nitro-*N*-bromobenzamide. On the other hand, *N*-substituted alkyl or aryl bromo- and chloro-acetamides do not react with mercury diphenyl any more than they undergo rearrangement with sodium hydroxide or ethoxide. The mercury diphenyl thus acts as a base in benzene solution, being a base of the benzene system in the same way as sodamide is of the ammonium system.

The author does not consider that the electronic structure for mercury diaryl compounds proposed by Jones and Werner (A., 1918, i, 483) has any sound theoretical or experimental basis, and proposes as an alternative structure, $\bar{R}-\overset{+}{\text{Hg}}-\bar{R}$. The formation of metallic mercury and benzyl acetate when mercury diphenyl is hydrolysed by glacial acetic acid at 200° (Jones and Werner, *loc. cit.*) is due to intramolecular oxidation and reduction. W. G.

Mercuri-organic Derivatives. The Mercurisation of Aromatic Amines and its Relation to the Theory of Substitution. MORRIS S. KHARASCH and ISADORE M. JACOBSON (J. Amer. Chem. Soc., 1921, 43, 1894—1903).—Schoeller, Schrauth, and Liese (cf. A., 1920, i, 120), in their theory of mercurisation, assume that the entrance of a group into the nucleus of an aromatic amine is always preceded by substitution on the amino-nitrogen. This theory does not explain, however, the mechanism of substitution in the case of tertiary amines, such as dimethylaniline, which contain no replaceable hydrogen. The authors propound the theory that of the aromatic amines only those which are capable of forming salts will mercurise and that mercurisation is always preceded by addition of a mercuric salt to the amino-nitrogen, with subsequent rearrangement of the mercury to the ortho- or para-position. This theory also applies equally well, without further postulates, to the introduction of other groups into the benzene nucleus in the case of aromatic amines. Where such salt formation is not possible, as in the quaternary ammonium salts, substitution must take place in the meta-position or, as in such special cases as that of mercurisation, it is not accomplished at all.

Thus *p*-nitrodimethylaniline, which is an extremely weak base and does not form salts, would not mercurise, whereas *p*-nitromethylaniline mercurised without difficulty. In further support of the theory, unpublished work is mentioned in which the intermediate additive compound from *m*-nitroaniline and mercuric acetate was isolated.

The following compounds are described. *o*-Nitro-*p*-acetoxymercuridimethylaniline, m. p. 160°; *o*-nitro-*p*-chloromercuridimethylaniline, m. p. 185° (decomp.); *m*-nitro-*p*-acetoxymercuridimethylaniline, m. p. 140°; *m*-nitro-*p*-chloromercurimethylaniline, m. p. 220° (decomp.); *p*-nitro-*o*-acetoxymercurimethylaniline, m. p. 197° (decomp.); *p*-nitro-*o*-chloromercurimethylaniline, m. p. 215° (decomp.); *p*-nitro-*o*-acetoxymercuriethylaniline, m. p. 183°; *p*-nitro-*o*-chloromercuriethylaniline, m. p. 218° (decomp.).

For purposes of characterisation, 2-bromo-4-nitroethylaniline, m. p. 65—66°; and 2 : 6-dibromo-4-nitroethylaniline, m. p. 75—76°, were prepared by brominating *p*-nitroethylaniline in acetic acid solution, using the requisite proportions of bromine. W. G.

An Indirect Method of Preparation of Organic Mercuric Derivatives and a Method of Linking Carbon to Carbon. MORRIS S. KHARASCH (J. Amer. Chem. Soc., 1921, 43, 2238—2243).—When mercuric salts of certain carboxylic acids are heated, carbon

dioxide is split off and the mercury takes the place originally occupied by the carboxyl group. Thus *mercuric 2:4-dinitrophenylacetate* when heated at 180° gives *mercury 2:4:2':4'-tetranitrodibenzyl*, $\text{C}_6\text{H}_3(\text{NO}_2)_2 \cdot \text{CH}_2 \cdot \text{Hg} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_3(\text{NO}_2)_2$, m. p. 235° ; and *mercuric 2:4:6-trinitrobenzoate* gives *mercury 2:4:6:2':4':6'-hexanitrodiphenyl*, m. p. 272° . The latter compound when heated in alcohol with mercuric chloride gives *2:4:6-trinitrophenyl mercurichloride*, $\text{C}_6\text{H}_2(\text{NO}_2)_3 \cdot \text{HgCl}$, m. p. 202° , which, when treated in aqueous suspension with iodine in potassium iodide solution gives *2:4:6-trinitroiodobenzene* and a compound which is probably *2:4:6:2':4':6'-hexanitrodiphenyl*. It is thought that by heating these mercury compounds in the dry state or in some solvent the mercury would oxidise one of the carbon atoms and thereby link the two carbon atoms together. This was observed in the case of *2:4:2':4'-tetranitromercurydibenzyl*, tetranitrodibenzyl being obtained.

This work is being extended to mercury salts of various types of carboxylic acids.

W. G.

Physiological Chemistry.

The Excretion of Acetone from the Lungs. A. P. BRIGGS and PHILIP A. SHAFFER (*J. Biol. Chem.*, 1921, **48**, 413—428).—Experiments on human diabetics, normal fasting subjects, and dogs after injection of large doses of acetone, show (1) that acetone is distributed between blood and alveolar air in approximately the same ratio as between water and air, (2) that the concentration of acetone in urine is approximately the same as in blood. These results confirm Widmark's conclusion (*Biochem. J.*, 1920, **14**, 379) that acetone is excreted from the lungs and kidneys by the physical process of diffusion. E. S.

Physical Chemistry of Cell Respiration. OTTO WARBURG (*Biochem. Z.*, 1921, **119**, 134—166).—The adsorption and oxidation of cystine by blood charcoal was investigated in the presence of various narcotics. There is an inhibition of both properties due to a displacement of the amino-acid and of oxygen from the charcoal surface by the narcotic. Hydrocyanic acid also inhibits adsorption and oxidation, but the same explanation does not hold good. A comparison was made of blood charcoal and charcoal prepared from benzoic acid. In composition and qualities of adsorption they differ markedly. From analogy with the charcoal experiments, cell respiration is considered to be essentially associated with the solid constituents of the cells. H. K.

Blood-gas Analysis. IX. Narcosis and Charge on the Colloids. KLOTHILDE MEIER and W. KRÖNIG (*Biochem. Z.*, 1921, **119**, 1—15).—By following the curve of combination of carbon dioxide with corpuscles as used in previous papers (A., 1920, i, 200), the authors show that addition of narcotics favours the neutralisation of the charge on the surface colloids of the erythrocytes. Corpuscles suspended in saline solution are discharged at P_H 6.67, but at the optimum concentration in the saline of methylurethane, ethylurethane, and ethyl alcohol the discharge takes place at P_H 6.95, 6.90, and 6.85 respectively. H. K.

The Dextrose Concentration in the Arterial Blood and in the Venous Blood from the Muscles. V. HENRIQUES and R. EGE (*Biochem. Z.*, 1921, **119**, 121—133).—No great difference of dextrose content between arterial and venous blood is to be expected. The process is complicated by a reservoir of carbohydrate in the muscles. Under special conditions, a difference can be observed. In a condition of hyperglycæmia, there is a large disappearance of dextrose during passage through the muscles, and when the dextrose concentration in the blood has again fallen the venous blood may contain more than the arterial. H. K.

The Ammonia Content of the Blood and its Bearing on the Mechanism of Acid Neutralisation in the Animal Organism. THOMAS P. NASH, jun., and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1921, **48**, 463—488).—The work of previous investigators on the ammonia content of the blood is discussed, and an improved technique for its estimation is described. The ammonia is removed from the blood by aeration, collected in acidified water, and estimated by means of Nessler's reagent.

By means of this method, the authors find concentrations of ammonia nitrogen varying from 0.03 to 0.20 mg. per 100 c.c. The concentration of ammonia in the blood is unaffected by the administration of phloridzin, the removal of the kidneys, and the injection of acid or alkali; the concentration in the renal venous blood is about twice as great as that in the systemic arterial blood.

From these results, the authors conclude that the kidney is the seat of formation of ammonia, and on this basis they offer an explanation of the different types of acidosis met with in various clinical conditions. C. R. H.

Inorganic Blood Phosphate. EDWIN P. LEHMAN (*J. Biol. Chem.*, 1921, **48**, 293—303).—A number of estimations of inorganic phosphate in the whole blood of normal rabbits by the method of Bell and Doisy (A., 1920, ii, 769) show that this constituent is practically constant and amounts to between 4 and 6 mg. per 100 c.c. When the concentration of phosphate is increased by the injection of large amounts of di-sodium hydrogen phosphate (sufficient in some cases to cause tetany) a normal concentration is reached again in four hours. C. R. H.

The Blood Calcium Content in Normal Children and in Tetany. I. B. DE VRIES ROBLES (*Nederl. Tijdschr. Geneesk.*, 1919, **63**, [i], 1663).—Despite statements to the contrary, there appears to be no abnormality in the content of calcium of the blood of children with tetany. CHEMICAL ABSTRACTS.

The Blood-sugar in Narcosis and Diseases of the Nervous System. H. CHANTRAINE (*Zentr. inn. Med.*, 1920, **41**, 521—529).—During ether narcosis, the blood-sugar is increased, the increase ranging from 30 to 50%. During narcosis with ethyl chloride, in patients with nervous diseases, and in rabbits with experimentally produced concussion of the brain, the proportion of blood-sugar remains normal. CHEMICAL ABSTRACTS.

Acetone Substances in the Blood in Diabetes. R. FITZ (*Trans. Assoc. Amer. Physicians*, 1917, **32**, 154—158).—Simultaneous estimation of the total acetone substances in the blood plasma and the degree of acidosis revealed no quantitative relationship between increased concentration of acetone and lowering of blood bicarbonate, although in general the proportion of the acetone rose as that of the bicarbonate fell. The total acetone was increased by large amounts of fat, the maximum occurring several hours after ingestion and after visible lipæmia had disappeared. Small amounts of fat depressed blood acetone. Fasting and pure carbohydrate diet diminished a high acetone value. Sodium hydrogen carbonate increased the output of acetone, but its effect on blood acetone was uncertain. In three fatal cases of coma, a rapid pre-mortal rise of blood acetone occurred; in one case this was independent of acidosis. CHEMICAL ABSTRACTS.

Effect of Subcutaneous Injections of Solutions of Potassium Cyanide on the Catalase Content of the Blood. WILLIAM H. WELKER and J. L. BOLLMAN (*J. Biol. Chem.*, 1921, **48**, 445—451).—The subcutaneous injection in dogs of lethal doses of potassium cyanide has little, if any, effect on the catalase content of the blood. E. S.

A Direct Demonstration of the Impermeability of the Corpuscles of Man and of the Rabbit for Dextrose. S. VAN CREVELD and R. BRINKMAN (*Biochem. Z.*, 1921, **119**, 65—72).—Corpuscles obtained by the jugular method from rabbits or by the paraffined tube method from man, are always free from dextrose. Faulty technique is the basis of the discrepant results of other workers. H. K.

Colloidal Structure of Red Blood Corpuscles and Hæmolysis. III. Ultramicroscopic Investigation of Lipoids. KENZO HATTORI (*Biochem. Z.*, 1921, **119**, 45—64).—The colloidal balance of an optically homogeneous cholesterol-lecithin mixture is altered by water owing to swelling of the lecithin and separation of the cholesterol. By saline solution, however, the degree of swelling of lecithin is limited and there is no separation of cholesterol. Reagents which affect the colloidal balance are hæmolytic, but the parallelism is only approximate. H. K.

The Combinations of Hæmoglobin with Oxygen and Carbon Monoxide, and the Effects of Acid and Carbon Dioxide.

ARCHIBALD VIVIAN HILL (*Biochem. J.*, 1921, 15, 577—586).—A theoretical paper which suggests an explanation for the S-shaped dissociation curves of oxy-hæmoglobin and of carboxy-hæmoglobin and the identical effects of carbon dioxide on these curves. The chief assumptions made are (1) that hæmoglobin dissociates slightly into protein molecules and molecules containing iron, and (2) that in the presence of salts the osmotic pressure of the complex hæmoglobin and of the simpler protein is reduced to $1/n$ of its value, calculated on the basis of one atom of iron per molecule of hæmoglobin. This reduction is not necessarily due to aggregation of molecules, as was previously assumed (*J. Physiol.*, 1910, 40, Proc. iv). It is shown that the effects of acid and of carbon dioxide on the dissociation curve of blood can be deduced from the hypothesis that the available alkali inside the corpuscle is competed for by oxy-hæmoglobin, reduced hæmoglobin, and the acid or carbon dioxide, the first being a far stronger acid than the second. The rectangular hyperbola relating carbon monoxide saturation to carbon monoxide pressure, or oxygen saturation to oxygen pressure, in blood or hæmoglobin fully saturated with a mixture of these gases, is also explained by the theory, as are various other points.
G. B.

Acceleration of Blood-clotting by Euphylline. R. MEISSNER (*Biochem. Z.*, 1921, 120, 197—202).—Euphylline (an additive product of theophylline and ethylenediamine) can accelerate blood-clotting even up to 50%. The components have individually a weak action.
H. K.

The Basal Metabolism and the Specific Dynamic Action of Protein in Liver Disease. JOSEPH C. AUB and JAMES H. MEANS (*Arch. Intern. Med.*, 1921, 28, 173—191).—The basal metabolism in twelve cases of liver disease (gallstones, cirrhosis, carcinoma, acute catarrhal jaundice) was essentially within normal limits. The liver is, therefore, either not an important regulator of the metabolic rate, or it is adequate for this purpose even when severely diseased. The rate of absorption and utilisation of protein in large quantities was usually normal, even in severe cirrhosis. In two cases of cirrhosis and one of gallstones, the utilisation of the protein was delayed or absent. Marked portal obstruction caused no delay in the appearance of the specific dynamic action of protein. The cases of cirrhosis showed, on the whole, the highest metabolic response to protein katabolism. The conclusion seems justified that either the liver is not the main site of the specific dynamic action of protein, or that it can adequately perform that function even in disease. The specific dynamic action of protein results from an increased combustion of protein and carbohydrate, rather than of fat. The observations of Du Bois (*ibid.*, 1916, 17, 915), that in exophthalmic goitre a normal increase in heat production, due to protein, is superimposed on the high basal rate, is confirmed.
CHEMICAL ABSTRACTS.

The Influence of Food Ingestion on Endogenous Purine Metabolism. I and II. WILLIAM C. ROSE (*J. Biol. Chem.*, 1921, **48**, 563—573 and 575—590).—The uric acid output remains constant under constant dietetic conditions, but is influenced by the quantity and nature of the food. In particular, it is increased by the amino-acids. The precursors of the purines are probably arginine and histidine; in the absence of these precursors, variations in the purine output may be brought about by the re-utilisation for anabolic purposes of purines produced in catabolism.

C. R. H.

Mechanism of Reduction of Nitrates and Nitrites in Processes of Assimilation. OSKAR BAUDISCH (*J. Biol. Chem.*, 1921, **48**, 489—502).—A summary of the author's previously published work on the subject.

E. S.

Quantitative Estimation of the Fat-soluble Factor. SYLVESTER SOLOMON ZILVA and MASATARO MIURA (*Biochem. J.*, 1921, **15**, 654—659).—Rats are used which have been kept 3—4 weeks on the basal diet without growing; their weight should not exceed 70 grams. The minimum dose of the active substance is then determined which just induces a definite growth. For instance, 1.7 mg. of the most active cod liver oil per day did this, and 1.4 mg. did not. The minimum doses of various samples of cod liver oil varied from 1.7—5 mg., of butter from 200—400 mg.

G. B.

Pharmacological and Chemical Study of the Roes of the Barbel and Pike. FRANCIS H. MCCRUDDEN (*Arch. exp. Path. Pharm.*, 1921, **91**, 46—80).—Fish poisoning produced by consumption of the barbel or pike is due to a toxic substance contained mainly, if not exclusively, in the hard roes of these fishes. For the investigation of its properties the globulin and albumin were extracted from the roes by salt solution. On separation of these by the usual methods, the toxic action was found to be confined to the albumin fraction. Injected intravenously into rabbits, it produced paralysis of the central nervous system, death finally resulting from paralysis of respiration. The effects produced by extracts of the roes of either fish were similar, but more marked in the case of the pike. The toxicity is destroyed by heat. A comparison is made of the globulins (ichthulins) from eggs of various fish and the difference between their chemical properties and those of vitellin from birds' eggs emphasised.

E. S.

Zinc and Copper Content of the Human Brain. MEYER BODANSKY (*J. Biol. Chem.*, 1921, **48**, 361—364).—Analyses of one foetal and four adult brains indicate that zinc and copper are normal constituents of the human brain.

E. S.

Acetone in Cerebrospinal Fluid. J. KOOPMAN (*Nederl. Tijdschr. Geneesk.*, 1920, **64**, 1346—1350).—Acetone is present in the cerebrospinal fluid during diabetic coma, diabetic acidosis, and adrenal apoplexy; in the first two cases it is accompanied by acetoacetic acid.

CHEMICAL ABSTRACTS.

The Spacial Separation of Glycogen and Diastase in the Liver Cells. E. J. LESSER (*Biochem. Z.*, 1921, **119**, 108—120).—Perfusion of a frog's liver in the months August to January with hypertonic salt solutions leads to a fourfold excretion of dextrose over that produced by isotonic salt solutions. The dextrose production rises to a maximum after four hours. In the spring and summer months, there is no great difference between the effect of isotonic and hypertonic salines. This effect is independent of the ions of the salts used, and is only slightly affected by the hydrogen-ion concentration. The action appears to be purely osmotic.

H. K.

Sea-wolf Liver Oil. THOR LEXOW (*Chem. Umschau*, 1921, **28**, 213—214).—The livers were obtained from both male and female of the species *Anarrhichas lupus*, L.; the oil, extracted separately, was of a clear golden brown colour and had a curious odour unlike that of other liver oils. The oils from the male and female livers gave respectively the following characters: d_{4}^{25} 0.9162, 0.9179; n_D^{25} 1.4733, 1.4702; acid number 13.11, 14.37; saponification number 182.8, 185.2; iodine number (Wijs) 131.2, 118.1; unsaponifiable matter 5.23, 3.86; fatty acids 92.4%, 92.2%; m. p. of fatty acids 24.5°, 24.7°; mean molecular weight of the fatty acids 276.8, 279.9.

The oil is used in Russia mixed with coal-fish liver oil in tanning and can easily be distinguished from the sea-wolf liver oil by its low iodine number and high content of unsaponifiable matter.

H. C. R.

Variations in the Amylolytic Activity of the Pancreas and Liver in Avian Polyneuritis. R. TIGER and H. SIMONNET (*Bull. Soc. Chim. Biol.*, 1921, **3**, 580—582).—The amylolytic activity of the pancreas in pigeons with polyneuritis is slightly less than in normal birds. Experiments with the liver did not yield concordant results.

E. S.

The Function of the Pancreas. LEO ADLER (*Arch. exp. Path. Pharm.*, 1921, **91**, 110—124).—The author has previously shown that hibernating hedgehogs are roused and the body temperature brought to summer level by subcutaneous injection of extracts of thyroid or thymus, adrenaline, or certain amines derived from proteins. In the present paper, it is shown that a simultaneous injection of pancreas extract made from the pancreas of hibernating hedgehogs more or less completely suppresses the action of these substances. The suppression is less complete in the case of adrenaline than in the other cases.

E. S.

Heterogenetic Antigen and Hapten. XV. KARL LANDSTEINER (*Biochem. Z.*, 1921, **119**, 294—306).—The soluble heterogenetic antigens obtained from horse kidney by alcohol extraction are as active in vitro as the unchanged materials, but when injected into animals do not produce hæmolsin.

H. K.

The Enzymes of the Abdominal Adipose Tissue of the Common Turkey, *Meleagris gallinavo*. JOSEPH SAMUEL HEPBURN (*J. Amer. Chem. Soc.*, 1921, **43**, 1963—1965).—Using the method previously applied to chicken fat (cf. Pennington and Hepburn, A., 1912, ii, 275), but taking tributyrin as the substrate for lipase and ethyl butyrate for esterase, catalase, lipase, and esterase were always found in the adipose tissue. Simple reductase and oxydase acting on phenolphthalein were usually present. Tests for oxydases acting on α -naphthol and tricresol, and for protease gave negative results. Aldehyde reductase and peroxydases were found in several of the samples. W. G.

The Selective Absorption of Potassium by Animal Cells. II. The Cause of Potassium Selection as Indicated by the Absorption of Rubidium and Cæsium. PHILIP H. MITCHELL, J. WALTER WILSON, and RALPH E. STANTON (*J. gen. Physiol.*, 1921, **4**, 141—148).—Frog muscles, perfused with Ringer solution in which potassium has been replaced by cæsium (or rubidium) in equivalent amount, and stimulated electrically during the perfusion, absorb the cæsium (or rubidium) in such a way as to be retained during a subsequent perfusion with potassium-free Ringer solution. The substitution of cæsium (or rubidium) for potassium in the diet of rats leads to a replacement of potassium by that metal in the tissues. Rubidium and cæsium are toxic, and in the presence or absence of potassium cause death. The physiological peculiarities of these metals may be related to their electronic structure, and hence to their comparative migration velocities. W. O. K.

Physiological Significance of the Change in the Condition of Permeability in the Limiting Membrane of the Muscle Fibres. GUSTAV EMBDEN and ERICH ADLER (*Z. physiol. Chem.*, 1922, **118**, 1—49).—The permeability of the limiting sheath of the muscle fibres of the gastrocnemius of the frog was studied under different physiological conditions. The diffusion of phosphoric acid from the muscle into Ringer's solution was adopted as the method for the estimation of the permeability. S. S. Z.

Investigations on Potassium Paralysis. HANS VOGEL (*Z. physiol. Chem.*, 1922, **118**, 50—95).—The speed with which potassium paralysis intervenes in the gastrocnemius of the frog runs parallel with the permeability of the limiting membrane of the muscle fibres as determined by the diffusion of phosphoric acid out of the muscle (see preceding abstract). This, of course, depends on the physiological condition of the muscle. The onset of the potassium paralysis of the muscle can therefore be utilised as a standard for the permeability of the limiting membrane of the muscle fibres. The author utilises the above observation to explain the different conclusions drawn by himself and Overton in an earlier investigation. S. S. Z.

The Influence of Asphyxiation on the Permeability of the Limiting Membrane of the Muscle Fibres. MAX SIMON (*Z. physiol. Chem.*, 1922, **118**, 96—122).—Asphyxiation increases

the permeability of the limiting membrane of the muscle fibres in the gastrocnemius of the frog. This can be demonstrated by replacing oxygen by hydrogen. The change is reversible. The permeability was determined both by the diffusion of phosphoric acid and by the production of paralysis by the potassium ion (see preceding abstracts). S. S. Z.

The Influence of the Chemical Composition and the Physico-chemical Structure on the Function of Frog Muscles. HANS BEHRENDT (*Z. physiol. Chem.*, 1922, **118**, 123—167).—The lactacidogen content of the gastrocnemius and the adductor muscles of the frog is the same. The adductor muscles, however, contain sometimes more free phosphoric acid than the gastrocnemius. The “residual phosphoric acid” (restphosphorsaure) and the glycogen content is higher in the gastrocnemius than in the adductors. The physico-chemical properties of the two muscles as obtained by physiological methods are also compared. S. S. Z.

Chemistry of the Formation and Ripening of Honey. E. SARIN (*Biochem. Z.*, 1921, **120**, 250—258).—Bees were fed with sucrose syrup, the honey collected and re-fed to the bees. This process was repeated three times. Examination of the honey at each stage indicated that invertase and diastase are specific products of the bees, but catalase, which only occurs in natural honey, is of plant origin. H. K.

Influence of Organic Acids on the Formation and Ripening of Sugar-honey. E. SARIN (*Biochem. Z.*, 1921, **120**, 259—264).—The addition of acids to the sugar syrups used for feeding bees exerts a harmful effect on the biochemical processes of the formation and ripening of honey. H. K.

Citric Acid Content of Milk and Milk Products. G. C. SUPPLEE and B. BELLIS (*J. Biol. Chem.*, 1921, **48**, 453—461).—From a series of estimations, it is shown (1) that the citric acid content of milk from different cows on the same ration shows a marked variation, (2) that there is no loss of citric acid during the process of drying or concentrating milk, (3) that the citric acid content decreases during ageing in the presence of highly developed acidity (cf. Sommer and Hart, A., 1918, i, 465). E. S.

Day and Night Urine during Complete Rest, Laboratory Routine, Light Muscular Work, and Oxygen Administration. JAMES ARGYLL CAMPBELL and THOMAS ARTHUR WEBSTER (*Biochem. J.*, 1921, **15**, 660—664).—The night urine contained always less total nitrogen, more ammonia, less creatinine, urea, uric acid, and amino-acids, and was more acid than during the day. The phosphate tide is considered to be due to the increased acidity, which in its turn is attributed to delayed excretion of certain fixed acids, formed in the cells during the day. The sulphur was evenly distributed between the day and the night. Administration of 35—40% oxygen did not affect the composition of the urine. G. B.

Viscometric and Stalagmometric Measurements of Urine. ERNST JOËL (*Biochem. Z.*, 1921, **119**, 93—107).—The viscosity of normal urine is 1·0 to 1·05. The presence of colloidal materials has a considerable influence on this value. H. K.

Which Carbohydrates are excreted in the Urine of Sucklings when the Sucrose in the Food Exceeds the Assimilation Limit? A Method for the Quantitative Estimation of several Carbohydrates simultaneously in the Urine. HANS MURSCHAUSER (*Biochem. Z.*, 1921, **119**, 328—338).—Experiments with babes under one year of age showed that sucrose administered in excess of the assimilation value appeared in the urine, partly unchanged and partly as dextrose and lævulose. The three sugars are estimated by determining the rotation and reducing power before and after inversion. H. K.

Alkapton Chromogen. G. KATSCH and GÉZA NÉMET (*Biochem. Z.*, 1921, **120**, 212—217).—The ethereal extract of an alkapton urine poured on to unburnt lime acquires an evanescent vivid blue colour. The reaction is very sensitive. The urine of many individuals, after administration of homogentisic acid, slowly darkens, but homogentisic acid is not detectable. The supposed derivatives of this acid which give rise to this reaction are called alkapton chromogens. H. K.

Chemistry of Diabetic Glycosuria. AL. IONESCU (*Bul. Soc. Chim. România*, 1921, **3**, 97—104).—A theoretical paper, suggesting that glycosuria is due to a disturbance of the normal equilibrium between the diastatic reactions occurring in the blood. Thus, excessive hydrolytic action would result in the formation of considerable quantities of acids, ketones, and aldehydes, in the disposal of which the alkalinity of the blood would assist, but these would probably be chiefly converted into dextrose in quantities greater than could be dealt with by the liver. The blood would be affected in regard to the distribution of electrolytes between the white corpuscles and the serum, and, as a consequence, the activity of the liver in converting dextrose into glycogen would be diminished. J. K.

The Types of Reaction of the Bile Pigments and the Quantitative Relation of Bilirubin to Cholesterol in the Blood during different Forms of Jaundice. F. ROSENTHAL and K. MEIER (*Arch. expt. Path. Pharm.*, 1921, **91**, 246—271).—The forms of jaundice investigated were mainly experimental. In each case the type of diazonium reaction (cf. van den Bergh and Muller, A., 1917, ii, 58) given by the serum was determined and the cholesterol content of the latter estimated. The readiness with which bilirubin appears in the urine in each case was also noted. E. S.

The Theory of Narcosis. I. TRAUBE and P. KLEIN (*Biochem. Z.*, 1921, **120**, 111—124).—The authors have examined the Tyndall effect and the ultramicroscopic behaviour of aqueous solutions

of a number of organic substances of slight or moderate solubility and find that some substances show two widely differing degrees of dispersity. Stalagmometric experiments on these show that the higher the dispersity the greater the effect on the surface tension of water. The results show that other factors besides those postulated in Traube's theory of narcosis must play a part, for the hydrocarbons and alkyl haloids have little effect on the surface tension and yet are powerful narcotics. H. K.

The Effective Strengths of Narcotics. I. Experiments on the Isolated Frog's Heart. H. FÜHNER (*Biochem. Z.*, 1921, 120, 143—163).—The isonarcotic concentration of 40 narcotics has been determined on the isolated frog's heart and the drop numbers have been compared, by means of Traube's stalagmometer. Alcohols and their derivatives, paracetaldehyde, acetone, and ethyl ether have a marked effect on the surface tension. Esters are less active, but benzene and many alkyl haloids are inactive even in saturated solution. Apart from the alcohols and related derivatives, there is no correspondence between narcotic action and depression of surface activity as postulated by Traube's theory. The narcotic concentrations, however, show a parallelism with the aqueous solubility in salt solutions. H. K.

The Action of some Derivatives of Chloroform with Special Reference to Traube's Theory of the Action of Narcotics of the Aliphatic Series. GEORG JOACHIMOGLU (*Biochem. Z.*, 1921, 120, 203—211).—Traube's theory of narcosis is untenable. Among the chloro-derivatives of methane and ethane or ethylene, the narcotic action and surface activity are by no means parallel. H. K.

Barium Chloride Poisoning. AL. IONESCU (*Bul. Soc. Chim. România*, 1921, 3, 94—97).—Investigation of a number of recent fatal cases of poisoning due to barium chloride confirms the observations of Ogier and others that a very small proportion of the fatal dose is discoverable in the organs, positive results being only obtained by the Flandin-Danger method, and not by a combination of dialysis with the Fresenius-Babo process. It is suggested that it will be advisable in such cases to examine the bones, since these appear to take up the overwhelming proportion of the poison. The action of this is attributed, in agreement with previous workers, to irritation of the neuro-motor system. J. K.

Toad Venom. HEINRICH WIELAND (*Sitzber. bayer. Akad. Wiss.*, 1920, 329—343).—The formulæ given to bufotalin and some of its derivatives by Wieland and Weil (A., 1913, i, 1343) must be changed, since it is found that bufotalin retains organic solvents of crystallisation most energetically. Bufotalin crystallised from alcohol is not $C_{16}H_{24}O_4$, but $C_{26}H_{36}O_6 \cdot C_2H_6O$ (which has the same percentage composition). Crystals from ethyl acetate melt at 154° and have the composition $2C_{26}H_{36}O_6 \cdot C_4H_8O_2$. The solvent is given off slowly in a high vacuum at 150° , and on careful heating in a high vacuum at 225 — 230° bufotalin sublimes. Of the six

oxygen atoms, two are present as a lactone group, two as an acetyl group, and two are hydroxylic. Of the latter groups, one is capable of acetylation, which yields *acetyl bufotalin*, $C_{28}H_{38}O_7$, m. p. 254° , and the other can be oxidised to a ketone group, present in *bufotalone*, $C_{26}H_{34}O_6$, m. p. 261° . Bufotalin is reduced by palladium black and hydrogen to *tetrahydrobufotalin*, $C_{26}H_{40}O_6$, m. p. $204-205^\circ$. Bufotalin, formed by the action of concentrated hydrochloric acid on bufotalin, is $C_{24}H_{30}O_3$ (not $C_{16}H_{20}O_2$, as previously supposed). In its formation one molecular proportion of acetic acid and one of water are removed from bufotalin. Bufotalin melts at $222-223^\circ$ and is yellow in colour. It is reduced catalytically by palladium to colourless *bufotalan*, $C_{24}H_{38}O_3$, m. p. $198-199^\circ$, and hence contains four double bonds. Unlike its precursors, bufotalan does not give Liebermann's cholesterol reaction with acetic anhydride and sulphuric acid.

The carbon skeleton of bufotalin (apart from the acetyl group) is derived from a saturated hydrocarbon, $C_{24}H_{42}$, with eight hydrogen atoms less than the corresponding aliphatic one. Hence bufotalin contains four carbon rings. Now the bile acids are also derived from a complex, C_{24} , with four rings, and, as was shown by Windaus and Neukirchen (A., 1920, i, 41), cholesterol differs from the bile acids by an additional *isopropyl* group at the end of a side-chain, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe-$, which in cholic acid is represented by $CO_2H \cdot CH_2 \cdot CH_2 \cdot CHMe-$. Wieland considers it very probable that in bufotalin this side-chain is further oxidised to a γ -lactone, $\begin{array}{c} CH_2 \cdot CMe \\ | \quad \diagup \\ CH_2 - CO > O \end{array}$, and the chief problem at present is to convert bufotalan, $C_{24}H_{38}O_3$, into cholanic acid, $C_{24}H_{40}O_2$, the parent substance of the bile acids.

A second crystalline toxic substance from the skin of the toad, previously called bufotalein by Wieland and Weil, is now named *bufotalidin*, $C_{26}H_{36}O_7$, probably oxybufotalin. With alcohol of crystallisation, it melts at 175° and after heating in a high vacuum at $228-230^\circ$.

Bufagin, the venom of the tropical toad *Bufo aqua*, isolated by Abel and Macht (A., 1912, ii, 1193), is certainly not identical with bufotalin, and according to Faust, has only one-tenth of the physiological action of the latter. Wieland is not convinced that the molecular weight of bufagin has been correctly determined, and considers that Abel and Macht's formula, $C_{18}H_{24}O_4$, may require alteration to $C_{27}H_{38}O_6$, which is that of a methyl ether of bufotalin.

[The above toad venoms are heart poisons and pharmacologically similar to digitalis and strophanthus. Digitoxigenin is, according to Cloetta (A., 1921, i, 39), $C_{24}H_{36}O_4$, and strophanthidin (cymarigenin, A., 1915, i, 704) has 23 or possibly also 24 carbon atoms. All these heart poisons from various animal and vegetable sources seem to be related to cholesterol and the bile acids.] G. B.

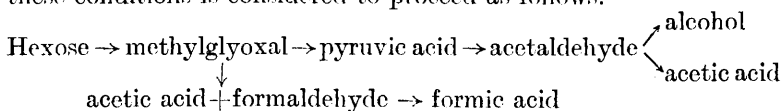
Chemistry of Vegetable Physiology and Agriculture.

The Effect of Hydrogen-ion Concentration on the Production of Carbon Dioxide by *Bacillus butyricus* and *Bacillus subtilis*. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1921, **4**, 177—186).—The rate of production of carbon dioxide by *Bacillus butyricus* and *Bacillus subtilis* is a maximum at P_H 7 and 6·8 respectively. If alkali be added to the culture at its optimum P_H recovery in the rate of production takes place; if acid be added, recovery takes place only if the amount added be small and if it be neutralised by an equivalent amount of acid. W. O. K.

Bacteria as a Source of the Water-Soluble B-Vitamin. SAMUEL R. DAMON (*J. Biol. Chem.*, 1921, **48**, 379—384).—Feeding experiments on rats indicate that *B. paratyphosus*, *B. coli*, and *B. subtilis* do not produce vitamin-B (cf. Pacini and Russell, *A.*, 1918, i, 329). E. S.

Characteristics of certain Pentose-destroying Bacteria, especially as Concerns their Action on Arabinose and Xylose. E. B. FRED, W. H. PETERSON, and J. A. ANDERSON (*J. Biol. Chem.*, 1921, **48**, 385—411; cf. *A.*, 1920, i, 406, 513, 911).—Pure cultures of twelve strains of lactic acid bacteria were isolated from corn silage and sauerkraut. They are classified in two main divisions, according as they ferment lævulose with or without the production of mannitol, further subdivision depending on their fermentative ability towards various sugars. The fermentation of arabinose and xylose by these bacteria results in the formation of acetic acid, lactic acid, and carbon dioxide. The two acids are formed in approximately equimolecular proportions, the main line of fermentation being, apparently, simple cleavage into acetic and lactic acids. The mannitol-forming bacteria also slowly ferment lactic acid to acetic acid and carbon dioxide. E. S.

The Attack of Dextrose and Lævulose by the Pyocyanic Bacillus. E. AUBEL (*Compt. rend.*, 1921, **173**, 1493—1495).—Amongst the products of the decomposition of dextrose and lævulose by the pyocyanic bacillus, alcohol, acetic acid, and formic acid have invariably been found. Lactic acid has also been found as a by-product from lævulose. The degradation of the two hexoses under these conditions is considered to proceed as follows.



W. G.

Action of Acids on Fermentation by Yeast. R. SOMOGYI (*Biochem. Z.*, 1921, **120**, 100—102).—Acids exert a harmful effect on fermentation by yeast. This is proved by the examination of

the action of thirteen acids, organic and inorganic, at concentrations between $N/6$ and $N/1500$. The inhibitory action does not appear to be solely dependent on the hydrogen-ion concentration, but on other physical properties as well. H. K.

The Change undergone by Nitrogenous Substances in the Final Phases of Yeast Autolysis. NICOLAUS N. IVANOV (*Biochem. Z.*, 1921, **120**, 1—24; cf. A., 1918, i, 365).—If, after yeast autolysis has proceeded for some time the solution be made alkaline, the ensuing autolysis is accompanied by an increase of protein nitrogen (as estimated by Stutzer's method), at the expense of the original protein decomposition products which are precipitable by lead acetate and phosphotungstic acid. The amino-nitrogen, however, as determined by Van Slyke's method, is unchanged. If the autolysis in alkaline solution is allowed to continue at a higher temperature, for example, 60° , there is a loss of amino-nitrogen unaccompanied by any increase of protein-nitrogen. This is interpreted as being due to the formation of humin-like substances at the expense of the amino-acids of the autolysate and carbohydrates. H. K.

The Influence of Fermentation Products on the Decomposition of Proteins in Yeast. NICOLAUS N. IVANOV (*Biochem. Z.*, 1921, **120**, 62—80).—During the process of fermentation substances are formed which inhibit the decomposition of protein. It is shown experimentally that the inhibition is the result of two factors, (1) production of alcohol during fermentation, (2) development of acidity; the former plays the greater rôle. H. K.

Protein Decomposition in Yeast during Fermentation. NICOLAUS N. IVANOV (*Biochem. Z.*, 1921, **120**, 25—61).—Stutzer's method (*J. Landw.*, 1880, **28**, 103) for the estimation of proteins in solutions by precipitation with cupric hydroxide does not differentiate between proteins and humins. During the fermentation of sugar by yeast there is decomposition of protein, earlier statements to the contrary being based on results obtained by Stutzer's method, the humins formed being stable to the proteolytic enzymes present and compensating for the loss of protein. Meyer's "excrements of fermentation" are probably humin-like substances. H. K.

Effect of certain Stimulating Substances on the Invertase Activity of Yeast. ELIZABETH W. MILLER (*J. Biol. Chem.*, 1921, **48**, 329—346).—The addition of an alcoholic or aqueous yeast extract to growing yeast is known to stimulate both growth and formation of invertase. It is now shown that these two effects are produced by different substances, a partial separation of which may be effected by removal of the growth stimulant by extraction with benzene, adsorption with Fuller's earth, or precipitation with phosphotungstic acid. The substance accelerating invertase formation is also contained in high concentration in a gummy precipitate which separates from alcoholic extracts of yeast. Its action is not of the nature of a co-enzyme, since it is without influence on

invertase itself; moreover, although Abderhalden and Schaumann (A., 1919, i, 108) found that yeast extract increased the invertase activity of both dried yeast and maceration juice, the increase was so small as to fall within the limits of experimental error. Extracts of wheat germ also stimulate growth but do not increase the invertase concentration in yeast. E. S.

The Lactase Content and the Fermenting Power of Lactose-fermenting Yeasts. RICHARD WILLSTÄTTER and GERTRUD OPPENHEIMER (*Z. physiol. Chem.*, 1922, **118**, 168—188).—Lactase can be obtained from fresh yeast without previously destroying the cell, providing that the acidity is neutralised. The lactose-splitting activity of yeasts, sometimes even of the same strain, varies within very wide limits. In some cases lactose is fermented more quickly than an equivalent mixture of dextrose and galactose. It is also shown that in certain cases the fermentation of lactose proceeds almost as quickly as, or perhaps more quickly than, the hydrolysis of the disaccharide. When the fermentation is interrupted in such cases no monosaccharides are found in the fermenting medium. This differs from the mechanism of the fermentation of sucrose, when hydrolysis takes place almost immediately. It is concluded that lactose-fermenting yeasts can ferment that sugar without hydrolysing it and therefore contain a lactose-*zymase*. S. S. Z.

Vitamin Requirements of certain Yeasts and Bacteria. CASIMIR FUNK and HARRY E. DUBIN (*J. Biol. Chem.*, 1921, **48**, 437—443).—By shaking autolysed yeast with either Fuller's earth or "norit" vitamin-*B* is completely removed; the filtrate, however, still promotes the growth of yeast. The authors conclude that a hitherto unknown vitamin, for which the name vitamin-*D* is suggested, is present in yeast. E. S.

The Rôle of Acetaldehyde in Alcoholic Fermentation. A. FERNBACH and M. SCHOEN (*Bull. inst. Pasteur*, 1920, **18**, 385—406).—A review of the present state of knowledge of the subject, with special reference to the work, already published, of Neubauer and Fromherz, Neuberg and others, Mazé and Lintner, Liebig, J. B. Dumas, Connstein, Leudeke, and the authors.

CHEMICAL ABSTRACTS.

The Lipase of *Aspergillus niger* (van Tiegh). ROBERT SCHENKER (*Biochem. Z.*, 1921, **120**, 164—196).—A pure culture of *Aspergillus niger* (identical with Brenner's β -strain) showed growth on various glycerides, especially triacetin, but no growth on ethyl esters. The lipase present can be extracted, with water or glycerol, in the form of a press-juice, or as a stable acetone-treated preparation. Fatty media favour the development of the enzyme more than media containing glycerol or sucrose. The optimum temperature for the enzyme is 40°, and the optimum reaction of the solution, for its activity, neutral or weakly acid. H. K.

The Toxicity of Different Nitrophenols towards *Aspergillus niger*. L. PLANTEFOL (*Compt. rend.*, 1922, **174**, 123—126).—Phenol and its nitro-derivatives are toxic towards *Aspergillus niger*, the nitro-derivatives being more toxic than phenol itself. Of the three mononitrophenols, the ortho is the least and the para the most toxic. 2:4-Dinitrophenol is one hundred times more toxic than phenol and ten times more toxic than the most toxic mononitrophenol. 2:4:6-Trinitrophenol is about as toxic as *m*-nitrophenol. W. G.

Bactericidal Action of the Quinones and Allied Compounds. GILBERT THOMAS MORGAN and EVELYN ASHLEY COOPER (*Biochem. J.*, 1921, **15**, 587—594).—When proteins are added to solutions of *p*-benzoquinone, the latter slowly disappears and quinol can be detected; the quinone seems to react as a peroxide and differs fundamentally from phenols, which are merely protein precipitants. *p*-Benzoquinone is 80—190 times as effective in destroying *B. typhosus* as quinol or phenol. In ascending a homologous series, the quinones become less, the phenols more bactericidal; thymoquinone is less effective than thymol. The authors incline to the view that the high bactericidal power of benzoquinone is connected with the interaction of *nascent* peroxide molecules with the bacterial protoplasm. G. B.

Theory of Disinfection. I. TRAUBE and R. SOMOGYI (*Biochem. Z.*, 1921, **120**, 90—99).—Experiments with *Staphylococcus* and *Bacillus coli* show that apart from disinfectants of the type of potassium permanganate and hydrogen peroxide, which act chemically, physical forces are the deciding factor, such as surface activity, adsorption, flocculation, and other properties. H. K.

P_H Again. I. TRAUBE (*Biochem. Z.*, 1921, **120**, 108—110).—The author's contention is that P_H is too much in the foreground to the exclusion of other factors. H. K.

Conditions for the Biological Action of Röntgen Rays. I. EUGEN PETRY (*Biochem. Z.*, 1921, **119**, 23—44).—The inhibitory action of Röntgen rays on the growth of seeds could not be influenced by temperature changes, lack of oxygen, or by the presence of potassium cyanide. The action is therefore not connected with the respiratory processes. The small temperature coefficient points to the action being photochemical. H. K.

The Action of Bases and Salts on Biocolloids and Cell Masses. D. T. MACDOUGALL (*Proc. Amer. Phil. Soc.*, 1921, **60**, 15—30).—A study of the swelling of biocolloids in dilute salt solutions in connexion with the suggestion that the chief effect of salts in nutrient solutions is in restricting, limiting, or defining the hydration of the cell colloids. Hydroxides of the metallic bases were found to decrease the swelling of plates of agar in the order: calcium, potassium, sodium, in concentrations of 0.01 molar. The chlorides show the same relative action. Hydration of agar is increased by

the hydroxides of these metals at 0.001*N*, but no well-defined differences between the metals could be observed. Similar effects were produced by chlorides of calcium, magnesium, potassium, and sodium at 0.0001*M*, and potassium and sodium at 0.001*M*. The purified agar used in the experiments has a p_H value of 6.5 and swells more in hydrochloric acid of p_H 4.2 than in pure water. The p_H range over which large swelling of the agar occurs is from 4.2 to 11. It also swells largely in 0.0001*M* sodium and potassium nitrates, but not in the sulphates. Similar measurements were also made on the swelling of gelatin. The gelatin used had a p_H value of 5.2 and it was noted that both hydrogen and hydroxyl ions caused increasing swelling with reference to the isoelectric point, at which minimum swelling occurred. The swelling in 0.0001*M* potassium chloride ($p_H=5.7$) was not much greater than in water; the swelling in potassium chloride 0.001*M* ($p_H=5.8$) is about double that in water. Calcium chloride solutions induce maximum swelling at 0.001*M*, but depress hydration as the concentration increases or decreases from 0.001*M*. The interest of these results lies in the fact that a mixture of a vegetable mucilage (pentosan) type of colloid with a protein colloid exemplifies many of the reactions of living or dead cell masses. Experiments were therefore continued with plates of gelatin 3 : agar 2 parts, and gelatin 2 : agar 3 parts. In the latter, sensitiveness to hydrogen ions was more marked than in the case of agar alone, but the effect of potassium chloride is about the same as that upon agar alone. The mixture in which gelatin predominated showed increase of swelling as p_H was increased to 2.01, whilst potassium chloride showed an effect similar to its effect on agar. The work was then extended to living and dead cell masses, such as sections from the roots of *Zea mais* (dominantly pentosan), which were closely parallel to those of the agar 3 : gelatin 2 mixture. Roots of strawberry showed different hydration reactions depending on whether they were grown in saline soils or in sand, the latter showing greater hydration. Joints of *Opuntia* (dominantly pentosan) showed maximum swelling in 0.01*N*-potassium hydroxide, hydrogen chloride at 0.001*N*, and potassium chloride at 0.0001*M*, all in excess of the swelling in water. The changes in volume of living cell masses in hydrating solutions include osmotic-plasmolytic effects in the alteration of the volume of the included cells. The hydration of dead cell masses includes possible osmotic action of cell-walls.

CHEMICAL ABSTRACTS.

Action of Neutral Salts on Plant Plasma. II. HUGO KAHHO (*Biochem. Z.*, 1921, **120**, 125—142).—The coagulating action of neutral salts on plant plasma (sections of *Tradescantia zebrina*) depends on both ions, the anions playing a greater part than the kations. The coagulating property of anions falls off in the order $CNS > I > Br > NO_3 > Acetate > Cl > Tartrate > Citrate > SO_4$ and of the kations $K > NH_4 > Na > Sr, Mg, Ba, Ca$. The order of the ions is substantially the lyotrope series, but in the reverse order of their action on protein. The possible reasons for this are discussed.

H. K.

The Occurrence and Action of Saccharophosphatase in the Organism of the Plant. ANTONIN NĚMEC and FRANTIŠEK DUCHOŇ (*Biochem. Z.*, 1921, **119**, 73—80).—The sodium and calcium salts of artificially prepared saccharophosphoric acid are hydrolysed with formation of free phosphoric acid by the resting seeds of the higher cultivated plants as well as by the leaves of *Solanum tuberosum*. Aqueous extracts of the seeds have the same power, but to a lesser degree. Alkali is inimical to the action of the enzyme, the optimum acidity being 0.03*N* for saccharophosphatase and 0.004*N* for the autolytic phosphatase of the seeds. H. K.

Pectic Substances of Plants. II. Preliminary Investigation of the Chemistry of the Cell-walls of Plants. DONALD HERBERT FRANK CLAYSON, FREDERICK WALTER NORRIS, and SAMUEL BARNETT SCHRYVER (*Biochem. J.*, 1921, **15**, 643—653; cf. A., 1917, i, 245).—The authors call *cytopentans* substances related to Schulze's hemicelluloses, which are extracted by cold *N*-sodium hydroxide and then precipitated by addition of alcohol. They are coloured blue by iodine, and do not reduce Fehling's solution until after hydrolysis by acids, when they give 40—85% of pentosans. Cytopentans form a relatively small part of crude pectin, and the name *cytopectic acid* is suggested for the rest. The samples of this acid from six species of plants contained 41.22—42.88% C, 5.31—5.71% H, and 0.15—0.85% ash. $[\alpha]_D^{20} + 260^\circ$ to $+280^\circ$. The percentage of methyl alcohol set free by sodium hydroxide was 0.16—0.42% (cf. von Fellenberg, A., 1918, i, 215, and Tutin, A., 1921, i, 751). G. B.

Incrustive Substances of Plants. II. ERICH SCHMIDT and FRANZ DUYSEN (*Ber.*, 1921, **54**, [B], 3241—3244; cf. A., 1921, i, 912).—The removal of incrustive substances is effected more conveniently by means of a solution of chlorine dioxide in acetic acid (50%) than by alternate treatment with chlorine peroxide and sodium sulphite; the method has the advantage that the attacked incrustations remain dissolved in the acid. Subsequently, the presence of polysaccharides which give a blue coloration in the tissues can be demonstrated readily by means of zinc chloride-iodine solution which gives untrustworthy results in the presence of the incrustations. The simple manipulation required and the stability of the solutions render the chlorine dioxide-acetic acid valuable for micro-chemical investigations. The reagent causes the cell-walls to swell slightly, but this action occurs so uniformly that the anatomical features of the plant are not altered thereby. H. W.

The Detection of the Pseudo-bases of Anthocyanidins in Plant-tissues. RAOUL COMBES (*Compt. rend.*, 1921, **174**, 58—61).—The substances characterised by Noack in the amyl alcohol extracts of leaves of *Polygonum compactum* and *Ampelopsis hederacea* and the pericarps of *Aesculus hippocastanum* as anthocyanidin pseudo-bases (cf. *Z. Botanik*, 1918, **10**, 561) were probably

phlobatannins and the red substances he obtained by the action of acids which he considered as anthocyanidins were probably phlobaphens. The author does not consider that Willstätter's method for the separation of anthocyanidins and anthocyanins by means of amyl alcohol can be applied to the detection of pseudo-bases of anthocyanidin in plant-tissues. It is necessary to extract the pigments and characterise them by examining the pure products to obtain conclusive results. W. G.

Effect of Temperature and of the Concentration of Hydrogen Ions on the Rate of Destruction of Antiscorbutic Vitamin (Vitamin-C). H. C. SHERMAN, V. K. LA MER, and H. L. CAMPBELL (*Proc. Nat. Acad. Sci.*, 1921, **7**, 279—281).—Guinea pigs were used and both the survival period and post-mortem findings were taken into account in estimating activity of solutions. Boiling tomato juice (P_H 4.3) for one hour destroyed 50%, for four hours 68%; the curve is much flatter than for a unimolecular reaction. The temperature coefficient for 10° between 60° and 80° was 1.23, between 80° and 100°, 1.12. Partial neutralisation or making alkaline causes the vitamin to be destroyed at a somewhat greater rate. Ninety to ninety-five % is destroyed in five days even at 10°, at an alkalinity of only $P_H=9$ (cf. Delf, A., 1920, i, 460). G. B.

Occurrence of a Crystalline Tannin in the Leaves of the *Acer ginnala*. ARTHUR GEORGE PERKIN and YOSHISUKE UYEDA (*T.*, 1922, **121**, 66—76).

Barbassu Nuts. HENRI JUMELLE (*Mat. grasses*, 1921, **13**, 5878—5879).—The nuts (genus *Orbignia*) contain: Water 4.21%, oil 66.12%, carbohydrates 14.47%, protein 7.18%, cellulose 5.99%, ash 2.03%. The oil has the following constants: m. p. 26°, solidification point, 22.7°, saponification number, 247.7, ether number, 242.9, iodine number, 16.83, Reichert-Meissl number, 6.2, Polenske number, 11.3, glycerol 13.2%. The cake has the following composition: Water 11.59, oil 6.50, proteins 19.81, carbohydrates 40, cellulose 16.50, ash 5.60%. CHEMICAL ABSTRACTS.

Application of Bourquelot's Biochemical Method to some Members of the *Caryophyllaceae* and *Papilionaceae*. CHARLES VERGELOT (*Bull. Soc. chim. Biol.*, 1921, **3**, 513—519).—By the successive action of invertase and emulsin on plant extracts, and observation of the rotation and reducing power, the author concludes that *Stellaria holostea* contains sucrose, but *Saponaria officinalis*, *Genista sagittalis*, *Ervum hirsutum*, and *Anthyllis vulneraria* contain other unknown sugars. Glucosides are indicated in most cases, and their extraction might be attempted from *Genista sagittalis*, *Ervum tetraspermum*, and *Saponaria officinalis*. G. B.

The Food Relations of *Fusarium lini*. YOSHIHIKO TOCHINAI (*Ann. Phytopath. Soc. Japan*, 1920, **1**, 22—33).—The fungus utilises carbohydrates as sources of carbon in the following descending order: inulin, dextrose, maltose, arabin, soluble starch, lævulose,

galactose, sucrose, and lactose. As indicated by the growth made, organic acids as sources of carbon are unfavourable to the fungus; the descending order of utilisation is as follows: succinic, malic, citric, fumaric, maleic, and racemic acids. *d*-Tartaric acid is more readily assimilated than *l*-tartaric acid. Mannitol, but not glycerol, is a favourable source of carbon. Phenol derivatives prevent growth. Organic nitrogen compounds, particularly amides, are far better sources of nitrogen than inorganic compounds.

CHEMICAL ABSTRACTS.

Hazel-nut oil and the Estimation of Arachidic acid. J. PRITZKER and R. JUNGKUNZ (*Z. Unters. Nahr. Genussm.*, 1921, **42**, 232—241).—The following characters were given by two samples of hazel-nut oil prepared in the laboratory: d_{4}^{15} 0.9152, 0.9156; n_D 54.2, 54.4; acid number 0.8, 1.7; saponification number 191.8, 189.1; iodine number (Hanus) 83.8, 85.4; Reichert-Meissl number 1.54; Polenske number 0.5; unsaponifiable matter 0.58%. Thorough investigation showed that there was no arachidic acid present. The following acetone method was used for the estimation of arachidic acid: 20 grams of the oil were saponified with 40 c.c. of 20% potassium hydroxide, and the clear solution was diluted with 50 c.c. of hot water and 20 c.c. of 25% hydrochloric acid were added. After fifteen minutes, the fatty acids were separated and dissolved in 180 c.c. of boiling acetone. Twenty c.c. of *N*-aqueous potassium hydroxide were added and the solution was allowed to cool and kept at 15° for half an hour. The crystals obtained were washed several times with small quantities of acetone, dissolved in water, the fatty acids liberated with hydrochloric acid, and dissolved by warming with 50 c.c. of 90% alcohol. The solution was slowly cooled and left for three hours at 15°. If arachidic acid is present, the precipitate consists of fine laminae. It is filtered, washed three times with 10 c.c. of 90% alcohol, and transferred to a weighed flask by dissolving in boiling alcohol. The alcohol is evaporated and the residue dried at 100° and weighed. Crude arachidic acid has m. p. 72—75°. If the m. p. is below 70°, the residue must be again recrystallised from 90% alcohol and reweighed. The quantity obtained is corrected for its solubility in 90% alcohol. This method does not require large quantities of alcohol and ether, and the troublesome manipulation of the lead soap is avoided. Schädler and Knorr's colour reactions for hazel-nut oil are found to be untrustworthy.

H. C. R.

The Chemical Constituents of some *Loranthaceae*. D. H. WESTER (*Rec. trav. chim.*, 1921, **40**, 707—723).—Leaves of *Loranthus pentandrus*, *L. globosus*, *L. atropurpureus*, and *Viscum album* were examined with respect to their chemical constituents. The ash of the leaves was determined and also the percentage of manganese in the ash, figures for the latter being rather high. From the first two species a glucoside identical with quercitrin was isolated, although its properties were not in all respects identical with those

previously described. The author states that a previous specimen of quercitrin prepared by him showed similar discrepancies, m. p. being 174—176°, not 182—185°, and the benzoate has m. p. 187—189°, not 239°, whilst the author's specimens recombine with water of crystallisation which is lost on heating and the solubility in 95% alcohol is 1 part in 70·5 parts, not 1 in 229.

The m. p. of quercitrin from *Loranthus* is lowered as the substance is purified. Its solubility in various solvents is described qualitatively and, in some cases, quantitatively. Three reactions are given which serve to distinguish quercitrin from quercetin: with ferric chloride and ether, the latter gives characteristic colours, the former no reaction; with zinc and hydrochloric acid in presence of amyl alcohol, the former gives a red coloration after some hours, the latter a yellow tint; with a soluble silver salt, the former gives no reaction, the latter a red coloration which turns blue and finally gives a black precipitate of metallic silver. The last test is stated to confirm the formula for quercitrin suggested by Perkin and Everest ("The Natural Colouring Matters," 1918). The brown coloration given by both substances on boiling with ferric chloride is due to separation of colloidal ferric hydroxide. Quercetin has *d* 1·6; that of quercitrin is lower.

The glucoside sugar consists entirely of rhamnose. Wax from *Loranthus* species is complex; the only constituent definitely identified is melissic alcohol, but this was not found in *L. atropurpureus*, neither was quercitrin obtained from this species. *Viscum album* does not contain invertase, reductase, amylase, emulsin, tannin, nor glucoside; however, xanthophyllin and a volatile alkaloid were obtained, but the experience of previous workers that it is difficult to extract pure substances from this species is confirmed.

H. J. E.

The Presence of Sucrose and Aucubin in the Seeds of *Melampyrum arvense*, L. MARC BRIDEL and (Mlle) MARIE BRAECKE (*Compt. rend.*, 1921, **173**, 1403—1405; cf. A., 1921, i, 840).—The presence of a glucoside in the seeds of *Melampyrum arvense*, decomposable by emulsin giving a black product has previously been indicated (*loc. cit.*). Aucubin has now been extracted in definite crystalline form from these seeds, and sucrose has also been isolated. Ludwig and Muller have isolated a glucoside from these seeds (cf. *Archiv Pharm.*, 1872, **199**, 6), which they considered to be identical with rhinanthin obtained from the seeds of *Rhinanthus Crista-Galli*, L. (*Archiv Pharm.*, 1870, **192**, 199), but the authors consider further work is necessary to establish the identity or otherwise of aucubin and rhinanthin.

W. G.

The Changes which Oranges Undergo on Keeping. G. ANDRÉ (*Compt. rend.*, 1921, **173**, 1399—1401).—When oranges, cut in halves, are kept under sterile conditions they undergo a slight loss in weight, which is accompanied by a marked loss in acidity and a slighter diminution in sugar content together with inversion of some of the sucrose. These changes are not entirely

due to oxidation, as they proceed to a less extent in a vacuum. It is probable that there is also some diastatic action. W. G.

Presence in Several Indigenous Orchids of Glucosides yielding Coumarin on Hydrolysis. H. HÉRISSEY and P. DELAUNEY (*Bull. Soc. Chim. Biol.*, 1921, **3**, 573—579).—A glucoside yielding coumarin on hydrolysis by dilute sulphuric acid or by emulsin is contained in the following three species of orchids: *Orchis purpurea*, Huds., *O. Simia*, Lam., *O. militaris*, L. (cf. Bourquelot and Hérissé, A., 1920, i, 586). This glucoside is not identical with loriglossin (Bourquelot and Bridel, A., 1919, i, 243; Delauney, A., 1920, i, 801, and A., 1921, i, 296), which does not yield coumarin on hydrolysis. E. S.

Occurrence of Ellagic Acid in *Rubus Idaeus*. The Cause of the Clouding of Raspberry Juice. HERMANN KUNZ-KRAUSE (*Arch. Pharm.*, 1921, **259**, 193—206).—Raspberry juice on keeping becomes cloudy owing to the deposition of a small quantity of a microcrystalline substance, the formation of which is accelerated by the addition of small quantities of a mineral acid. This deposit was collected, and decolorised and purified by warming in sodium hydroxide solution with hydrogen peroxide, and reprecipitating with acetic acid, and was identified as ellagic acid by analysis of its pyridine compound, $(C_{14}H_6O_8 \cdot H_2O) \cdot 2C_5H_5N$, and by characteristic reactions with alkali hydroxides, ferric chloride, nitrous acid, etc. The ellagic acid does not apparently exist as such in the fruit itself or initially in the fruit juice, but originates from a molecular complex of a higher order such as a tannoid or, possibly even, from the red colouring matter of the fruit.

G. F. M.

Water-soluble Colouring Matters of the *Schizophyceae*. KARL BORESCH (*Biochem. Z.*, 1921, **119**, 166—214).—The aqueous extracts of the water-soluble colouring matters of pure cultures of numerous species of *Schizophyceae* were examined spectrophotometrically. Phycocyan, a blue colouring matter with a maximum absorption between the *C* and *D* lines, occurred alone in some species, in others mixed with phycoerythrin, a red colouring matter with an orange-yellow fluorescence and an absorption maximum in the green between the lines *D* and *E*. The latter pigment also occurred singly in certain species. When mixed, the two pigments were separable by capillary analysis. H. K.

Sakoa Oil from Madagascar. HENRI JUMELLE (*Mat. grasses*, 1921, **13**, 5854—5855).—Sakoa is the name given to *Sclerocarpa caffra*. The fruits are drupes and have an acid pulp owing to the presence of citric acid. The seeds contain 56% of oil having the following constants: d^{15}_4 0.9167, n^{40}_D 1.460, saponification number 193.5, iodine number 76.6, Reichert-Meissl number 0.1, Polenske number 0.45, unsaponifiable matter 0.6%, m. p. of fatty acids 25°. The oil is non-drying. CHEMICAL ABSTRACTS.

Alcohol-soluble Protein of the Caryopsis of *Sorghum vulgare*. I. **Extraction and Identification.** SABATO VISCO (*Arch. Farm. sperim. Sci. aff.*, 1921, **31**, 173—176).—Hot 70% aqueous alcohol extracts from the ground caryopsis of *Sorghum vulgare* about 3·5% of a nitrogenous substance, which is named *sorgein* and is classified with the prolamines. It gives the principal colour reactions of the proteins, but not the Adamkiewicz or the Liebermann reaction. In the isolation of the compound, two fractions were obtained which contain respectively 11·19% and 13·61% of nitrogen and may be different compounds. T. H. P.

The Biochemistry of Tobacco. II. **Tobacco Seeds.** G. PARIS (*Bot. tec. [R. ist. sci. sper. tabacco, Scafati]*, 1920, **17**, 101—115; cf. A., 1917, ii, 227).—The entire seed contains: water, 9·17%; crude protein, 21·87%; fat, 37·68%; amides and sugar, 6·05%; pentosans, 2·9%; cellulose, 7·15%, and ash, 3·84%. The ash contains SO_3 , 1·97%; P_2O_5 , 22·12%; Na_2O , 3·48%; K_2O , 28·5%; CaO , 9·54%; MgO , 14·63%. A sample of oil from Kentucky tobacco seed had d^{15}_4 0·9408; temperature of solidification, 12°; acid number, 4; saponification number, 196; iodine number, 132·8; ether number, 192. The oil consisted of about 52·4% of olein, 22·1% of linolein, and 23·9% of palmitin. No nicotine was found in tobacco seed, except in slight quantities in the germinating seed. The dry, fat-free seed contained 6·5% of total nitrogen, 3·76% of protein nitrogen, 2·39% of nuclein nitrogen, and 0·35% of non-protein nitrogen. The presence of arginine was established. CHEMICAL ABSTRACTS.

Hesperidine-like Substances in the *Umbelliferae*. HAROLD NILSSON (*Svensk Farm. Tidskr.*, 1921, **25**, 233—238).—The paper gives a brief résumé of the chemistry, properties, and tests for hesperidine. Microscopic sections are best made after fixing with lactic acid and freezing. Microscopically the alkaloid is detected as spherocrysts and sheaves. These are soluble in pyridine and quinoline. Seventy specimens were examined; either the spherocrysts or sheaves were noted in the leaves and stems of the following: *Angelica archangelica*, *A. atropurpurea*, *A. decurrens*, *A. litoralis*, *A. silvestris*, *Acthusa cynapium*, *Bubon galbanum*, *Conium maculatum*, *Ferula communis*, *F. neapolitana*, *F. scorodosma*, *Imperatoria ostruthium*, *I. hispanica*, *Libanotis siberica*, *Ligusticum scoticum*, *Sesili glaucum*, *S. tenuifolium*, *Trinia vulgaris*. The presence of the alkaloid was also confirmed by chemical tests. In the fourth, sixth, and eighth there was also a positive test for the fruit. CHEMICAL ABSTRACTS.

Action of Coal Gas on Plants. C. WEHMER (*Bied. Zentr.*, 1921, **50**, 425—428).—The author has examined the effect of coal gas on three- to seven-year old trees grown in pots. In winter, the trees are scarcely affected, but in spring they wither and gradually die. Fir and elm trees are especially sensitive, then come maple, whilst lime trees are least sensitive. The trees survive

the action of coal gas in the autumn. From these experiments and further experiments on twigs immersed in water saturated with coal gas it is concluded that the harmful effect of coal gas is most pronounced when the root system commences its activity after winter, and is not due to action on the foliage. The harmful effect is due to certain constituents in the gas, particularly those which impart an odour to the gas. Hydrocyanic acid is particularly harmful.

W. G.

Availability of Organic Nitrogenous Compounds. C. S. ROBINSON, O. B. WINTER, and E. J. MILLER (*J. Ind. Eng. Chem.*, 1921, **13**, 933—936).—It is probable that all amino-nitrogen present in soil in the form of α -amino-acids and a portion of that nitrogen present as acid amides may be added to the class of substances constituting the source of immediately available nitrogen, the chief members of this class being inorganic compounds of ammonia and nitric acid. Peptides may form a class of potentially available compounds; in some cases the peptides in fertilisers are readily hydrolysed to amino-acids and primary and secondary amines.

W. P. S.

Effect of Alum on Silicate Colloids. C. S. SCOFIELD (*J. Washington Acad. Sci.*, 1921, **11**, 438—439).—The removal of soluble salts from certain soils of the western United States by irrigation and drainage leads to serious trouble through the effect of colloidal silicates, principally sodium silicate, on soil texture. By the addition of alum as a dressing insoluble aluminium silicates are formed and sodium sulphate thereby formed is removable in drainage. Analyses of the drainage from soils to which aluminium sulphate had been applied showed that practically all the aluminium had been precipitated by the soil and that equivalent amounts of sodium, calcium, and magnesium had been liberated combined with the sulphate radicle.

G. W. R.

The Flocculation of Soils. II. NORMAN M. COMBER (*J. Agric. Sci.*, 1921, **11**, 450—471).—"Direct" flocculation of the clay soils by salts of iron and aluminium occurs in a manner precisely similar to the coagulation of electro-negative suspensoids by electrolytes. "Indirect" flocculation by neutral salts and some acids results from interaction with the constituents of the clay particle whereby normal flocculating agents are produced. The "abnormal" flocculation of clay by calcium hydroxide is a result of the reaction of lime with the emulsoid surface layer of the clay particle, and does not depend on the formation of calcium carbonate. The difference in the action of flocculating agents on clay and silt particles depends entirely on the relative proportions of emulsoid surface layer to core in the particle. (See also *J. Soc. Chem. Ind.*, 1922, 69A.)

A. G. P.

Organic Chemistry.

The Chemical Nature of Mineral Lubricating Oils. A. E. DUNSTAN and F. B. THOLE (*J. Inst. Petroleum Tech.*, 1921, 7, 417—421).—Mineral lubricating oils appear to contain but a small percentage of paraffin hydrocarbons of the C_nH_{2n+2} series, and consist chiefly of compounds the formulæ of which range from C_nH_{2n} to C_nH_{2n-8} . The olefine contents cannot be determined by extraction with sulphuric acid, as they are thereby converted into condensation products insoluble in the acid. A partial separation of unsaturated hydrocarbons can be achieved by extraction with liquid sulphur dioxide, an oil with an iodine value 46 giving, for example, a residue with iodine value 33 and an extract with iodine value 73. The reaction of mineral oils towards iodine differs profoundly from that of fatty oils, as no constant iodine value can be obtained, an increase in the proportion of reagent to oil invariably augmenting the value. This fact, coupled with the reluctance exhibited to hydrogenation, seems to lead to the conclusion that the unsaturated hydrocarbons in mineral oils consist only to a small degree of true olefines. The saturated compounds are principally naphthenic and probably polynuclear. Solid resinous components containing oxygen are present to the extent of a few parts per cent., and are probably an important cause of "gumming." Removal of these substances, and the more readily oxidisable unsaturated hydrocarbons reduces the gumming tendency, but in oil refining care should be taken not to destroy the more stable unsaturated hydrocarbons, to which the viscosity of the oil is largely due, it having been shown that an increase in viscosity occurs concurrently with a decrease in the hydrogen content.

G. F. M.

The Hydrogenation of Ethylene in Contact with Nickel. ERIC KEIGHTLEY RIDEAL (*T.*, 1922, 121, 309—318).

Bivalent Carbon. ALFRED GILLET (*Bull. Soc. chim. Belg.*, 1921, 30, 329—336).—A theoretical paper in which some evidence is adduced to show the existence of certain bivalent carbon compounds either as unstable intermediate substances or as isomerides of differing degrees of stability.

H. J. E.

The Exchange of Halogen in Unsaturated, Aliphatic Halogenated Hydrocarbons. I. H. P. KAUFMANN (*Ber.*, 1922, 55, [B], 249—267).—It is shown in a variety of ways that the iodine atoms of the stereoisomeric *s*-di-iodoethylenes are removed with much greater difficulty than those of similar saturated aliphatic iodo-compounds. The most probable explanation is that the unsaturated hydrocarbon residue in the immediate vicinity of the halogen atom makes such a complete demand on the affinity

of the latter that but little remains for the attraction of a new atom, whereas the saturated hydrocarbon residue saturates the affinity of the halogen atom less completely and so leaves it more disposed to react with reagents in general.

Solid $\alpha\beta$ -di-iodoethylene, m. p. 73° , is conveniently prepared by allowing a solution of iodine in absolute alcohol to remain in contact with acetylene gas under slightly increased pressure and at the atmospheric temperature; the liquid isomeride has b. p. 185° .

A solution of the solid di-iodide in anhydrous ether reacts quantitatively with activated magnesium in accordance with the equation: $C_2H_2I_2 + Mg = C_2H_2 + MgI_2$; in all probability, an unstable organo-metallic compound is formed primarily. Metallic potassium is slowly attacked by a boiling solution of solid di-iodoethylene in anhydrous ether with ultimate production of acetylene and potassium iodide; the formation of $\alpha\alpha$ -di-iodoethylene (see below) during the reaction is established. The latter is prepared more conveniently by allowing the ethereal solution of the solid di-iodide (or more rapidly from the liquid isomeride) to remain in contact with metallic sodium at the atmospheric temperature. It forms colourless crystals which sublime with great ease, m. p. 56° ; the vapours have an extremely unpleasant odour and attack the eyes with great violence. When dissolved in carbon tetrachloride and treated with bromine in direct sunlight, it is transformed into $\alpha\alpha$ -dibromoethylene, yellow leaflets, m. p. 90° , which is thus prepared in the dimeric form, $(C_2H_2Br_2)_2$. If an excess of bromine is used, $\alpha\alpha\alpha\beta$ -tetrabromoethane is produced, which is formed also by the further action of bromine on the solid, dimeric dibromide. Similar $\alpha\alpha$ -di-iodoethylene is converted by an excess of chlorine in the presence of bright sunlight into $\alpha\alpha\alpha\beta$ -tetrachloroethane, b. p. 135° , and iodine trichloride. $\alpha\alpha$ -Di-iodoethylene is decomposed by potassium or activated magnesium in the presence of anhydrous ether with quantitative formation of acetylene.

trans- and *cis*- $\alpha\beta$ -Di-iodoethylene and $\alpha\alpha$ -di-iodoethylene are decomposed with liberation of iodine when their ethereal solutions are exposed to ultra-violet light, the velocity of the reaction in the case of the compound first named being approximately twice as great as that in the remaining two cases.

[With F. SCHWEITZER.]—A solution of solid $\alpha\beta$ -di-iodoethylene in anhydrous ether is attacked slowly by zinc ethyl when the mixture is heated until it becomes slightly turbid and subsequently exposed to direct sunlight during several weeks; the main product is α -iodo- Δ^a -butylene, $CHI:CHEt$, a pale yellow liquid which decomposes gradually when exposed to light, b. p. 127 – 128° /atmospheric pressure, or 57° /30 mm. The same product is mainly obtained in a similar manner from the liquid $\alpha\beta$ -di-iodoethylene, but, in this case, an *isomeride* (probably the *cis*-modification), b. p. 168° , is produced in minor amount. It is converted by an excess of bromine in the presence of carbon tetrachloride into $\alpha\alpha\beta$ -tribromobutane, $CHBr_2 \cdot CHBr \cdot CH_2 \cdot CH_3$, a pale yellow liquid, b. p. 158° (partial decomp.)/normal pressure, or 98° /25 mm. The chief evidence with regard to the constitution of the iodobutylene rests on the observation

that it is converted by sodium into the *hydrocarbon* [Δ^8 -octadiene], C_8H_{14} , a colourless, slightly refractive liquid, b. p. 138—140°. The latter is transformed by ozone into the explosive *ozonide*, a yellowish-red, viscous liquid, which is decomposed by boiling water into glyoxal, propaldehyde, and hydrogen peroxide.

The transformation of the liquid (*cis*) $\alpha\beta$ -di-iodoethylene into the solid (*trans*-) modification has been observed repeatedly. The reverse change occurs to the extent of 45° in six hours, when the solid isomeride is heated carefully at 190°; slight decomposition with elimination of iodine occurs simultaneously. H. W.

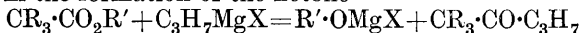
The System Water-Ethyl Alcohol-Chloroform: Miscibility of the Three Components in Different Proportions and some Practical Applications. N. SCHOORL and (MLLE) A. REGENBOGEN (*Rec. trav. chim.*, 1922, **41**, 1—14).—The ternary system has been examined and a diagram is given showing the limits of homogeneous mixtures at temperatures of 0°, 10°, 20°, and 66°. The results obtained by Bancroft (A., 1895, ii, 157) are criticised on the ground of incomplete drying of the alcohol used. The authors suggest that their data may be of use in the examination of spirits of wine for water content, and of chloroform for the detection of impurities. Details of some typical estimations carried out in this manner are given. H. J. E.

The System Ethyl Alcohol-Water-Aromatic Hydrocarbons from 30° to -30°. W. R. ORMANDY and E. C. CRAVEN (*J. Inst. Petroleum Tech.*, 1921, **7**, 422—439).—The freezing-point curves of binary mixtures of benzene with ethyl alcohol, toluene, and xylene, and of ternary mixtures of benzene, alcohol, and water, and of "benzole" (benzene 3, toluene 1), alcohol, and water were determined, and also the liquid separation points of ternary mixtures of benzene, toluene, and xylene with alcohol and water at temperatures ranging from -30° to +30°. The method adopted was to add from a burette dilute aqueous alcohol to known mixtures of absolute alcohol and the hydrocarbon, maintained at a constant temperature, until separation occurred. The full numerical results are given in numerous tables, and results obtained by graphical interpolation are also given showing the strengths of ethyl alcohol necessary to dissolve various proportions of benzene and toluene at 15° and xylene at 0°. For these, the original paper should be consulted. In regard to the binary mixtures of benzene and toluene, the depression of the freezing point of benzene follows the cryoscopic law over a considerable range. The results of the liquid separation point determinations on the ternary mixtures showed that at any temperature above the melting point of benzene the solubilities of the three hydrocarbons in an alcohol of given strength are in the order benzene-toluene-xylene. At temperatures below this, separation of solid phase occurs and the solubility of benzene falls below that of its homologues. G. F. M.

Some Properties of $\alpha\alpha$ -Disubstituted Esters. J. LEROIDE (*Ann. Chim.*, 1921, [ix], **16**, 354—410).— $\alpha\alpha$ -Disubstituted ketones react with magnesium alkyl haloids, in which the alkyl group has

a normal chain and not more than four carbon atoms, to give excellent yields of the corresponding secondary alcohols. Thus pinacolin reacts with magnesium propyl chloride to give $\beta\beta$ -dimethylbutan- γ -ol. Under similar conditions, camphenylone gives camphenylol. With magnesium propyl bromide, fenchone gives fenchyl alcohol and camphor gives a mixture of borneol and isoborneol.

The esters of $\alpha\alpha$ -disubstituted monobasic acids react with the same magnesium alkyl haloids to give principally secondary and not tertiary alcohols. This action is more marked with the magnesium alkyl iodides than with the bromides or chlorides. In all cases it is very slow, and the yields are by no means quantitative. This is probably due to the fact that the first part of the change consists in the formation of the ketone



which only takes place very slowly.

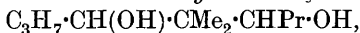
Ethyl pivalate reacts with magnesium ethyl iodide to give $\beta\beta$ -dimethylpentan- γ -ol, $\text{CMe}_3\cdot\text{CHEt}\cdot\text{OH}$, b. p. 140—148°, giving a *phenylurethane*, m. p. 83°; with magnesium propyl iodide, bromide, or chloride the products are $\beta\beta$ -dimethylhexan- γ -ol, $\text{CMe}_3\cdot\text{CHPr}\cdot\text{OH}$, b. p. 153—156°/755 mm.; n_D^{17} 1.4280; d^{17} 0.830, giving a *phenylurethane*, m. p. 68—69°; and $\beta\beta$ -dimethyl- γ -propylhexan- γ -ol, $\text{CMe}_3\cdot\text{CPr}_2\cdot\text{OH}$, b. p. 90°/20 mm.; n_D^{18} 1.4455; d^{18} 0.853. The ratio of the yield of secondary alcohol to that of the tertiary alcohol is greatest with magnesium propyl iodide and least with magnesium propyl chloride. On oxidation with chromic acid in acetic acid solution, $\beta\beta$ -dimethylhexan- γ -ol gives *tert.-butyl propyl ketone*, $\text{CMe}_3\cdot\text{COPr}$, b. p. 145—148°; n_D^{17} 1.4148; d^{17} 0.8225.

Ethyl pivalate reacts with magnesium butyl iodide to give $\beta\beta$ -dimethylheptan- γ -ol, $\text{CMe}_3\cdot\text{CH(OH)}\cdot\text{C}_4\text{H}_9$, b. p. 76—79°/16 mm., giving a *phenylurethane*, m. p. 65°.

To examine the effect of heavier groups in the α -position in the disubstituted esters, ethyl α -methyl- α -propylvalerate has been prepared as follows and used. α -Propylvaleric acid yields with thionyl chloride the *acid chloride*, b. p. 77—79°/20 mm., which with benzene in the presence of aluminium chloride gives *phenyl α -propylbutyl ketone*, $\text{CHPr}_2\cdot\text{COPh}$, b. p. 157—159°/25 mm.; n_D^{18} 1.5064; d^{18} 0.9492 which with sodamide followed by methyl iodide gives some impure phenyl α -methyl- α -propylbutyl ketone. The latter ketone is better prepared by propylating propiophenone, which gives *phenyl α -methylbutyl ketone*, $\text{CHMePr}\cdot\text{COPh}$, b. p. 122—125°/14 mm.; n_D^{17} 1.5109; d^{17} 0.964, and this on further propylation yields *phenyl α -methyl- α -propylbutyl ketone*, $\text{CMePr}_2\cdot\text{COPh}$, b. p. 149—152°/13 mm.; n_D^{18} 1.5063; d^{18} 0.9502. The latter ketone on treatment with sodamide and subsequent hydrolysis with hydrochloric acid yields α -methyl- α -propylvaleric acid, $\text{CMePr}_2\cdot\text{CO}_2\text{H}$, m. p. 43—44°; b. p. 124—128°/18 mm., giving an *amide* and an *ethyl ester*, b. p. 90—92°/18 mm., which with magnesium propyl bromide yields δ -methyl- δ -propyloctan- ϵ -ol, $\text{CH}_2\text{Me}\cdot\text{CH}_2\cdot\text{CMePr}\cdot\text{CHPr}\cdot\text{OH}$, b. p. 109—112°/18 mm.; $n_D^{16.5}$ 1.4421; $d^{16.25}$ 0.8455; giving a *phenylurethane*, m. p. 96°, and its *hydrate*, m. p. 89—91°.

Ethyl campholate gives with magnesium propyl chloride or bromide 1 : 2 : 2 : 3-tetramethylcyclopentylpropylcarbinol, $\text{CHMe} \cdot \text{CMe}_2 > \text{CH}_2 - \text{CH}_2 > \text{CMe} \cdot \text{CHPr} \cdot \text{OH}$, m. p. 58°; b. p. 126—129°/15 mm. Using a straight chain ester of high molecular weight, namely, ethyl palmitate, a secondary alcohol was also obtained with magnesium propyl bromide, the product being *nonadecan-8-ol*, $\text{C}_{15}\text{H}_{31} \cdot \text{CHPr} \cdot \text{OH}$, m. p. 19°; b. p. 221—224°/15 mm., giving a *phenylurethane*, m. p. 50—51°.

The behaviour of the esters of $\alpha\alpha$ -disubstituted dibasic acids towards magnesium alkyl haloids is variable. Ethyl dimethylmalonate gives with magnesium propyl chloride a number of derivatives including a small amount of a bissecondary glycol, ethyl *isobutyrate*, dipropyl ketone, propyl *isopropyl ketone*, tripropylcarbinol, and dipropylcarbinol. There are thus apparently two reactions; one in which the molecule is split up giving tripropylcarbinol and the hydrocarbon resulting from its dehydration, and the other in which hydrogenation occurs. The new compounds isolated are : *εε*-dimethylnonan-8,9-diol,



m. p. 73°; b. p. 150—152°/18 mm.; *tripropylcarbinol phenylurethane*, m. p. 74—75°; *dipropylisopropylcarbinol phenylurethane*, m. p. 71—72°. To confirm the formation of dipropyl and propyl *isopropyl ketones*, a similar condensation of magnesium *isobutyl chloride* and ethyl dimethylmalonate was carried out and from the products *diisobutyl ketone semicarbazone*, m. p. 119°, and *isopropyl isobutyl ketone semicarbazone*, m. p. 139—140°, were isolated. To prove the constitution of the nonandiol described above, the following preparations were made. Ethyl butyrate was condensed with methyl propyl ketone in the presence of sodium ethoxide to give *dibutyrylmethane*, $\text{C}_3\text{H}_7 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_3\text{H}_7$, b. p. 96—98°/21 mm.; $n_D^{16.5}$ 1.46125; $d_4^{16.5}$ 0.9218, giving a *copper derivative*, m. p. 157—158°. On methylation, it yielded *αα*-dibutyrylethane, $\text{CH}_3 \cdot \text{CH}(\text{COPr})_2$, b. p. 124—126°/21 mm., giving a *copper derivative*, m. p. 140—141°, and on further methylation *ββ*-dibutyrylpropane, $\text{CMe}_2(\text{COPr})_2$, b. p. 129—130°/18 mm., which gave a *disemicarbazone*, m. p. 216°, identical with that obtained from the nonandiol.

With a view to elucidating the course of the reaction of the dimethylmalonic ester and magnesium propyl chloride, dipropyl ketone was condensed with ethyl bromoisobutyrate in dry benzene in the presence of zinc, giving *ethyl β-hydroxy-αα*-dimethyl-β-propylhexoate, $\text{HO} \cdot \text{CPr}_2 \cdot \text{CMe}_2 \cdot \text{CO}_2\text{Et}$, b. p. 135—136°/26 mm., which, when treated with magnesium propyl bromide, has its molecule ruptured in such a way as to give tripropylcarbinol and a magnesium additive compound.

Ethyl *αα*-dimethylsuccinate and magnesium propyl chloride yield 3 : 3-dimethyl-2 : 5 : 5-tripropyltetrahydrofuran, $\begin{matrix} \text{CH}_2 - \text{CPr}_2 \\ | \\ \text{CMe}_2 \cdot \text{CHPr} \end{matrix} > \text{O}$, b. p. 114—118°/15 mm.; n_D^{18} 1.4531; d_4^{18} 0.8629.

Ethyl *αα*-dimethylglutarate and magnesium propyl bromide give

$\alpha\alpha$ -dimethyl- $\delta\delta$ -dipropylvalerolactone, $\begin{array}{c} \text{CH}_2 \cdot \text{CMe}_2 \cdot \text{CO} \\ | \qquad \qquad \qquad | \\ \text{CH} \text{---} \text{CPr}_2 \end{array} > \text{O}$, b. p. 153—157/16 mm., n_D^{18} 1.4585, d_4^{18} 0.9311, giving a barium salt. Similarly, ethyl camphorate yields *dipropylcampholactone*, m. p. 58°; b. p. 177—180°/18 mm., giving a copper salt.

The presence of an alkyloxy-group in the ester results in the general reaction pursuing its normal course, giving a tertiary alcohol. Thus ethylethoxy- α -methylpropionate and magnesium propyl chloride give β -ethoxy- β -methyl- γ -propylhexan- γ -ol, $\text{OEt} \cdot \text{CMe}_2 \cdot \text{CPr}_2 \cdot \text{OH}$, b. p. 118—122°/35 mm.; n_D^{17} 1.4392; d_4^{17} 0.8864. Under similar conditions, ethyl β -hydroxy- $\alpha\alpha\beta$ -trimethylbutyrate gives $\beta\gamma\gamma$ -trimethyl- δ -propylheptan- $\beta\delta$ -diol, $\text{HO} \cdot \text{CMe}_2 \cdot \text{CMe}_2 \cdot \text{CPr}_2 \cdot \text{OH}$, m. p. 91°.

W. G.

Symmetrical Dichlorodimethyl Sulphide. IGNAZ BLOCH and FRITZ HÖHN (*Ber.*, 1922, **55**, [B], 53—57).—*Dichlorodimethyl sulphide* is prepared by cautious admixture of trithioformaldehyde and sulphur chloride and subsequent heating of the mixture under reflux after the initial violent action has subsided. It is an almost colourless liquid, b. p. 156—156.5°/765 mm., or 51°/11 mm. Its formation appears to take place in accordance with the equation: $(\text{CH}_2\text{S})_3 + 2\text{S}_2\text{Cl}_2 = \text{C}_2\text{H}_4\text{Cl}_2\text{S} + \text{CS}_2 + 2\text{HCl} + 4\text{S}$. It is converted by hot water into trithioformaldehyde and amorphous polyoxymethylene, and by methyl-alcoholic potassium hydroxide or ammonia solution into (?) polyoxymethylene and *s*-dimethoxydimethyl sulphide, b. p. 152°/760 mm. (cf. de Lattre, A., 1912, i, 745).

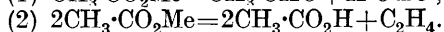
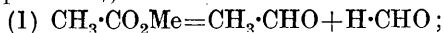
The formation of *s*-dichlorodimethyl sulphide from trithioformaldehyde brings additional confirmation of the constitution, $\text{S} < \begin{array}{c} \text{CH}_2 \cdot \text{S} \\ \text{CH}_2 \cdot \text{S} \end{array} > \text{CH}_2$, generally assigned to this compound. H. W.

Production of Alcohols, Ketones, and the Like [Lithium Formate, Methyl Alcohol, Acetone, etc.]. BADISCHE ANILIN- & SODA-FABRIK (Brit. Pat. 173097).—Carbon monoxide may be utilised for the production of alcohols, ketones, etc., through the intermediate formation of lithium formate, which when heated at 380—420°, preferably in a current of moist hydrogen under diminished pressure, is decomposed with the formation of methyl alcohol, acetone, formaldehyde, etc., in addition to oily and empyreumatic substances. Lithium formate is obtained by the action of carbon monoxide on lithium hydroxide or carbonate in presence of water at a temperature of 120—250° and a pressure of 20—70 atm. When absorption is complete, the solution is evaporated and the dry salt powdered and transferred to the decomposition plant, which may consist of a tube-shaped vessel with a conveyor worm, or of shallow pans or revolving drums heated in a bath of fused potassium nitrate. The residue after decomposition, consisting of lithium carbonate and carbon, may be utilised again for the production of formate, but provision must be made, by washing the gases or otherwise, for the removal of the carbon dioxide pro-

duced during absorption of the monoxide: $\text{Li}_2\text{CO}_3 + \text{H}_2\text{O} + 2\text{CO} = 2\text{HCO}_2\text{Li} + \text{CO}_2$.
G. F. M.

The Mode of Sudden Pyrogenic Decomposition of Acetic Acid at High Temperature. (MLLE) ÉGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1922, [iv], **31**, 113—118; cf. A., 1918, i, 1; 1920, i, 217; 1921, i, 156, 166).—The sudden decomposition of acetic acid vapour at 1150° takes place in such a way that the molecule is deformed as little as possible. There are three reactions of the first order, namely, (1) $2\text{CH}_3\cdot\text{CO}_2\text{H} = (\text{CH}_3\cdot\text{CO})_2\text{O} + \text{H}_2\text{O}$; (2) $\text{CH}_3\cdot\text{CO}_2\text{H} = \text{CO}_2 + \text{CH}_4$; (3) $2\text{CH}_3\cdot\text{CO}_2\text{H} = 2\text{H}_2\text{O} + 2\text{CO} + \text{C}_2\text{H}_4$; and two reactions of the second order, namely, (4) $\text{CO}_2 + \text{CH}_4 = \text{CO} + \text{H}_2 + \text{H}_2\text{O} + \text{C}$; (5) $\text{C}_2\text{H}_4 = \text{C}_2\text{H}_2 + \text{H}_2$. The importance of reaction (1) is greater as the velocity of flow of the acetic acid vapour is greater. In reaction (4), instead of the formation of free carbon, very condensed hydrocarbons are probably formed. W. G.

The Mode of Pyrogenic Decomposition of Methyl Acetate at High Temperature. (MLLE) ÉGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1922, [iv], **31**, 118—122; cf. preceding abstract).—In the pyrogenic decomposition of methyl acetate at high temperatures the two principal changes are:



The acetaldehyde formed in reaction (1) tends to decompose, giving methane and carbon monoxide, and the formaldehyde gives hydrogen and carbon monoxide. The acetic acid formed in reaction (2), which is less important than reaction (1), tends to decompose in the manner already described (*loc. cit.*). W. G.

Carboxylic Esters as Amphoteric Electrolytes. H. v. EULER and OLOF SVANBERG (*Z. physiol. Chem.*, 1921, **115**, 139—146).—Ethyl acetate acts as an amphoteric electrolyte, the constant K_a being about 10^{-16} and K_b about 10^{-20} . S. S. Z.

Manufacture of Chloro-acids. KIKUNAE IKEDA and SHINTARO KODAMA (Jap. Pat. 37211).—By the action of sodium nitrite, solid or in concentrated solution, on amino-acid hydrochlorides or their ester hydrochlorides in the presence of hydrogen chloride, chloro-acids or their esters are easily produced. For example, 1 part of leucine or its hydrochloride is dissolved in 1—2 parts of the water layer obtained in the previous manufacture of the chloro-acid from leucine, and saturated with hydrogen chloride; the corresponding quantity of 30% sodium nitrite solution is gradually added at the ordinary temperature. Chlorohexoic acid separates as an oil. It is separated from the water layer, dried with sodium sulphate, and distilled in a vacuum. The method is applied to crude leucine, phenylalanine, valine, alanine, etc. CHEMICAL ABSTRACTS.

Reactions between the Higher Fatty Acids and Salts of the Lower Fatty Acids. ARTHUR W. KNAPP and RAYMOND V. WADSWORTH (*Chem. News*, 1922, **124**, 44—45).—If finely-powdered sodium acetate is added to oils or melted fats, a gelatinous precipitate is

generally produced. Sodium propionate and sodium butyrate give similar results. Castor oil does not give a jelly. Pure glycerides do not give this reaction, which is due to the free fatty acids present. The jelly consists of soaps formed by the interaction of the salt and the free fatty acids. It is a reversible colloid. Sodium acetate is soluble in oleic acid, forming a viscous solution. When cooled this becomes a thick jelly. If the fatty acid is dissolved in absolute alcohol and the acetate added, a gelatinous precipitate of soap is formed almost immediately. The reaction is reversed by adding water.

H. C. R.

The Preparation of Acrylic Acid and some of its Derivatives.

J. H. N. VAN DER BURG (*Rec. trav. chim.*, 1922, **41**, 21—23; cf. Gaspary and Tollens, A., 1872, 814, and Moureu, A., 1893, i, 548).—The methods of preparation used hitherto are inconvenient when large quantities are required or give poor yields. The acid itself and some of its derivatives tend to polymerise on keeping and must therefore be freshly prepared. The sodium salt will keep indefinitely, and may be used as a starting-point. It is prepared from ethylene glycol, which gives a 70—80% yield of chlorohydrin. The latter is treated with sodium cyanide, the resulting nitrile being transformed into hydracrylic acid. The sodium salt of the latter, carefully dried, gives, on distillation with sulphuric acid, very pure acrylic acid, and on treatment with phosphorus oxychloride, the chloride of the acid.

H. J. E.

Two New Ammonium Molybdomalates. E. DARMOIS (*Compt. rend.*, 1922, **174**, 294—296; cf. A., 1920, ii, 575; 1921, i, 539).—From a study of the optical activity of solutions of different proportions of molybdic acid, malic acid, and ammonia, the existence of two laevorotatory compounds having the compositions $\text{MoO}_3 \cdot 2\text{C}_4\text{H}_6\text{O}_5 \cdot 2\text{NH}_3$ and $\text{MoO}_3 \cdot 2\text{C}_4\text{H}_6\text{O}_5 \cdot 4\text{NH}_3$, respectively, has been proved and these two compounds and the corresponding sodium and potassium salts have been isolated.

W. G.

Equilibrium in Solution of the Desmotropic-Isomeric Diacetylsuccinic Esters and its Colorimetric Estimation.

L. KNORR and H. P. KAUFMANN (*Ber.*, 1922, **55**, [B], 232—248).—Ethyl diacetylsuccinate has been isolated in two diketonic forms, namely, β -ester, m. p. 89° , γ -ester (formerly α_3 -ester), m. p. 30° , one dienolic form, α -ester (formerly α_4 -ester), and two keto-enolic forms, $\alpha\beta$ -ester (formerly α_1 -ester), a liquid and $\alpha_2\beta$ -ester (formerly α_2 -ester), m. p. 20° . The equilibrium in solution in various solvents and the rate of transformation of the isomerides have been measured at 30° with the aid of the deeply-coloured enolic iron salts according to the method of Wislicenus (cf. also Knorr and Schubert, A., 1911, i, 948). In methyl and ethyl alcohols, acetone, and chloroform, the rate of enolisation of the β -ester at 30° diminishes with decreasing dielectric constant of the solvent; in hexane, ether, or benzene, the change takes place too slowly to permit its measurement. The influence of temperature on the velocity of transformation and the relative proportions in the equilibrium mixtures has

been examined, mainly by comparison of the data obtained at 30° and at the boiling points of the solutions. The velocity of enolisation is found to increase with increasing temperature, but the composition of the equilibrium mixture is approximately constant. In $N/5$, $N/10$, and $N/20$ solution, the concentration of the β -ester is without influence on the velocity of transformation or the composition of the equilibrium mixture. The influence of the dielectric constant of the solvent on the composition of the equilibrium mixture could not be elucidated definitely.

Examination of the equilibrium in hexane and ether led to the observation of an unexpectedly high enolic content, indicating the possible presence of the dienol, m. p. 45°. This is shown by mechanical separation of the products to be actually the case. The presence of this ester in molten mixtures or in dissolved equilibrium mixtures has not been established previously.

The iron salt of ethyl α -diacetylsuccinate is obtained when a solution of the β -ester in absolute alcohol is treated successively with an alcoholic solution of sodium ethoxide and an ethereal solution of ferric chloride; it is a brown powder. The analysed product, however, appears to be basic in character. The salt, $\text{FeCl}_2 \cdot \text{O} \cdot \text{CMe} \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{CMe} \cdot \text{O} \cdot \text{FeCl}_2$, a voluminous, unstable, violet-black powder, is prepared by agitating the brown salt with a solution of ferric chloride in anhydrous ether.

H. W.

New Method of Preparing Gluconic Acid. ARTHUR R. LING and DINSHAW RATTONJI NANJI (*J. Soc. Chem. Ind.*, 1922, 41, 28—29T; cf. Herzfeld and Lenart, A., 1920, i, 143).—A slow, well-regulated current of chlorine (about one bubble per second) is passed through a solution of dextrose (20%) containing 0.025% of cobalt nitrate as catalyst and a quantity of calcium bromide corresponding in potential bromine content with 26% of the bromine used by Herzfeld and Lenart (*loc. cit.*). The temperature is maintained at 45—50°, and care is taken that this limit is not exceeded, otherwise the hypobromous acid may be converted into bromate. As the reaction proceeds, there is a constant accumulation of halogen acids, and to avoid their retarding action calcium carbonate is added from time to time. The reaction is complete in about four hours. The final solution when reaction has proceeded normally contains calcium gluconate, calcium chloride, and calcium bromide, and when concentrated appropriately deposits the former in the course of a few days, the yield being about 90% of that theoretically possible.

The use of calcium bromide and chlorine is preferable to that of bromine, since the latter acts more efficiently in the nascent state, and there is no loss of bromine by volatilisation under the correct experimental conditions.

H. W.

Colophenic Acid. OSSIAN ASCHAN (*Ber.*, 1922, 55, [B], 1—3; cf. A., 1921, i, 512).—The author is unable to share Fahrion's view of the identity of colophenic acid with oxyabiatic acid prepared by the autoxidation of colophony (A., 1907, i, 329; 1921, i, 792)

and points out that it is not possible for Fahrion's product to be homogeneous.

Colophenic acid is an excellent material for the preparation of varnishes. H. W.

Sulphiformin (Methanalsulphurous Acid). PHILIPPE MALVEZIN (*Ind. chimique*, 1921, 8, 311—314; from *Chem. Zentr.*, 1921, iii, 1118).—Sulphiformin, obtained by the distillation of formaldehyde in the presence of sulphur dioxide, has the formula $\text{OH}\cdot\text{CH}_2\cdot\text{O}\cdot\text{SO}\cdot\text{OH}$. It reduces Millon's reagent, and gives a violet coloration and precipitate with magenta solution. It decomposes readily, giving sulphur dioxide and formic acid. With aniline alone, a yellow dye is formed; in the presence of hydrochloric acid a red caoutchouc-like mass is formed; in the presence of acetic acid, a dye is obtained which is yellowish-green in the cold and orange-red on warming. Sulphiformin has antiseptic properties. G. W. R.

Laboratory Preparation of Acetaldehyde. CHESTER E. ADAMS and ROGER J. WILLIAMS (*J. Amer. Chem. Soc.*, 1921, 43, 2420—2421).—In the preparation of acetaldehyde by the oxidation of ethyl alcohol with sodium dichromate the yield is practically doubled if the mixture is stirred vigorously to disengage the acetaldehyde as fast as it is formed. The best proportions to use are 200 grams of sodium dichromate for 100 grams of alcohol.

W. G.

Production of Butaldehyde and Butyric Acid therefrom. MATTHEW ATKINSON ADAM and DAVID ALLISTON LEGG (Brit. Pat. 173004).—Butaldehyde is obtained by the dehydrogenation of *n*-butyl alcohol by passing it in a state of vapour over a fused copper oxide catalyst heated at 280—320°, and fractionally distilling the product. About 75% conversion is obtainable by one passage over the catalyst at a good speed; for example, 240 c.c. per hour using a $\frac{3}{4}$ -inch copper tube packed for 26 inches of its length with the catalyst. Butyric acid is prepared from the liquid aldehyde by adding a small proportion of an oxygen-carrying catalyst, for example, manganese butyrate, and introducing air or oxygen at either ordinary or higher pressures, with suitable cooling to maintain the liquid below the boiling point of the aldehyde.

G. F. M.

The Mode of Pyrogenic Decomposition of Acetone at High Temperature. (MLLE) ÉGLANTINE PEYTRAL (*Bull. Soc. chim.*, 1922, [iv], 31, 122—124; cf. this vol., i, 219).—The sudden pyrogenic decomposition of acetone at high temperatures consists almost exclusively of a simple scission of the molecule into keten, $\text{CH}_2\cdot\text{CO}$, and methane. The keten then decomposes, giving carbon monoxide and ethylene.

W. G.

Monosulphates of Dextrose and Sucrose. III. CARL NEUBERG and LUDWIG LIEBERMANN (*Biochem. Z.*, 1921, 121, 326—332).—By the action of chlorosulphonic acid in pure chloroform

at -10° on a pyridine solution of dextrose or sucrose, the mono-sulphates of these carbohydrates are obtained and can be isolated as the calcium salts, which are amorphous. The calcium salt from sucrose sulphate has $[\alpha]_D +48.0$, that from dextrose sulphate $[\alpha]_D +44.43$. Lactose reacts similarly, but no details are given.

H. K.

The Action of Ozone on Pure Solutions of Dextrose, Lævulose, and Sucrose. C. W. SCHONEBAUM (*Rec. trav. chim.*, 1922, **41**, 44—48).—Various workers in this field have obtained results which are mutually contradictory. The author finds that dextrose, lævulose, and sucrose in alkaline solution are decomposed quantitatively when ozonised, the products being carbon dioxide and water. Formic acid is obtained as an intermediate product. The reaction takes a considerable time, and, for this reason, various technical applications are suggested.

H. J. E.

New Observations on the Chemistry of the Sugars. II. H. KILIANI (*Ber.*, 1922, **55**, [B], 75—101; cf. A., 1921, i, 304).—Further experience of the oxidation of sugars and polyhydroxy-acids by nitric acid at the atmospheric temperature has emphasised the necessity of excluding air during the process. This is effected conveniently by performing the operation in Erlenmeyer flasks provided with ground-glass stoppers and inserting at one point between the neck and the stopper a small plug of long-fibred glass wool. It is now recognised that the oxidation may lead to the production of α -keto-acids, the predominance of aldehydic or ketonic product appearing to depend on the configuration of the original material.

Attempts to replace the use of bromine and sodium hydroxide by that of a filtered solution of bleaching powder in the oxidation of the primary alcoholic to the aldehydic group in the sugars have not been quite satisfactory, possibly owing to deficient alkalinity of the solution.

Action of Nitric Acid on Dextrose and d-Gluconic Acid.—The product of the oxidation is, in all probability, α -ketogluconic acid, $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}(\text{OH})]_3\cdot\text{CO}\cdot\text{CO}_2\text{H}$; the acid is unstable when preserved at the atmospheric temperature, and evolves carbon dioxide when its aqueous solution is boiled. After successive addition of hydrocyanic acid and hydrolysis, a dibasic acid is produced which evolves carbon dioxide more freely than the parent acid; inability to effect the completion of the latter change has prevented its definite characterisation as a substituted malonic acid.

Preparation of Rhammonic Acid.—The acid is prepared more conveniently by the older bromine method than by the new oxidation process. It is emphasised that the oxidation of aldoses by bromine is never quantitative and that with freely soluble acids and lactones it is advisable to boil the solution of the acid (which has been freed from hydrobromic acid) with chalk for at least three-quarters of an hour; the solution is evaporated to small bulk and the calcium salt is precipitated with alcohol and

decomposed subsequently with oxalic acid. Contrary to the statements of the literature, pure rhamnolactone does not reduce alkaline copper solutions.

Action of Nitric Acid on Rhamnonic Acid and Rhamnose.—The oxidation of either substance at the atmospheric temperature gives the lactone of α -ketorhamnonic acid in good yield. The product has m. p. (indefinite) 188° (decomp.) after becoming discoloured at 168° , $[\alpha]_D -25.2^\circ$. The solubility in water is about 1 part in 20 parts at 20° . It gives a *p*-nitrophenylhydrazone, $C_{12}H_{13}O_6N_3 \cdot H_2O$, long, yellow needles, m. p. 150° after softening and darkening above 130° . It retains the terminal methyl group of rhamnonic acid, since it is not oxidised by bromine water and yields acetic acid when treated with an aqueous suspension of silver oxide. The presence of the ketonic group in the α -position is deduced from the ability of the keto-lactone to evolve carbon dioxide from its boiling aqueous solution and the greater readiness with which the gas is evolved from the hydrolysed cyanohydrin of the keto-lactone.

Oxidation of α -Galaheptonic Acid by Nitric Acid.—*l*-Mannohepturonic lactone (from *d*-galactose), m. p. 205 – 206° (decomp.) after becoming discoloured at about 190° , is obtained in good yield from α -galaheptonic acid; the aldehydic nature of the product has been established.

Configuration of Digitoxone and Digitoxosecarboxylic Acid.—Digitoxose, $CH_2 \cdot [CH(OH)]_3 \cdot CH_2 \cdot CHO$, is oxidised by nitric acid to a dihydroxyglutaric acid and *meso*-tartaric acid, thus showing that the hydroxyl groups, 3 and 4, are in the *meso*-position to one another. Since the lactone of digitoxonic acid has been shown previously to be *l*ævorotatory, the annexed configuration can be assigned to digitoxonic acid on the basis of Hudson's rule. On the other hand, the proof of the *meso*-position of the 3- and 4-hydroxyl groups of digitoxonic acid can now be extended. The well-crystallised lactone of digitoxosecarboxylic acid is *l*ævorotatory ($[\alpha]_D -13.67^\circ$), as is also the *phenylhydrazone* of digitoxosecarboxylic acid (groups of needles, m. p. 145 – 148° , $[\alpha]_D -37.7^\circ$). In consequence, the newly-formed hydroxyl group in the production of cyanohydrin must be to the left and digitoxosecarboxylic acid receives the annexed configuration, in which the configuration of the 6-CH \cdot OH remains unelucidated.

Formation of Digitalonic Acid from Digitalose (cf. A., 1916, i, 493).—Digitalonic acid gives a well-crystallised, *l*ævorotatory lactone, and must therefore contain a hydroxyl group attached to carbon atom 4. The methoxyl group cannot be in position 5, since the acid does not give pure trihydroxyglutaric acid when oxidised by nitric acid. It must therefore have the latter group in position 3 or 2. The former possibility is discounted by the apparent inability of digitalose to yield an osazone. Since the *phenylhydrazone* of digitalonic acid is *l*ævorotatory ($[\alpha]_D$ about -16°)

the configuration $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \overset{\text{OH}}{\underset{\text{H}}{\text{C}}} \cdot \text{CH}(\text{OH}) \cdot \overset{\text{OMe}}{\underset{\text{H}}{\text{C}}} \cdot \text{CO}_2\text{H}$ may be assigned

to the parent acid.

Salts of Trihydroxyadipic Acid (from Metasaccharin).—The following salts are described, generally with particular reference to their solubility in water: calcium, strontium ($+4\text{H}_2\text{O}$), magnesium ($+3\text{H}_2\text{O}$), barium, potassium, $\text{C}_6\text{H}_8\text{O}_7\text{K}_2 \cdot \text{H}_2\text{O}$, silver, cadmium ($+2\text{H}_2\text{O}$), quinine. The behaviour of the calcium and quinine salts of *l*-trihydroxyglutaric acid is described in detail. The cadmium, barium, and calcium salts of α -galaheptanepentoldicarboxylic acid have been further investigated.

The crystallisation of *d*-galactonic acid is readily effected by evaporation of solutions of the acid (from the calcium salt and oxalic acid) in an open dish and subsequent treatment of the paste obtained in this manner with alcohol under conditions which are specified in detail in the original.

The preparation of the galaheptonic acid from *d*-galactone is described in detail, the process depending on a modification of Fischer's phenylhydrazide method.

The production of *l*-mannonic and *l*-gluconic acids from arabinose has been investigated further. Under conditions which are fully described, the cyanohydrin synthesis leads to the crystallisation of *l*-mannonamide, which is smoothly converted into *l*-mannonic acid by boiling barium hydroxide solution. The isolation of *l*-gluconic acid from the mother-liquors is conveniently effected by means of the brucine salt.

H. W.

The Partial Replacement of the Acid Groups in β -Penta-acetylglucose. PERCY BRIGL (*Z. physiol. Chem.*, 1921, **116**, 1—52).—The following compounds have been prepared:

α -Chloro- $\gamma\epsilon\zeta$ -triacetyl- β -trichloroacetylglucose from β -penta-acetylglucose and phosphorus pentachloride, forms long, white needles, m. p. 142° , $[\alpha]_{\text{D}}^{14} + 2.95^\circ$ in benzene. The position of the chlorine atoms was ascertained by various forms of saponification. $\beta\gamma\epsilon\zeta$ -Tetracetyl- α -trichloroacetylglucose from β -penta-acetylglucose, trichloroacetyl chloride, and phosphorus oxychloride, forms dense needles, m. p. 131° , $[\alpha]_{\text{D}}^{13} + 94.6^\circ$. $\alpha\gamma\epsilon\zeta$ -Tetracetyl- β -trichloroacetylglucose, by treating the tetrachloro-substance with anhydrous zinc chloride and acetic anhydride. A mixture of two isomerides obtained has m. p. 110 — 112° . The α -isomeride forms long, fine needles, m. p. 120° , $[\alpha]_{\text{D}}^{14} + 101.5^\circ$; the β -isomeride forms needles, m. p. 167° , $[\alpha]_{\text{D}}^{13-15} + 28.85^\circ$. α -Chloro- $\gamma\epsilon\zeta$ -triacetyl- β -monochloroacetylglucose, by reduction of tetrachlorine compound, needles, m. p. 81° . α -Chloro- $\gamma\epsilon\zeta$ -triacetylglucose, from the tetrachloro-compound with an ethereal solution of ammonia, crystallises in needles, m. p. 158° ; it exhibits multirotation, the initial $[\alpha]_{\text{D}}^{12} + 25.0^\circ$ rising to $+151.5^\circ$. α -Chloro- $\gamma\epsilon\zeta$ -triacetylglucose- β -chloro-

sulphinite, $\text{OAc} \cdot \text{CH}_2 \cdot \text{CH}(\text{OAc}) \cdot \text{CH} < \begin{array}{c} \text{CH}(\text{OAc}) \cdot \text{CH} \cdot \text{O} \cdot \text{SOCl} \\ \text{O} \text{ — — — } | \\ \text{CHCl} \end{array}$, by treating the last compound with thionyl chloride, has m. p. 103° (approx.).

$\alpha\beta$ -Dichloro- $\gamma\epsilon$ -triacetylglucose, from triacetylchloroglucose with phosphorus pentachloride, crystallises in platelets, m. p. 83° , $[\alpha]_D^{20} +65.6^\circ$. Triacetylglucal from triacetyldichloroglucose, by treatment with zinc dust. Acetobromoglucose was also converted into acetochloroglucose with mercuric chloride. S. S. Z.

The Synthesis of Disaccharides containing Sulphur and Selenium by combining two Dextrose Residues in the C⁶-position. Some New Derivatives of ζ -Bromoglucose. FRITZ WREDE (*Z. physiol. Chem.*, 1921, **115**, 284—304).—The following compounds have been prepared: Acetodibromoglucose from pentaacetyl glucose, $[\alpha]_D^{20} +184.1^\circ$ in ethyl acetate. Methylglucoside- ζ -bromohydrin triacetate, $[\alpha]_D^{20} -7.78^\circ$ in ethyl acetate, from the last compound. Triacetyl-ethylglucoside- ζ -bromohydrin from acetodibromoglucose and ethyl alcohol in the presence of dry silver carbonate, crystallises from methyl alcohol in compact needles, m. p. 154° (uncorr.); $[\alpha]_D^{18} -11.78^\circ$ in ethyl acetate. β -Tetra-acetyl- ζ -bromoglucose, by heating acetodibromoglucose with acetic anhydride and sodium acetate at 100° , melts at 127° (corr.). The α -form, produced at the same time, crystallises from methyl alcohol in fine, white needles, m. p. 171° , $[\alpha]_D^{18} +107.2^\circ$ in ethyl acetate. Dimethylglucoside of bisglucosyl ζ -sulphide hexa-acetate, from triacetylmethylglucoside- ζ -bromohydrin and alcoholic potassium sulphide by heating in a sealed tube, crystallises in white needles, m. p. 168° , $[\alpha]_D^{15} -10.51^\circ$ in ethyl acetate. Dimethylglucoside of bisglucosyl ζ -sulphide, from the hexa-acetate by treating it with absolute methyl alcohol and ammonia in the cold, crystallises in dense masses, m. p. 188° , $[\alpha]_D^{18} +6.53^\circ$ in water. Bisglucosyl ζ -sulphide, by heating the last compound with 5% sulphuric acid in a sealed tube, sinters at approximately 135° and liquefies at approximately 150° , $[\alpha]_D^{20} +80.9^\circ$ in water. Octa-acetyl-bisglucosyl ζ -sulphide, by acetylating the last compound, crystallises in nodules, m. p. 163° , $[\alpha]_D^{18} +56.2^\circ$ in ethyl acetate. Dimethylglucoside of bisglucosyl ζ -selenide hexa-acetate, prepared in the same way as the sulphide, crystallises in long, white needles, m. p. 179 — 180° . Dimethylglucoside of bisglucosyl ζ -selenide, prepared in the same way as the sulphide, crystallises from 90% alcohol in dense aggregates, m. p. 138° , $[\alpha]_D^{15} +14.59^\circ$ in water. Bisglucosyl ζ -selenide, by hydrolysis from the glucoside, sinters at approximately 160° , decomposes at approximately 200° , $[\alpha]_D^{14} +69.5^\circ$ in water. Octa-acetyl-bisglucosyl ζ -selenide, by acetylating the selenide with acetic anhydride, crystallises from ether and light petroleum in nodules, m. p. 150 — 155° , $\alpha_D +40^\circ$ (approx.). Dimethylglucoside of bisglucosyl ζ -diselenide hexa-acetate, by treatment of acetyl-methylglucoside- ζ -bromohydrin with an alcoholic solution of potassium diselenide, has m. p. 148° , $[\alpha]_D^{17} +49.74^\circ$ in ethyl acetate. Dimethylglucoside of bisglucosyl ζ -diselenide, by treatment with methyl alcohol solution and gaseous ammonia, crystallises from 98% alcohol in dense needles, m. p. 96 — 97° , $[\alpha]_D^{14} +75.65^\circ$ in water. Bisglucosyl ζ -diselenide, by hydrolysis of the methyl glucoside, decomposes at

approximately 125° , $[\alpha]_D^{18} +145.6^\circ$ in water. *Octa-acetyl-bis-glucosyl ζ -diselenide*, by acetylation of the last compound with acetic anhydride, forms small crystals which sintered at $175\text{--}179^\circ$.
S. S. Z.

Unsaturated Reduction Products of the Sugars and their Transformations. III. 2-Deoxyglucose (Glucodesose). MAX BERGMANN, HERBERT SCHOTTE, and WOLFGANG LECHINSKY (*Ber.*, 1922, 55, [B], 158—172; cf. A., 1921, i, 307, 648).—With the object of obtaining a derivative of dextrose so modified that a hydroxyl group is not present in position 2, glucal (A., 1913, i, 445; 1914, i, 252; 1920, i, 420) has been converted by dilute acid into 2-deoxyglucose, $\text{OH}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, which

has only been isolated previously in the form of its phenylbenzylhydrazone. In connexion with this substance, it is proposed to define a simple sugar as an aldehyde-alcohol or keto-alcohol with an open carbon chain and one or more hydroxyl groups, of which at least one is in the direct neighbourhood of the carbonyl radicle; deoxyglucose and Kiliani's digitoxose are therefore not within the class. It is also proposed to establish a nomenclature for the 2-deoxy-sugars by inserting the syllable "des" between the name of the sugar from which they are derived and the characteristic ending of all sugars "ose"; thus 2-deoxyglucose is termed "glucodesose."

2-Deoxyglucose is prepared by hydrolysing triacetylglucal by means of methyl-alcoholic ammonia to glucal and treatment of the latter with 2*N*-sulphuric acid at 0° . Alternatively, triacetylglucal is treated directly with 2*N*-sulphuric acid at $10\text{--}15^\circ$ and the deoxyglucose is converted into its phenylbenzylhydrazone, m. p. $158\text{--}159^\circ$, from which it is regenerated by treatment with benzaldehyde containing 10% of benzoic acid. The first method is preferred. 2-Deoxyglucose is a white, anhydrous powder, m. p. 148° (corr.), to a turbid liquid which decomposes at about 155° , $[\alpha]_D^{18} +46.59^\circ$ in water, $+17.56^\circ$ in pyridine. It does not appear to be mutarotatory in aqueous solution, although it has been isolated in two forms with differing specific rotation (details will be given later). It behaves in the same manner as dextrose towards Fehling's solution, alkaline silver solution, and magenta-sulphurous acid. It gives a yellow coloration with warm alkali hydroxides. It is very readily decomposed by not too dilute acid, with separation of greyish-green or darker amorphous substances; the reaction may be used for the detection of deoxyglucose and for distinguishing it from the true sugars. A pine shaving dipped into a solution of deoxyglucose and then exposed to hydrogen chloride becomes intensely green (these reactions are also shown by Kiliani's digitoxose). *Deoxyglucosephenylmethylhydrazone* crystallises in colourless needles or prisms, m. p. $157\text{--}158^\circ$ (corr.), decomp. about 195° ; the corresponding *p*-nitrophenylhydrazone forms small, canary-yellow prisms, m. p. $190\text{--}191^\circ$ (corr., decomp.). Deoxyglucose could not be fermented by a number of varieties of yeast.

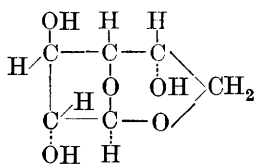
Deoxyglucose is distinguished by the extreme ease with which it is converted into glucosido-derivatives by acids in the presence of alcohols. Small amounts of acetic acid cause the production of glucoside in a short time at 100°, whilst with methyl alcohol containing 0.25—1% of hydrogen chloride the formation of the methylglucoside is complete in less than fifteen minutes at the atmospheric temperature. The product has m. p. 91—92° after softening at 87°, $[\alpha]_D^{25} +137.8^\circ$ in aqueous solution, whereas the isomeride described previously has m. p. 122—123°, $[\alpha]_D -48.2^\circ$. The difference in the specific rotation (186°) is approximately the same as that between α - and β -methylglucosides (189°). Since in all probability the two methyldeoxyglucosides are similarly related to one another and contain the oxygen bridge between the 1 and 4 carbon atoms, it is proposed to designate the first-named substance α -2-deoxymethylglucoside [α -methylglucodesoside] and the latter β -2-deoxymethylglucoside. The sensitiveness of the two substances towards acidic hydrolysing agents is similar, and closely resembles that of γ -methylglucoside. Fission of the glucoside appears to be facilitated by the absence of the hydroxyl group from position 2. α -2-Deoxymethylglucoside, like the β -isomeride, is not affected by yeast or emulsin.

Glucodesose tetrabenzoate is prepared by the action of benzoyl chloride on glucodesose in the presence of pyridine and chloroform; it crystallises in rectangular plates or short, broad prisms. The preparation, m. p. 136—145°, appears to be a mixture of isomerides.

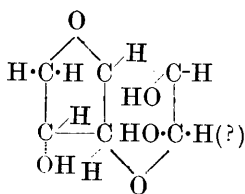
H. W.

The Constitution and Configuration of the Anhydro-sugars.

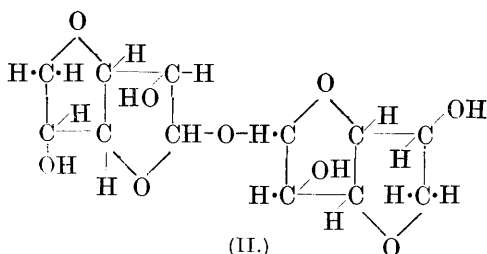
P. KARRER and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1922, 5, 124—128).—Triacetyl-lævoglucosan is converted by liquid hydrogen bromide at the atmospheric temperature in the course of a few days into acetodibromoglucose (A., 1912, i, 239), thus confirming the constitution assigned to lævoglucosan by Pictet (A., 1920, i, 819). The reaction is effected more advantageously by the use of phosphorus pentabromide, and, in this form, is the readiest and best method of preparing acetodibromoglucose. Assuming that a displacement of the oxygen bridge and of an acetyl residue does not occur during the change (which is very improbable by reason of the relative stability of lævoglucosan and the non-convertibility of penta-acetylglucose



into acetodibromoglucose by means of phosphorus pentabromide), the annexed configuration can be assigned to lævoglucosan. Anhydroglucose has the configuration I, in which the disposition of the hydrogen and hydroxyl attached to the α -carbon atom is undecided. The formula accounts for the unusual stability of the compound, since it is composed of two five-membered rings and shows further that anhydro-compounds are only to be expected from sugars which have the γ - and δ -hydroxy-groups on opposite sides of the carbon chain.

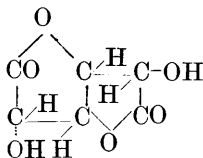


(I.)

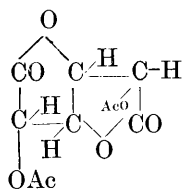


(II.)

Diglucan and *isodiglucan* (A., 1921, i, 765) are represented by formula II, in which the configuration at the α -carbon atoms remains undetermined.



(III.)



(IV.)

The dilactones of the saccharic acids must have a configuration similar to that of anhydroglucose. The dilactone of mannosaccharic acid and the diacetyl derivative of saccharic acid dilactone are

therefore represented by the formulæ III and IV.

H. W.

Polysaccharides. XIII. Inulin and the Alkali Hydroxide Compounds of the Anhydro-sugars. P. KARRER, MAX STAUB, and A. WÄLTJ (*Helv. Chim. Acta*, 1922, 5, 129—139; cf. this vol., i, 11).—It has been shown previously (A., 1921, i, 765) that polymeric anhydro-sugars form additive compounds with sodium hydroxide of the type $(C_{12}H_{20}O_{10}, NaOH)_x$, which are dissociated more or less readily by water. It is now shown that these compounds can be prepared conveniently by precipitating them from their solutions in sodium hydroxide (8—10%) by alcohol and washing the precipitates thoroughly with alcohol (96%). The use of absolute alcohol does not generally effect the complete removal of absorbed sodium hydroxide. The compounds of α -diamylose, α -tetra-amylose, β -hexa-amylose, and α -octa-amylose with potassium hydroxide have been prepared in a similar manner and conform to the type $(C_{12}H_{20}O_{10}, KOH)_x$. *Inulin sodium hydroxide*, $(C_6H_{10}O_5, NaOH)_x$, is prepared by dissolving inulin in sodium hydroxide solution (8%) and adding the product to a large volume of alcohol, and is purified by re-solution in a little water and re-precipitation by alcohol. *Inulin potassium hydroxide*, $(C_6H_{10}O_5, KOH)_x$, is more readily dissociated than the corresponding sodium compound, and is prepared from solution containing 15% or more of potassium hydroxide. The isolation of these compounds brings additional evidence in favour of the view that inulin is a polymeric form of anhydro-fructose. Further confirmation is found in the behaviour of inulin towards fission with acetyl bromide under conditions which cause only slight disintegration of disaccharides such as maltose; the only compound obtained was fructose, although the action was carried out at 0° to $+5^\circ$, and for only such time as was necessary to effect the solution of the inulin.

H. W.

Speed of Reaction in Concentrated Solutions and the Mechanism of the Inversion of Sucrose. GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1921, **43**, 2387—2406).—A theoretical paper in which a method is outlined for calculating the activity of water in sucrose solutions of any concentration at temperatures near the ordinary temperature. The method is also extended to solutions containing a small amount of another solute, such as sulphuric acid. A formula for the speed of the reaction in solution in terms of the activities of the reacting substances is developed, and it is suggested as the most logical formula for solutions. By the application of this formula to the inversion of sucrose, it is shown that the available data indicate that the reaction is of the sixth order with respect to water. The results are interpreted as indicating the existence of a hexahydrate of sucrose. The effect of the addition of sucrose in increasing the activity of the hydrogen ion is explained as being very largely due to an increase in the molar fraction of hydrogen ions without any large change in the actual degree of ionisation. Precautions, necessary in calculating the catalytic effect of the non-ionised portion of the acid by the customary method, are pointed out. J. F. S.

Hydration of Sucrose in Water Solution as Calculated from Vapour Pressure Measurements. GEORGE SCATCHARD (*J. Amer. Chem. Soc.*, 1921, **43**, 2406—2418; cf. preceding abstract).—The average degree of hydration of sucrose in water solution at 0° and 30° is calculated from the vapour pressures of sucrose solutions. The hypothesis is advanced that sucrose solutions are equilibrium mixtures of water, unhydrated sucrose, and a single hydrate of sucrose, and that the relative quantities of these substances are determined by the law of mass action. This hypothesis is tested by comparison of the experimental results with those calculated from the law of mass action. The agreement is fair for either a hexahydrate or a heptahydrate. The hypothesis is further tested by a comparison of the activity of the sucrose calculated from its degree of hydration and that calculated by the Duhem-Margules equation. The results confirm those obtained by the use of the law of mass action method. The present results are in keeping with those obtained from the inversion of sucrose (*loc. cit.*). J. F. S.

Preservation of Starch Solution. NAOTSUNA KANÔ (*J. Chem. Soc. Japan*, 1921, **42**, 974—975).—Starch solution (50 c.c.) for use as an indicator in iodometry can be preserved for more than eight months by the addition of 0.5 c.c. of 2*N*-hydrochloric acid, or of a drop of carbon disulphide. K. K.

The Constitution of Polysaccharides. J. J. LYNST ZWIKKER (*Rec. trav. chim.*, 1922, **41**, 49—53).—On the assumption that the polysaccharide molecule may be regarded as formed from a small number of hexose molecules, each of which consists of a straight chain of carbon atoms, the author shows that a regular tetrahedron and a triangular prism, each bounded by such a straight chain

lying along the junction of each pair of sides, gives a structural formula which is in accordance with the properties of cellulose and starch respectively. Such a structure involves the homogeneous filling of space, and is consistent with the opinion that the polysaccharide molecule is not built up of long chains of sugar molecules. H. J. E.

The Composition of Agar. M. SAMEC and V. SSAJEVIČ (*Compt. rend.*, 1921, **173**, 1474—1475).—Evidence is given in support of the view that agar is a sulphuric ester of gelose in much the same way as amylopectin is a phosphoric ester of the amyloses. A gram-atom of sulphur in the gelose ester corresponds with 9320 grams of organic matter. The great viscosity of agar is probably due to its relatively high content of the SO_4'' ion. W. G.

Alkali-cellulose and the Structure of Cellulose. P. KARRER (*Cellulosechemie*, 1921, **2**, 125—128).—The experimental results of Gladstone are confirmed, namely, that the product of the action of strong sodium hydroxide solution on cellulose, after complete washing with alcohol, has a constant composition corresponding with the formula $\text{C}_{12}\text{H}_{20}\text{O}_{10}\cdot\text{NaOH}$. This is regarded as a definite additive compound, which is hydrolysed by water, so that the products obtained with dilute sodium hydroxide are the results of equilibria. Alkali-cellulose therefore falls into line with analogous compounds obtained with starch, inulin, and the various polymerides of anhydro-maltose classed as amyloses. All these combine with sodium hydroxide in the same proportions, regardless of the degree of polymerisation. Cellulose is a polymeride of cellobiose anhydride, and it is probable from analogies based on the heats of combustion and the Röntgen spectrum (cf. A., 1921, i, 310, 397, 771) that the degree of polymerisation is not high. It is suggested that the cellulose formula may be written $(\text{C}_{12}\text{H}_{20}\text{O}_{10})_2$ and that the polymerisation of the anhydro-sugar takes place through subsidiary valencies without the rupture of the oxygen bridges. The cellulose fibre-substance has a configuration analogous to a crystal structure with nuclei of these dimeride molecules in co-ordinated arrangements. The molecules are held together in the crystal by other valency forces of unusual strength, and this strong cohesion accounts for the properties hitherto attributed to a highly polymerised molecule. The tendency is for the cellulose matter to concentrate its mass into the smallest possible volume and to assume a co-ordinated arrangement of its molecules.

J. F. B.

A New Degradation of Cellulose ; Conversion of Cellulose into a Biose Anhydride. P. KARRER (*Ber.*, 1922, **55**, [B], 153—156).—A reply to the criticisms of Hess (this vol., i, 12). The conversion of amylose by acetyl bromide into acetylbromomaltose is "quantitative" in the sense that the same yield of this substance is obtained from maltose, amylose, or starch. The process of the depolymerisation of starch does not appear to be involved in this matter. H. W.

Saccharification of Cellulose. A. WOHL and H. KRULL (*Cellulosechemie*, 1921, 2, 1—7).—When cellulose is moistened with 3 parts of water, cooled with ice, saturated with hydrogen chloride, kept for five hours at 20°, the acid removed by evaporation in a vacuum at temperatures up to 70°, the residue dissolved in water to form a 10% solution containing 1% of hydrogen chloride and boiled for eight hours, 97% of the theoretical quantity of reducing sugars is obtained and can be estimated by cupric reduction. The process may be applied to the estimation of cellulose. In view of discrepancies in the yields of alcohol obtained by fermentation of the reducing sugars from pine wood and from pure cellulose respectively, it is probable that the hydrolysis of the cellulose in the former is impeded by incrusting substances which cannot be removed by preliminary treatment, whilst prolonged action of the acid leads to the formation of non-fermentable reversion products in relatively large quantity.

CHEMICAL ABSTRACTS.

Viscosity of some Cellulose Acetate Solutions. GUY BARR and L. L. BIRCUMSHAW (*Trans. Faraday Soc.*, 1921, 16, Appendix, 72—75).—The viscosity and density of 5% solutions of cellulose acetate have been determined in acetone and mixtures of acetone and water, benzene, and ethyl alcohol respectively. The second solvent was added in all concentrations up to the point where cellulose acetate was precipitated. The viscosity-concentration (of second solvent) curves are markedly different. Benzene causes a progressive increase in the viscosity with increase in the concentration, whereas water and ethyl alcohol give an initial rapid fall in viscosity, which in the case of water reaches a minimum and then rises fairly rapidly but with alcohol remains fairly constant at the minimum value.

J. F. S.

Syntheses with Chloroacetyl Chloride. W. LEIGH BARNETT (*J. Soc. Chem. Ind.*, 1921, 40, 286; cf. A., 1921, i, 847).—Examination of the gases evolved during the reaction between chloroacetyl chloride and cellulose showed that hydrogen chloride alone is formed in the absence of water, but on treating the acetic acid solution of the cellulose esters with water, large quantities of formic acid are produced. The author concludes that the reaction proceeds in four distinct stages, and has succeeded in preparing compounds corresponding with all these stages in the case of glycerol.

W. P. S.

The Elimination of Furfuraldehyde from Oxycelluloses. The Solubility in Alkali and the Reduction Capacity of Oxycelluloses. CARL G. SCHWALBE and ERNST BECKER (*Zellstoff u. Papier*, 1921, 1, 100—103; 135—139).—The yield of furfuraldehyde on treatment with barium hydroxide is not a characteristic property of oxycelluloses, and there are marked differences in their copper number, acidity, and resistance to alkali. The values obtained indicate the existence of two classes of oxycelluloses, in which the predominating character is acidic and aldehydic respectively, whilst the former character is almost completely lacking

in the hydrocelluloses. Denitrated wood pulp and denitrated nitro-silk (Chardonnnet silk) have the chemical character of the oxycelluloses and the hydrocelluloses respectively.

CHEMICAL ABSTRACTS.

Physico-chemical Characterisation of Lignin from Winter Rye Straw. ERNST BECKMANN, OTTO LIESCHE, and FRITZ LEHMANN (*Biochem. Z.*, 1921, **124**, 293—310; cf. A., 1921, i, 546).—The formula $C_{40}H_{44}O_{15}$ for lignin has been confirmed in a number of ways. There are four methoxyl groups present and on benzylation four benzoyl groups enter the molecule. The sodium salt of lignin contains slightly less than two sodium atoms. The molecular weight in phenol and in boiling acetic acid and that of the sodium salt in water agrees with the above formula. Conductivity measurements show that lignin obeys the Ostwald valency rule. H. K.

The Lignin-like Resins and Tannins of Spruce Needles. A. CLEVE VON EULER (*Cellulosechemie*, 1921, **2**, 128—135; 1922, **3**, 1—7; cf. A., 1921, i, 769, 849; 1922, i, 100).—Powdered spruce needles were exhaustively extracted with 93% commercial methyl alcohol and the concentrated extract was divided into three fractions by means of ether. There were thus obtained: "crude fat," soluble in ether, "molasses," the brown, aqueous bottom layer, and "crude resin," an intermediate layer soluble in alcohol but not in ether. The crude fat contained, besides true resins and fats, about 29% of humus-like substances classified under the name of abiophyllic acids, consisting of allied derivatives of coniferyl aldehyde more or less condensed and partly hydrogenised. The crude resin, which amounted to not less than 10% of the weight of the needles, might be described as a hydrated form, partly hydrogenised, of lignin; that is to say, it is an allied substance, at a lower stage of condensation than the ordinary lignin of wood. Its composition, C=60.6, H=7.12%, has no relation to that of a true resin; it is, moreover, extremely susceptible to change, either spontaneously or by solution in alkali and reprecipitation by acid, giving a brownish-red product not unlike the phlobaphens derived from tannic acid. The alcoholic solution of the crude resin has the property of precipitating gelatin. A study of the constituents of the "molasses" soluble in water yielded a whole series of definitely pronounced tannins which have been fractionated and classified into components soluble and insoluble in ethyl acetate, some yielding uncoloured lead salts and others lemon-yellow lead salts. A comparison of this series of needle tannins with the series of bark tannins studied by Etti and Böttinger (*Ber.*, **22**, 753; **23**, 647) revealed many analogies. The spruce-needle tannins are ketonic acids, most of them hydroaromatic, related to *p*-cumarylferulic acid or feruylferulic acid at various degrees of hydrogenation; derivatives related to caffeic acid are also represented. Those giving colourless lead salts and insoluble in ethyl acetate are richest in hydrogen and those giving yellow lead salts are poorest. According to Klason's hypothesis (A., 1920, i, 821), β -lignin is a ketonic acid, not hydroaromatic, but otherwise very closely related

to this series of water-soluble spruce-needle tannins. The author formulates β -lignin as a dihydroxyhydrocaffeylferulic acid. All these tannins and β -lignin are built up from more or less hydrogenised hydroxycinnamic acids. The author does not accept Klason's flavone constitution for α -lignin; he regards it as being very similar to β -lignin, but built up from more or less hydrogenised hydroxycinnamic acids and aldehydes; the abiophylllic acids are built up of similar aldehydes, and the tannins of the crude resin of similar aldehydes and alcohols. The following formula might represent α -lignin, except that it includes two hydroxyls, instead of one as determined by Klason,

$\text{OMe} \cdot \text{C}_6\text{H}_3(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_2(\text{OH})(\text{OMe}) \cdot \text{CH} \cdot \text{CH} \cdot \text{CHO}$,
and the tannins of the crude resin and abiophylllic acids would be derived from this by various additions of H_2O and H_2 . J. F. B.

Preparation of Amines from Alcohols and Ammonia.

EUGENIE SMOLENSKI and KAZIMIR SMOLENSKI (*Roczniki Chemji*, 1921, **1**, 232—243).—When the vapours of methyl, ethyl, or amyl alcohol react with ammonia in the presence of a dehydrating catalyst such as alumina or kaolin at about 300° , a satisfactory yield of primary, secondary, and tertiary amines is obtained. In the case of ethyl alcohol, secondary products consisting of ethylene and ethyl ether are also obtained. If the ratio of the quantities of alcohol to ammonia is about 2 mols : 1 mol, when the temperature is kept between 300° and 330° , a good yield of diethylamine is obtained. The total yield, after accounting for the alcohol which is regained, is 53% of amine, 25% of ether, and 20% of ethylene. Under the same conditions, ethyl ether and ammonia also give ethylamine. Good results are obtained with aromatic compounds; thus aniline and methyl alcohol at 350° in the proportion of 1 mol. : 4 mols. give toluidines and xylydines, but if the temperature is kept below 330° and 10—20% of a salt of aniline is added, the yield of the homologues of aniline is practically zero. J. F. S.

Action of some Acyclic Halogenated Derivatives on Hexamethylenetetramine. MARCEL DELÉPINE and (MME) PIERRE JAFFEUX (*Bull. Soc. chim.*, 1922, [iv], **31**, 108—112).—With the exception of isopropyl iodide, secondary and tertiary alkyl haloids do not form quaternary ammonium salts with hexamethylenetetramine. Primary alkyl haloids do, but the ease of the action diminishes as the molecular weight increases. Alkyl haloids having the same molecular weight but differing in the branching of the chain differ in their reactivity. W. G.

Condensation Products from Acid Haloids. IX. Ketenium Compounds. E. WEDEKIND and CL. WEINAND (*Ber.*, 1922, **55**, [B], 60—68; cf. Wedekind and Miller, A., 1909, i, 459).—It has been shown previously that isobutyryl chloride and phenylchloroacetyl chloride are converted by triethylamine into dimethylketetriethylilium, $\text{CMe}_2\text{CO} \cdot \text{NEt}_3$, and phenylchloroketentriethylilium, $\text{CPhCl} \cdot \text{CO} \cdot \text{NEt}_3$. The similar reactions with chloroacetyl chloride, bromoacetyl chloride, and dichloroacetyl chloride are now described. For this

type of compound the constitutions $\text{NEt}_3 \begin{smallmatrix} \text{CR}_2 \\ | \\ \text{CO} \end{smallmatrix}$ and $\text{NEt}_3 \begin{smallmatrix} \text{O} \\ | \\ \text{C}:\text{CR}_2 \end{smallmatrix}$ have been advanced tentatively. The first of these, however, is excluded by the observation that dimethylketentriethylum is smoothly hydrogenated in the presence of platinum black to isobutaldehyde and triethylamine: $\text{NEt}_3 \begin{smallmatrix} \text{O} \\ | \\ \text{C}:\text{CMe}_2 \end{smallmatrix} \rightarrow (\text{NEt}_3 \begin{smallmatrix} \text{O} \\ | \\ \text{CH} \cdot \text{CHMe}_2 \end{smallmatrix}) \rightarrow \text{CHMe}_2 \cdot \text{CHO} + \text{NEt}_3$. The incapability of

existence of the assumed intermediate compound, combined with the improbability of the direct addition of a saturated tertiary amine at a $\text{C}=\text{O}$ group, cause the authors to prefer the subsidiary valency formula, $\text{CR}_2:\text{C}:\text{O} \dots \text{NAlk}_3$. An explanation is thereby afforded of the inability of the pre-formed keten to combine with triethylamine, since it is probable that in it the subsidiary valencies have to some extent compensated one another.

[With M. MILLER.]—Solutions of the requisite acid chloride and triethylamine are gradually mixed, when a violent reaction occurs; the product is filtered and the residue extracted with benzene, whereby triethylamine hydrochloride remains undissolved. The ketenium compound is isolated by distillation of the residue left after removal of the solvent from the filtrate under diminished pressure. The yields are small.

Chloroketentriethylum, $\text{CHCl}:\text{CO}:\text{NEt}_3$, is an almost colourless liquid, b. p. $120\text{--}125^\circ/10$ mm. *Bromoketentriethylum*, a pale yellow liquid, b. p. $128\text{--}129.5^\circ/18$ mm., is transformed by hydrochloric acid at 135° into triethylamine hydrochloride and bromoacetic acid. It cannot be hydrogenated in the presence of palladium, towards which it behaves as a poison. *Dichloroketentriethylum* is a golden-yellow liquid, b. p. $142\text{--}145^\circ/18$ mm. It is decomposed by alcoholic potassium hydroxide solution with quantitative production of potassium chloride; carbon monoxide is not, however, evolved. H. W.

The Action of Amino-acids on Sugars. L. GRÜNHUT and J. WEBER (*Biochem. Z.*, 1921, **121**, 109—119).—The interaction between various amino-acids and sugars with special reference to melanoidin formation has been followed by a study of the formol titration, the optical activity, and reducing power. The reaction is in general very complex, and varies from case to case. H. K.

Alkylation of the Anhydrides of Amino-acids. P. KARRER, CH. GRÄNACHER, and A. SCHLOSSER (*Helv. Chim. Acta*, 1922, **5**, 139—141; cf. Sasaki and Hashimoto, this vol., i, 56).—Sarcosine anhydride is obtained in more than 50% yield by the protracted action of methyl iodide on the silver salt of glycine anhydride. An attempt to prepare the silver salt of leucine anhydride by the method used for the corresponding glycine compound was unsuccessful.

In general, very marked differences are found in the behaviour of the anhydrides of various amino-acids for which, at present, a

satisfactory explanation cannot be given. Thus, for example, glycine anhydride and phenylalanine anhydride give sparingly soluble additive compounds with solutions of calcium chloride in alcohol, but this behaviour is not exhibited by leucine anhydride.

H. W.

Monochlorocarbamide. Preparation of Chlorohydrins by its Action on Ethylenic Hydrocarbons. ANDRÉ DETEUF (*Bull. Soc. chim.*, 1922, [iv], **31**, 102—108).—Monochlorocarbamide may be obtained by the action of chlorine on carbamide in the presence of a small amount of water at 0°. By this method a certain amount of carbamide hydrochloride is also formed. The chlorocarbamide may be obtained in approximately 20% solution by passing chlorine through a solution of 120 grams of carbamide in 60 grams of water at 0°, in which 60 grams of powdered marble is suspended, until the theoretical amount of chlorine is taken up. The solution is then filtered. Such a solution, after the addition of 5% of acetic acid, readily reacts with ethylenic hydrocarbons, giving the corresponding chlorohydrins. For the latter action to take place, the solution of chlorocarbamide must be acid either from the addition of acetic acid or from the presence of carbamide hydrochloride.

W. G.

Preparation of Thiocarbamides. THE GOODYEAR TIRE AND RUBBER CO. (Brit. Pat. 164326).—In the preparation of substituted thiocarbamides by the action of carbon disulphide on a primary amine, the speed of the reaction is greatly increased and a product of greater purity is obtained if the reaction is carried out at a temperature above the boiling point of carbon disulphide, but below that of the amine, by passing, for example, the superheated vapours of carbon disulphide into the amine previously heated to the desired temperature.

G. F. M.

Isomeric Citraconyl Hydrazides. FREDERICK DANIEL CHATTAWAY and DERIC WILLIAM PARKES (T., 1922, **121**, 283—288).

Simultaneous Reduction and Oxidation. III. Transformation of Halogenaldehydes into Aldehydes and Acids through Ketenes. ARTHUR KÖTZ and H. RATHERT (*J. pr. Chem.*, 1921, [ii], **103**, 227—240; cf. A., 1913, i, 1309; 1915, i, 208).— $\beta\beta$ -Dichloro- α -acetoxyacrylonitrile when hydrolysed with strong sulphuric acid in the cold, gives $\beta\beta$ -dichloro- α -acetoxyacrylamide, $\text{CCl}_2\cdot\text{C}(\text{OAc})\cdot\text{CO}\cdot\text{NH}_2$, needles, m. p. 122—123°. The nitrile on boiling with water gives dichloroacetic acid, acetic acid, and hydrogen cyanide, and when heated with ethyl alcohol at 150°, it gives dichloroacetic acid, acetic ester, and hydrogen cyanide. It also reacts readily with aniline to give the corresponding anilides and hydrogen cyanide, and not dichloroketen. Ethyl β -dichloro- α -ethoxyacrylate, on the other hand, gives on boiling with water dichloroacetaldehyde, alcohol, and carbon dioxide. Dichloroacetoxyacrylonitrile, on reduction with hydrogen in presence of colloidal palladium or platinum black, gives $\beta\beta$ -dichloro- α -acetoxy propionitrile, $\text{CHCl}_2\cdot\text{CH}(\text{OAc})\cdot\text{CN}$, b. p. 42—43°/6 mm., and with

dry hydrogen chloride it gives $\alpha\beta\beta$ -trichloro- α -acetoxypropionitrile, $\text{CHCl}_2\cdot\text{CCl}(\text{OAc})\cdot\text{CN}$, b. p. 202° , which on hydrolysis gives dichloroacetic acid, hydrogen chloride, and hydrogen cyanide, thus proving its structure. Dichloroacetoxyacrylonitrile, with alcoholic hydrogen chloride, gives the *hydrochloride* of the *iminoether* of $\alpha\beta\beta$ -trichloro- α -acetoxyacetic acid, $\text{CCl}_2\text{H}\cdot\text{CCl}(\text{OAc})\cdot\text{C}(\text{OEt})\cdot\text{NH}_2\cdot\text{HCl}$, m. p. $93\text{--}94^\circ$. Bromoacetaldehyde, when heated in a sealed tube with triethylamine, gives diketocyclobutane, b. p. $125\text{--}126^\circ$. Chloral does not, under similar conditions, eliminate hydrogen chloride and give dichloroketen. W. O. K.

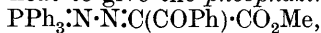
Aliphatic Diazo-compounds. XXIV. Organic Phosphorus Compounds. VI. Preparation and Reactions of Phosphazines. H. STAUDINGER and G. LÜSCHER (*Helv. Chim. Acta*, 1922, 5, 75—86).—A continuation of the work of Staudinger and Meyer (A., 1920, i, 105). The aliphatic diazo-compounds do not exhibit great differences in the readiness with which they combine with tertiary phosphines to give phosphazines. The latter are hydrolysed with greater or less readiness by water into hydrazones and phosphine oxides. They all decompose with evolution of nitrogen when heated, but the formation of phosphinemethylenes thereby is not observed except in the case of triphenylphosphine-benzophenoneazine (*loc. cit.*). Clear proof is adduced that the initial change consists of a dissociation of the compound into its constituents, since volatile diazo-compounds can be distilled unchanged from the difficultly volatile triphenylphosphine when the compounds are heated carefully in a vacuum.

Triphenylphosphinebenzilazine, $\text{PPh}_3\cdot\text{N}\cdot\text{N}\cdot\text{CPhBz}$, a yellow, crystalline powder, m. p. $115\text{--}117^\circ$ (decomp.), is obtained in 83% yield by mixing benzoylphenyldiazomethane and triphenylphosphine in ethereal solution. It is hydrolysed readily by alcohol (90%) to triphenylphosphine oxide and benzilhydrazone. It is decomposed by heat in a complicated manner, giving nitrogen, triphenylphosphine, triphenylphosphine oxide, possibly benzonitrile, and a dark brown resin.

Ethyl triphenylphosphineglyoxylate-azine [from triphenylphosphine and ethyl diazoacetate (cf. Staudinger and Meyer, *loc. cit.*)] is hydrolysed with great readiness to triphenylphosphine oxide and ethyl *anti*-glyoxylatehydrazone, m. p. 38° , thus indicating the anti-configuration, $\text{CO}_2\text{Et}\cdot\overset{\text{CH}}{\underset{\text{N}\cdot\text{N}\cdot\text{PPh}_3}{\parallel}}$, for the phosphazine. It

decomposes at 200° with liberation of about half the total quantity of nitrogen; when distilled at 140° in a vacuum, it yields ethyl diazoacetate and triphenylphosphine.

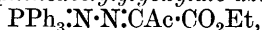
Triphenylphosphine and methyl benzoyldiazoacetate react without development of heat to give the *phosphazine*,



a pale yellow, crystalline powder, m. p. $132\cdot5\text{--}133^\circ$ (decomp.). It is converted by alcohol (90%) into the *substance*, $\text{C}_{28}\text{H}_{25}\text{O}_4\text{N}_2\text{P}$, m. p. $95\cdot5\text{--}96\cdot5^\circ$. It gives nitrogen, triphenylphosphine, triphenylphosphine oxide, and resinous matter when heated.

Triphenylphosphine and methyl cinnamoyldiazoacetate yield the *phosphazine*, $\text{PPh}_3 \cdot \text{N} \cdot \text{N} : \text{C}(\text{CO}_2\text{Me}) \cdot \text{CO} \cdot \text{CH} : \text{CHPh}$, a pale yellow solid, m. p. 174° .

Ethyl triphenylphosphineacetylglxyrate-azine,



yellow crystals, m. p. 90° , is hydrolysed readily by atmospheric moisture. It decomposes completely when heated under atmospheric pressure; it regenerates its components when heated in a vacuum.

Triphenylphosphine and ethyl diazomalonate react comparatively slowly to give the *phosphazine*, $\text{PPh}_3 \cdot \text{N} \cdot \text{N} : \text{C}(\text{CO}_2\text{Et})_2$, almost colourless crystals, m. p. 128° (decomp.). It is very sensitive towards moisture and is hydrolysed readily to ethyl mesoxalatehydrazone and triphenylphosphine oxide. Towards heat, it behaves in the same manner as the preceding compound. The corresponding *phosphazine*, $\text{PPh}_3 \cdot \text{N} \cdot \text{N} : \text{C}(\text{CO}_2\text{Me})_2$, a pale yellow, crystalline mass, m. p. about 92° , crystallises more readily than the ethyl compound, but, like the latter, is extremely sensitive to moisture. It dissociates into its components when heated in an absolute vacuum.

Triphenylphosphine and benzoylacetyldiazomethane give the *phosphazine*, $\text{PPh}_3 \cdot \text{N} \cdot \text{N} : \text{C} \text{Ac} \text{Bz}$, dark yellow crystals, m. p. 128° , which is hydrolysed by boiling dilute alcohol with the formation of *benzoylacetylketonehydrazone*, $\text{NH}_2 \cdot \text{N} : \text{C} \text{Ac} \text{Bz}$, colourless crystals, m. p. $111-112^\circ$; it decomposes completely when heated.

Triphenylphosphinedinitroquinoneazine (annexed formula), brilliant, red crystals, decomp. about 194° , is prepared from its components in chloroform solution. Relatively, it is an extremely stable substance, possibly owing to its sparing solubility; protracted heating with aqueous alcohol converts it into triphenylphosphine oxide and smeary products.

Further investigation of the decomposition of triphenylphosphinefluorenoneazine by heat has shown that the main product is the ketazine, m. p. 264° ; triphenylphosphinediphenylenemethylene, m. p. 274° , is produced in minor amount, but the method is unsuitable for its preparation for this reason, and also because of the difficulty of separating it from the ketazine by crystallisation.

H. W.

Aliphatic Diazo-compounds. XXV. Ketens. XXXVIII.

Aliphatic Diazo-compounds and Ketens. H. STAUDINGER (*Helv. Chim. Acta*, 1922, 5, 87—103).—A theoretical paper. Further investigation has led the author to modify his view of the constitution of the aliphatic diazo-compounds (A., 1916, i, 847), which are now formulated in accordance with the manner proposed by Angeli and Thiele. Compounds with the group $\text{N} : \text{N}$, which are derived from the unsaturated nitrogen molecule, are termed azens. This class of compound shows a great variety of chemical actions, some of which are common to all members of the class, whereas others are limited to particular members. The observations may be explained by the assumption that the azens contain two re-

active points, as indicated by the schemes $A:\ddot{N}:\ddot{N}<$ and $A:\ddot{N}:\ddot{N}$, respectively. Reactions occurring at the terminal nitrogen atom (first scheme), such as the addition of phosphines, reduction of aliphatic diazo-compounds and azides and addition of Grignard's reagents, are common to all azens, since an alteration in the nature or substitution of the first atom has relatively little influence on the third atom. Great differences in the reactivity of the different azens are observed, on the other hand, in many reactions which are considered to be based on compounds formulated in accordance with the second scheme; instances are afforded by (1) the addition of unsaturated compounds which is presumed to occur thus, $R_2\ddot{C}=\ddot{N}\equiv\ddot{N}+A=B \rightarrow \begin{matrix} R_2\ddot{C}-\ddot{N}=\ddot{N} \\ | \quad \quad | \\ A \quad \quad B \end{matrix} \rightarrow R_2\ddot{C}<\begin{matrix} A \\ | \\ B \end{matrix}$; (2) the action of compounds HR (acids, water, alcohols, and amines) proceeding according to the scheme $R_2\ddot{C}=\ddot{N}\equiv\ddot{N}+HCl \rightarrow \begin{matrix} R_2\ddot{C}-\ddot{N}=\ddot{N}H \\ | \\ Cl \end{matrix} \rightarrow$

$R_2CHCl+N_2$; (3) the addition of halogen, acid chloride, or nitrogen dioxide. Reduction may occur in accordance with either scheme, the course of the changes being dependent on the particular azen and the reducing agent employed. A number of reactions cannot be explained by either scheme; in all of these the azens react with salts.

Carbonylen compounds resemble the azens closely in their general reactions, which may be referred to the two schemes $R_2\overset{3}{\ddot{C}}=\overset{2}{\ddot{C}}=\overset{1}{\ddot{O}}$, $R\cdot\ddot{N}=\overset{3}{\ddot{C}}=\overset{1}{\ddot{O}}$ or $R_2\ddot{C}=\overset{3}{\ddot{C}}=\overset{1}{\ddot{O}}<$, $R\cdot\ddot{N}=\overset{3}{\ddot{C}}=\overset{1}{\ddot{O}}<$ and

$R_2\overset{3}{\ddot{C}}=\overset{2}{\ddot{C}}=\overset{1}{\ddot{O}}$, $R\cdot\ddot{N}=\overset{3}{\ddot{C}}=\overset{1}{\ddot{O}}$. Those occurring in accordance with the first scheme are but little affected by substituents at the third atom, and are exemplified by the action with phosphineimines, $CH_2=\overset{3}{\ddot{C}}=\overset{1}{\ddot{O}}+PR_3\cdot NPh \rightarrow CH_2\cdot\ddot{C}:NPh+PR_3O$, the addition of tertiary phosphines, $CPh_2=\overset{3}{\ddot{C}}=\overset{1}{\ddot{O}}<+PEt_3 \rightarrow CPh_2=\overset{3}{\ddot{C}}=\overset{1}{\ddot{O}}=PEt_3$, and the action of compounds of the type HR , such as water, alcohol, acids, and primary and secondary amines. Reactions occurring in accordance with the second scheme are affected greatly by the presence of substituents at atom 3; typical instances are afforded by the behaviour towards oxygen and unsaturated compounds such as ethylene derivatives, Schiff's bases, carbonyl compounds, thioketones, and nitroso-compounds, by the polymerisation of ketens and by the decomposition of carbonylens by heat.

The similarity of azens and carbonylens extends to colour and to absorption spectrum. Further consideration of unsaturated substances leads to the recognition of the existence of two distinct groups, which are influenced differently by substituents, frequently in a reversed direction; one class includes the ketens and diazo-compounds, whereas the other comprises the carbonyl compounds and their nitrogenous derivatives, such as the hydrazones, Schiff's bases, ketazines, and phosphazines. These differences are most readily explained in accordance with Thiele's theory of partial valencies. In the cases of the highly reactive *o*-diketones and

unsaturated ketones, there is a strengthened partial valency at the end of the conjugated system $\text{O}=\text{C}-\text{C}=\text{O}$, which accounts for both the increase in the colour and enhanced activity. In the less reactive carbonyl substituted ketens and carbonyl substituted and unsaturated diazo-compounds, conjugation influences the second atom, which has but little effect on the reactivity, whereas the third atom is weakened in its action by the neutralisation of the partial valencies, thus $\text{O}=\text{C}-\text{C}=\text{O}$ and $\text{O}=\text{C}-\text{C}=\text{N}=\text{N}$ instead of $\text{R}_2\text{C}=\text{C}=\text{O}$ and $\text{R}_2\text{C}=\text{N}=\text{N}$, respectively. H. W.

Ketens. XXXIX. Aliphatic Diazo-compounds. XXVI. Behaviour of Ring Systems. H. STAUDINGER (*Helv. Chim. Acta*, 1922, 5, 103—108).—A general review of the stability of cyclic compounds formed from carbonylens and azens and unsaturated substances.

The four-membered rings, obtained in large number from diphenylketen and unsaturated compounds, are shown in tabular form; a general conception of the dependence of stability of these structures on the members of the ring cannot be given, but the effect of substituents is very marked. Five-membered rings are formed from azens and unsaturated compounds, which, in general, are exceedingly unstable and immediately lose nitrogen, with the production of three-membered rings. The five-atom rings containing one double bond are less stable than similar rings with two double bonds. Heterocyclic rings containing three atoms are less stable than the trimethylene derivatives; the influence of substituents is very marked, and requires further investigation.

H. W.

A New Process for the Preparation of Cadmium Dimethyl. E. DE MAHLER (*Bull. Soc. chim.*, 1922, [iv], 31, 125).—Cadmium iodide and magnesium methyl iodide readily react in ethereal solution at the ordinary temperature, giving cadmium dimethyl and magnesium iodide. The cadmium dimethyl, b. p. $105^\circ/760$ mm., is readily separated by fractional distillation. W. G.

Stereoisomerism of Cyclic Hydrocarbons. A. SKITA and A. SCHENCK (*Ber.*, 1922, 55, [B], 144—152).—If Auwer's hypothesis (A., 1920, i, 721) that the reduction of aromatic hydrocarbons by Sabatier's method and in the presence of platinum leads to the formation of *trans*- and *cis*-derivatives respectively is correct, it must be possible to prepare a large number of previously unknown cyclic hexamethylenes by the latter process. For this purpose, a modification of the catalyst is, however, necessary, since the addition of water, which is necessary for the solution of the catalyst protected by gum arabic, causes the separation of the hydrocarbon. A glacial acetic acid reversible platinum colloid in which the metal is deposited on pure gelatin has therefore been introduced (the details of the preparation will be described later), with which it is possible to secure the smooth reduction of benzenoid hydrocarbons to hexamethylenes.

Reduction of the three xylenes is effected by dissolving the hydrocarbon in glacial acetic acid and adding successively solutions of chloroplatinic acid and gelatin in glacial acetic acid and colloidal platinum solution; hydrogenation is completed rapidly at 80° under an excess pressure of three atmospheres. In each case a mixture is obtained which is separated by repeated fractional distillation into its components, the purity of which is controlled by observation of the molecular coefficient of refraction. The following constants are recorded: $1^{\circ}:2^{\circ}$ -dimethylcyclohexane, b. p. 126.5° , d_4^{20} 0.786, n_D^{20} 1.43114; $1^{\circ}:2^{\circ}$ -dimethylcyclohexane, b. p. 124° , d_4^{20} 0.780, n_D^{20} 1.43037; $1^{\circ}:3^{\circ}$ -dimethylcyclohexane, b. p. 121.5° , d_4^{20} 0.775, n_D^{20} 1.42609; $1^{\circ}:3^{\circ}$ -dimethylcyclohexane, b. p. 119° , d_4^{20} 0.772, n_D^{20} 1.42470; $1^{\circ}:4^{\circ}$ -dimethylcyclohexane, b. p. 121.5° , d_4^{20} 0.773, n_D^{20} 1.42300; $1^{\circ}:4^{\circ}$ -dimethylcyclohexane, b. p. 119.5° , d_4^{20} 0.769, n_D^{20} 1.42095. The constants of the *trans*-series are identical with those of the products obtained by von Auwers by Sabatier's method. *p*-Cymene is reduced exclusively to 1° -methyl-4 $^{\circ}$ -isopropylcyclohexane, b. p. 168.5° , d_4^{20} 0.816, n_D^{20} 1.45149.

$1^{\circ}:2^{\circ}:4^{\circ}$ -Tetramethylcyclohexane, b. p. 146° , d_4^{20} 0.790, n_D^{20} 1.43314, is obtained a sole product of the reduction of ψ -cumene by the new process; it is identical with the substance obtained recently (A., 1919, i, 578) by the catalytic reduction of ψ -cumenol in acid solution, and differs markedly from the $1^{\circ}:2^{\circ}:4^{\circ}$ -isomeride obtained by von Auwers by Sabatier's method. The $1^{\circ}:2^{\circ}:4^{\circ}$ -isomeride, b. p. 140° , d_4^{20} 0.774, n_D^{20} 1.42916 is prepared by the reduction of tetrahydro- ψ -cumene (from *cis*-1-hydroxy-*cis*-2:4:5-trimethylcyclohexane) with sodium and alcohol.

The differences observed with the cyclohexenes are similar to those with the saturated cyclic hydrocarbons. Thus the 1:2:4-trimethylcyclohexene derived from *cis*-1-hydroxy-*cis*-2:4:5-trimethylcyclohexane in contrast to the stereoisomeric hydrocarbon obtained by von Auwers (*loc. cit.*) by Sabatier's method has a pronounced *cis*-form, the constants being b. p. 147° , d_4^{20} 0.814, n_D^{20} 1.44905 for the former and b. p. 145° , d_4^{20} 0.805, n_D^{20} 1.44820 for the latter.

cis-1-Hydroxy-*cis*-2:4:5-trimethylcyclohexane is converted into the corresponding ketone, which is converted by magnesium methyl iodide into the tertiary alcohol; the latter is transformed by phosphorus pentachloride into a tetrahydrodurene, b. p. 169° , d_4^{20} 0.828, n_D^{20} 1.46053. In all probability it is the $1^{\circ}:2^{\circ}:4:5$ -compound, whereas the isomeride, b. p. 166° , d_4^{20} 0.817, n_D^{20} 1.45722, obtained by von Auwers by Sabatier's method, has the $1^{\circ}:2^{\circ}:4:5$ -configuration.

H. W.

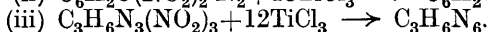
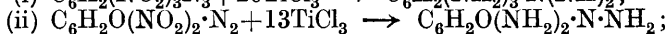
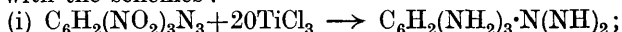
Action of Sodium Sulphite on Nitrobenzene. SEYEWETZ and VIGNAT (*Compt. rend.*, 1922, 174, 296—299).—When nitrobenzene in suspension is boiled with a 10—20% solution of sodium sulphite, it gradually disappears, the solution becoming orange-coloured and ammonia being evolved. From the solution, a compound can be isolated which is apparently identical with 4-aminophenol-3-sulphonic acid (cf. Schultz and Ståhle, A., 1904,

i, 597). Phenylhydroxylaminesulphonic acid is probably formed as an intermediate product, and, being unstable, is transformed into the aminophenolsulphonic acid. The coloration is probably due to the formation of an azoxybenzene, and may be suppressed by adding sodium hydrogen carbonate to the sulphite solution.

W. G.

The Products of Nitration of Toluene. WILLIAM HOWIESON GIBSON, REBECCA DUCKHAM, and RUTH FAIRBAIRN (T., 1922, 121, 270—283).

Reductions with Titanium Trichloride. HANS RATHSBURG (*Ber.*, 1921, 54, [B], 3183—3184).—The following nitro-compounds are completely reduced by titanium trichloride according to the method of Knecht and Hibbert in boiling, concentrated hydrochloric acid solution in a current of carbon dioxide: *s*-chloro-trinitrobenzene, trinitroresorcinol, trinitrophenylhydroxylamine, picramide, *m*-dinitro-*o*-dinitrosobenzene, picramic acid, tetranitrophenol (+4H₂O), trinitrophenolglucinol (+½H₂O). Over-reduction is observed with hexanitrotetrahydroxydiphenyl. If account is taken of the partial reduction of other groups which are present in addition to the nitro-radicles, trinitrophenyldiazo-imide, dinitrodiazophenol anhydride, and the substance, C₃H₆O₆N₆, from hexamethylenetetramine can be reduced smoothly in accordance with the schemes:



Complete reduction occurs also with the following salts and salt-like compounds, a disturbing influence due to the metallic ion not being observed: lead styphnate (+1H₂O), lead picrate, and the potassium compounds of dinitrodinitrosobenzene (+0.25H₂O) and tetranitrophenol (+1H₂O).

H. W.

The Electrochemical Oxidation of *o*-Toluenesulphonamide. FR. FICHTER and HANS LÖWE (*Helv. Chim. Acta*, 1922, 5, 60—69).—An examination of the possibility of converting *o*-toluenesulphonamide into "saccharin" by electrochemical oxidation.

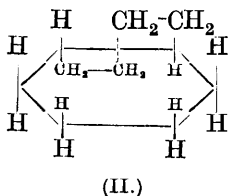
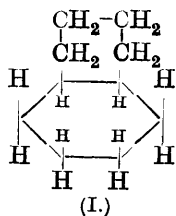
Electrolysis of solutions of *o*-toluenesulphonamide in an excess of aqueous sodium hydroxide at platinum, nickel, or copper anodes (cf. D.R.-P. 85491) does not lead to the formation of more than slight traces of "saccharin"; the sulphonamide appears to be completely decomposed with the formation of sodium sulphate as the sole isolable product.

Electrolysis of *o*-toluenesulphonamide, partly suspended and partly dissolved in 0.5*N*-sulphuric acid, at 60° with anodes of platinum gauze, graphite, or lead coated with lead peroxide in a divided cell in which the cathode is formed of a lead cylinder immersed in 2*N*-sulphuric acid causes the separation of ammonia, which is not due to hydrolysis and the production of small quantities of "saccharin." It is thus shown to be possible to oxidise the

methyl to the carboxy-group. For the successful production of "saccharin," however, it is necessary to secure the smooth oxidation of the methyl radicle and to protect the sulphonamide group during the process so as to secure the ultimate formation of the sulphonimide ring. The first point is investigated by examining the oxidation of *o*-toluenesulphonic acid in 0.5*N*-sulphuric acid solution at a rotating anode of lead covered with lead peroxide. It is found that the substance is not transformed smoothly into *o*-sulphobenzoic acid. A portion of it is oxidised to phenolic substances which still contain the sulphonic group; according to analyses of the barium salts, the phenolic substances and the products which are not precipitable with lead acetate are sulphocarboxylic acids. The electrolytic oxidation of *o*-toluenesulphonic acid proceeds therefore beyond the *o*-sulphobenzoic acid stage, and, for the preparation of "saccharin," it is necessary to protect the oxidised product by ring closure immediately the methyl is converted into carboxyl. Electrolysis of benzenesulphonamide, *o*-toluenesulphonamide, and "saccharin" in 0.5*N*-sulphuric acid solution at a platinum gauze anode proves that neither the sulphonamide nor the sulphonimide group is stable under these conditions. These groups, however, can be considerably protected by the use of ammoniacal solutions in which the ammonia functions as "relative depolariser"; thus, *o*-toluenesulphonamide is converted in 4*N*-ammoniacal solution in the presence of ammonium sulphate at 40° and at a platinum gauze anode into "saccharin," the material yield being 43.7% and the current yield 9.2%. The most favourable results, however (material yield 75.4%, current yield 42.6%), are obtained by the electrolysis of *o*-toluenesulphonamide dissolved and suspended in 2*N*-sodium carbonate solution at about 60° with a platinum gauze anode and rotating lead cathode, which secures efficient agitation of the mixture; a porous cell is unnecessary. The success of the method does not depend on the intermediate formation of potassium percarbonate.

H. W.

Theory of the *cis-trans*-Isomerism of Decahydronaphthalene. ERNST MOHR (*Ber.*, 1922, 55, [B], 230—231).—Willstätter and Waldschmidt-Leitz, in a recent discussion of the



theoretically possible number of isomerides in completely hydrogenated naphthalene derivatives, have expressed the opinion that only the *cis*-form (I) is capable of existence (A., 1921, i, 667). Since, however, the author has been

able to construct a model for both *cis*- and *trans*-tetrahydronaphthalene (II) which is completely free from strain (cf. A., 1919, ii, 229), he considers that the ultimate experimental realisation of the *trans*-isomeride is possible.

H. W.

Certain Chloronaphthalene Derivatives. P. FRIEDLÄNDER, S. KARAMESSINIS, and O. SCHENK (*Ber.*, 1922, **55**, [B], 45—52).—The chlorination of nitronaphthalenesulphonic acids leads to the elimination of the sulphonic group which is replaced by chlorine. The reaction is not quite quantitative, since, even with the calculated quantity of the reagents, a certain amount of oxidation occurs, leading apparently to the production of chloroquinones, which, however, are readily separated from the chloronitronaphthalenes by means of alkali.

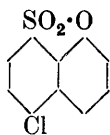
Gradual addition of an aqueous solution of sodium chlorate at 90—95° to a solution of sodium 1-nitronaphthalene-5-sulphonate in aqueous hydrochloric acid yields 5-chloro-1-nitronaphthalene, almost colourless needles, m. p. 111°; it is preferable to remove the chloronitronaphthalene from the mixture as it is formed by means of di-(tri-)chlorobenzene. 5-Chloro- α -naphthylamine crystallises in long, colourless needles, m. p. 85°, whilst its *acetyl* derivative forms hexagonal prisms, m. p. 128°. The crude chloronitronaphthalene contains small amounts of 1:4:5-trichloronaphthalene, m. p. 133°. 1-Nitronaphthalene-8-sulphonic acid is transformed similarly into 8-chloro-1-nitronaphthalene.

2-Nitronaphthalene-4:8-disulphonic acid is the main product of the nitration of naphthalene-1:5-disulphonic acid (the *sodium* salt, lustrous needles, and the sparingly soluble *barium* salt, $C_{10}H_5O_8NS_2Ba$, are described); it is converted by chlorination into 4:8-dichloro-2-nitronaphthalene, long, yellow needles, m. p. 132°. The latter is reduced by stannous chloride or iron and hydrochloric acid to 4:8-dichloro- β -naphthylamine, colourless needles, m. p. 132—133° (the *hydrochloride*, and the *acetyl* derivative, colourless needles, m. p. 265°, are described). The base can be diazotised in concentrated sulphuric acid solution, from which the *diazonium sulphate* is precipitated by addition of water in small, pale yellow needles. The latter couples normally with phenols and naphthols; it is transformed by boiling dilute sulphuric acid into 4:8-dichloro- β -naphthol, colourless needles, m. p. 158—159° (*methyl ether*, needles, m. p. 93°), and by hydrochloric acid and cuprous chloride into 2:4:8-trichloronaphthalene, yellow needles, m. p. 94°.

4:8-Dichloro-1-nitronaphthalene, pale yellow needles, m. p. 142°, is prepared by the chlorination of 1-nitronaphthalene-4:8-disulphonic acid or of 4-chloro-1-nitronaphthalene-8-sulphonic acid (the latter appears to be the sole product of the nitration of 1-chloronaphthalene-5-sulphonic acid; the *sodium* salt is described). It is reduced to 4-chloro- α -naphthylamine-8-sulphonic acid, rhombic crystals, the *sodium* salt of which is sparingly soluble in water). 4:8-Dichloro- α -naphthylamine crystallises in long, slender needles, m. p. 113°, and yields an *acetyl* derivative, m. p. 163°.

5:8-Dichloro-1-nitronaphthalene, m. p. 93° (5:8-dichloro- α -naphthylamine, m. p. 104°, and its *acetyl* derivative, hexagonal prisms, m. p. 202°), is prepared by the chlorination of the product of the nitration of 1-chloronaphthalene-4-sulphonic acid. The production of two isomeric nitro-acids during the latter process is most conclusively demonstrated by their reduction to the

readily soluble 8-chloro-1-aminonaphthalene-5-sulphonic acid (the constitution of which follows from its conversion by sodium amalgam into 8-chloro- α -naphthylamine) and the sparingly soluble 5-chloro-1-aminonaphthalene-8-sulphonic acid, which is converted by boiling its diazotised solution into the *sulphone* (annexed formula), colourless needles, m. p. 184°.



4-Chloro-1 : 8-dinitronaphthalene, m. p. 180°, is prepared from 1 : 8-dinitronaphthalene-4-sulphonic acid (the *sodium* salt and the corresponding *sulphonyl chloride*, pale yellow needles, m. p. 152·5°, of the latter are described).

When similarly chlorinated, 1 : 8-dinitronaphthalene-3 : 6-disulphonic acid and 1 : 5-dinitronaphthalene-3 : 7-disulphonic acid do not yield precipitates.

H. W.

Vapour Pressure Determinations on Naphthalene, Anthracene, Phenanthrene, and Anthraquinone between their Melting and Boiling Points. O. A. NELSON and C. E. SENSEMAN (*J. Ind. Eng. Chem.*, 1922, **14**, 58—62).—Few determinations of vapour pressure have been carried out with most of the solid hydrocarbons between the temperatures of their melting and boiling points, or above. Vapour-pressure determinations over a range of temperatures have now been carried out on naphthalene, anthracene, phenanthrene, and anthraquinone, using Smith and Menzies's dynamic isothermoscope (A., 1910, ii, 1037), and tables and curves of observed vapour pressures of these compounds are recorded. Boiling-point determinations on anthracene, phenanthrene, and anthraquinone gave anthracene, b. p. 342°; phenanthrene, b. p. 340·2°; anthraquinone, b. p. 379·8°.

F. M. R.

Perylene. F. HANSRIG (U.S. Pat. 1384615; cf. A., 1920, i, 541).—A high yield of perylene is obtained by treating 2-derivatives of naphthalene or of 1 : 1'-dinaphthyl with halogenating agents such as the halogen compounds of phosphorus, antimony, arsenic, or aluminium to obtain 2-substituted halogen derivatives, and then transforming the latter into perylene by the action of ring-closing reagents such as aluminium chloride or by the "pyrolysis synthesis." A reducing flux such as phosphorous acid is preferably used in the process and it may be carried out as a single operation with isolation of the intermediate halogen derivatives, or, if desired, the latter may be separately obtained and used as starting materials for the last stage of the process. Among the starting materials which may be used are 2 : 2'-hydroxy-1 : 1'-dinaphthyl and 2 : 2'-dichloro-1 : 1'-dinaphthyl.

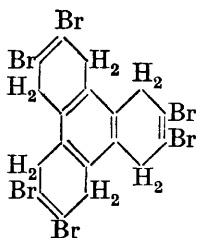
CHEMICAL ABSTRACTS.

Condensations of Acetylene. I. Elucidation of the Constitution of Cuprene. H. P. KAUFMANN and M. SCHNEIDER (*Ber.*, 1922, **55**, [B], 267—282).—Cuprene has been obtained previously by several observers by the decomposition of acetylene in the presence of reduced copper or oxides of copper, but the elucidation of its constitution has been rendered difficult by the poverty of the yield, the insolubility of the product, and the

difficulty with which it is attacked by reagents. A more potent catalyst has now been found in the residue obtained by heating anhydrous copper ferrocyanide in a current of air at 250° during fifteen minutes, which is approximately three times as active as reduced copper. The optimal temperatures for reduced copper, cupric oxide, cuprous oxide, and copper ferrocyanide residue are $240\text{--}250^{\circ}$, $230\text{--}240^{\circ}$, $230\text{--}240^{\circ}$, and $240\text{--}250^{\circ}$, respectively. The product of the reaction has a differing colour, dependent on the duration of heating and the particular contact agent. The residue obtained with decomposed copper ferrocyanide is yellow to pale brown, whereas that prepared with other catalysts is darker in shade, the portions richer in copper being dark brown to black. The latter are converted into paler products poorer in copper by further treatment with acetylene. With a short period of heating the product is loose and voluminous, but becomes more compact when the heating is protracted. It is frequently spontaneously inflammable at $100\text{--}150^{\circ}$, but this property is not due to cuprene itself, but to finely-divided pyrophoric metal. A liquid condensation product is deposited in green, oily drops on the cooler portions of the tube; the further investigation has been prevented by the small quantity available. Copper can only be removed from the solid product with great difficulty by treatment with hydrochloric acid (20%), and it is necessary to use aqua regia to obtain specimens the copper content of which is so small that it can be neglected in the analysis. The composition of cuprene is not uniform, varying between $(C_{11}H_{10})_x$ and $(C_{15}H_{10})_x$. The main factor in the formation of the different types of cuprene is the uncontrollable oxidative action of the oxygen. The formation of cuprene cannot at present be completely explained, but it appears most probable that a copper acetylide is formed intermediately which decomposes into cuprene without explosion; the uniform distribution of the metal throughout the product is otherwise difficult to account for.

Cuprene is attacked violently by very concentrated nitric acid. It dissolves very slowly in boiling 50% nitric acid, and the clear yellow solution, when neutralised with ammonia and concentrated, yields ammonium mellitate. If the acid solution is diluted largely with water, a brown, mellogen-like precipitate is obtained which is transformed into mellitic acid by nitric acid (80%) and into benzoic acid by dry distillation. The filtrate from the brown precipitate is neutralised by barium hydroxide, whereby an inseparable mixture of barium salts is obtained from which naphthalene is produced by dry distillation. Cuprene is not attacked by dilute solutions of bromine in water or organic media, whereas the action of elementary bromine causes carbonisation with elimination of hydrogen bromide. It may, however, be brominated by heating a paste of it with water and bromine at $100\text{--}130^{\circ}$ in the presence of iron bromide. Since cuprene itself is not homogeneous, it is not surprising that the composition of the brominated product depends on the experimental conditions adopted. One such *substance*, prepared by extracting the crude product with

alcohol and subsequent treatment of the residue from the alcoholic solution with ether, forms a pale yellow, amorphous powder, analyses and determinations of the molecular weight of which agree with the formula $C_{18}H_{12}Br_6$. It is converted by nitric acid into mellitic acid. It appears, therefore, to be a hexabromohexahydrotriphenylene (annexed formula), in which the position of the bromine atoms is not established. All attempts to isolate the parent hydrocarbon by removal of the bromine atoms were unsuccessful, since the residue (immediately after loss of bromine) became polymerised to a hydrocarbon resembling cuprene.



H. W.

The System : Acetanilide-Water. N. SCHOORL and F. N. B. DE WEERD (*Rec. trav. chim.*, 1922, **41**, 15—20).—The acetanilide-water system exhibits a region of heterogeneous equilibrium which is situated above the ordinary temperature and connects the solubility and depression of freezing-point curves. The temperature limits of this region are 83.2° and 144° , and the composition limits from 5.2% to 87% of acetanilide. At 144° , the highest temperature at which the system is heterogeneous, the composition is 40% acetanilide, 60% water.

H. J. E.

Aniline Glucoside (Glucose Anilide). TH. SABALITSCHKA (*Ber. deut. Pharm. Ges.*, 1921, **31**, 439—445).—Acetobromoglucose reacts with aniline at ordinary temperatures, and after twenty-four hours the initially clear solution sets to a solid mass from which *aniline tetracetyl-d-glucoside* was isolated in long needles, m. p. $95-96^\circ$, $[\alpha]_D^{24} -59.5$ (after twenty-four hours). On hydrolysis in methyl alcoholic solution with barium hydroxide, it was converted into *aniline-d-glucoside*, which accordingly has the γ -oxidic structure $OH \cdot CH_2 \cdot CH(OH) \cdot \underbrace{CH \cdot CH(OH) \cdot CH(OH) \cdot CH \cdot NPh}_{O}$. The

substance was deposited from organic solvents as a gelatinous mass which dried to a white, amorphous powder, m. p. 147° , $[\alpha]_D^{20} -52.4^\circ$ (in methyl alcohol) constant after four days. *Aniline-d-glucoside* thus prepared was identical with glucose anilide, obtained by the direct action of aniline on dextrose, to which the structure of a Schiff's base had originally been ascribed, and the correctness of Sorokin's (A., 1888, 807) and, later, of Irvine's views (T., 1908, **93**, 95, 1429) of the constitution of this substance as a glucoside is thus confirmed.

G. F. M.

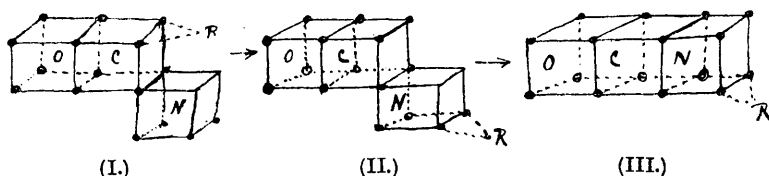
6-Amino- α -naphthol-5-sulphonic Acid (A-acid) and its Derivatives. HANS TH. BUCHERER and RUDOLF WAHL (*J. pr. Chem.*, 1921, [ii], **103**, 129—162).—2-Naphthylamine-1 : 5-disulphonic acid, which may be obtained by treating 2-naphthylamine-1-sulphonic acid with fuming sulphuric acid at $30-40^\circ$, is converted into its potassium salt and fused with potassium hydroxide to give 6-amino- α -naphthol-5-sulphonic acid (A-acid). The yield

k 2

and nature of the by-products (6-amino- α -naphthol, 1 : 6-dihydroxynaphthalene, and 1 : 6-dihydroxynaphthalene-5-sulphonic acid) vary with the exact conditions employed. *A*-acid forms a characteristic orange diazonium salt. 2-Naphthylamine-1 : 5-disulphonic acid, on heating with 75% sulphuric acid, gives β -naphthylamine and 2-naphthylamine-5-sulphonic acid and with sulphuric acid monohydrate, 2-naphthylamine-5-, -6-, and -7-sulphonic acids. *A*-acid with mineral acids gives 6-amino- α -naphthol. On sulphonation with concentrated sulphuric acid a mixture of 6-amino- α -naphthol-2 : 5-disulphonic acid and 6-amino- α -naphthol-4 : 5-disulphonic acid are obtained. With acetic anhydride, 6-acetyl-amino- α -naphthol-5-sulphonic acid is formed, with benzoyl chloride 6-dibenzoylamino- α -naphthol-5-sulphonic acid, with toluenesulphonyl chloride it forms the expected product, $C_{17}H_{15}O_6NS_2$, and with carbonyl chloride the carbamide.

W. O. K.

Rearrangements of some New Hydroxamic Acids Related to Heterocyclic Acids and to Diphenyl- and Triphenyl-acetic Acids. LAUDER W. JONES and CHARLES D. HURD (*J. Amer. Chem. Soc.*, 1921, **43**, 2422—2448).—An interpretation of the mechanism of the Beckmann rearrangement is proposed, based on Langmuir's theory of the atom. The stages in the rearrangement are pictured as follows, in which Fig. 1 represents the intermediate



univalent nitrogen derivative and Fig. III the carbimide stage in the rearrangement. As a further hypothesis to explain why one radicle, R, will migrate more readily than another radicle, R', the authors suggest that the relative ease of arrangements of the Beckmann type is dependent on the tendency for the radicle R, in the univalent nitrogen derivative, such as $[R \cdot CO \cdot N]$, to exist as a free radicle. This hypothesis finds support in the results obtained for the relative ease with which the sodium and potassium salts of the acyl esters of diphenylacethydroxamic acid and triphenylacethydroxamic acid undergo rearrangement. The salts of the triphenyl derivative undergo rearrangement the more readily.

Two new methods of preparing hydroxamic acids are described.


In the first, by the action of free hydroxylamine on a keten such as diphenylketen, the corresponding hydroxamic acid is obtained,

$$CPh_2 \cdot CO + NH_2 \cdot OH = CHPh_2 \cdot CO \cdot NH \cdot OH.$$


The second method is a modification of the one usually employed, namely, the action of acid chlorides on hydroxylamine in aqueous solution. If a neutral solvent, such as benzene, is used in place of water, a quantitative yield of the monohydroxamic acid is obtained.

Diphenylacethydroxamic acid, $\text{CHPh}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, m. p. 172° , is prepared by the action of hydroxylamine on ethyl diphenylacetate in the presence of sodium methoxide or by either of the above methods. It gives a *benzoyl* ester, m. p. 140 — 140.5° , the *sodium* and *potassium* salts of which could not be obtained in the pure state. The *silver* salt showed chromoisomerism. The alcohol-ether solution of the sodium salt, on evaporation, leaves a mixture of the salt with its products of decomposition and rearrangement, namely, *diphenylmethylcarbimide*, *diphenylmethylurethane*, m. p. 122 — 123° , and sodium benzoate. When this residue is extracted with cold water and the solution filtered and boiled, *s-bisdiphenylmethylcarbamide*, $\text{CO}(\text{NH}\cdot\text{CHPh}_2)_2$, m. p. 269.5 — 270° , is obtained. Diphenylacethydroxamic acid yields a *monoacetyl* derivative, m. p. 113 — 113.5° ; giving *potassium*, *sodium*, and *silver* salts, and a *diacetyl* derivative, m. p. 95.5 — 97.5° . Diphenylmethyl urethane reacts with phosphorus pentachloride, yielding *diphenylmethylcarbamyl chloride*, $\text{CHPh}_2\cdot\text{NH}\cdot\text{COCl}$, which when left in contact with calcium oxide gives diphenylmethylcarbimide and this when treated with benzoyl-hydroxylamine yields *s-bisdiphenylmethylcarbamide*.

Triphenylacetyl chloride reacts with hydroxylamine to give *triphenylacethydroxamic acid*, m. p. 175 — 176° , which yields a *benzoyl* ester giving *sodium*, *potassium*, and *silver* salts. The *silver* salt showed chromoisomerism, but the *sodium* and *potassium* salts could not be obtained pure owing to the readiness with which they decomposed, giving *triphenylmethylcarbimide*, m. p. 85 — 87° . The *acetyl* ester, m. p. 133.5 — 134° , gives *potassium*, *sodium*, and *silver* salts, the two former of which are somewhat more stable than the corresponding salts of the *benzoyl* ester. In these rearrangements, none of the *s-bistriphenylmethylcarbamide* was formed.

Pyromucylhydroxamic acid,  $\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$ (cf. Pickard and

Neville, T., 1901, **79**, 847), its *ammonium* salt, m. p. 130 — 131° , its *benzoyl* ester, m. p. 140° , and the *potassium*, *sodium*, and *silver* salts of the ester were prepared. When the *potassium* salt was warmed in aqueous solution, some of the ester was first precipitated, and when this was filtered off and the filtrate boiled, a red, resinous mass, presumably of difurylcarbamide, was obtained. The *acetyl* ester, m. p. 95 — 96° , of the hydroxamic acid gave *potassium*, *sodium*, and *silver* salts, the rearrangement and hydrolysis of these salts being similar to those of the corresponding salts of the *benzoyl* ester.

Thienoylhydroxamic acid,  $\cdot\text{CO}\cdot\text{NH}\cdot\text{OH}$, m. p. 123 — 124.5° , was

obtained either by the action of hydroxylamine on ethyl thiophenecarboxylate, $\text{C}_4\text{H}_3\text{S}\cdot\text{CO}_2\text{Et}$, or by the action of hydroxylamine on thienoyl chloride. It gave an *ammonium* salt, m. p. 142 — 143° (decomp.); a *benzoyl* ester, m. p. 143 — 144° , giving *potassium*, *sodium*, and *silver* salts; an *acetyl* ester, m. p. 96.5 — 97° , giving *potassium*, *sodium*, and *silver* salts; and a *thienoyl* ester [*dithienoyl*-

hydroxamic acid, $C_4H_3S \cdot CO \cdot NH \cdot O \cdot CO \cdot C_4H_3S$], which occurred in two forms, and gave *potassium*, *sodium*, and *silver* salts.

The salts of the esters of thienoylhydroxamic acid underwent slight hydrolysis in aqueous solution, but the main change was one of rearrangement to *sym*-dithienylcarbamide.

The *thienoyl* ester, m. p. 133—133.5°, of benzhydroxamic acid, which was isomeric with the benzoyl ester of thenhydroxamic acid, was prepared and its *potassium* and *silver* salts were investigated. The melting points of the esters and the decomposition temperatures of their salts, and the ease of rearrangement of the latter, were almost identical in the two cases. W. G.

Metallic Derivatives of Nitrophenolic Compounds. IV. Some Complex Nitrophenoxides of Magnesium, Silver, and Lead. ARCHIBALD EDWIN GODDARD and JAMES BERTRAM WARD (T., 1922, 121, 262—266).

Auto-oxidation : the Anti-oxygens. CHARLES MOUREU and CHARLES DUFRAISSE (*Compt. rend.*, 1922, 174, 258—264).—The auto-oxidation of a large number of substances may be checked by the presence of traces of certain compounds to which the authors give the name "anti-oxygens." Most of the substances which have been found to show this inhibiting action belong to the phenol group, and of these quinol, catechol, and pyrogallol are particularly active. This protecting action may be prolonged for two years at least, providing the substance capable of auto-oxidation does not sublime from the anti-oxygen. The secondary reactions which often accompany auto-oxidation are also inhibited by the presence of the anti-oxygens. The action of the anti-oxygens is apparently catalytic, and it is of interest to note that traces of pyrogallol, a substance commonly used as an absorbent of oxygen, oppose the action of this gas.

The bearing of these observations on the phenomena of life in the animal and the vegetable kingdom is discussed. It is suggested that the toxic properties of phenols are connected with their activities as anti-oxygens. W. G.

The Quadrivalence of Tin in its Mercaptides. H. WUYTS and A. VANGINDERTAELEN (*Bull. Soc. chim. Belg.*, 1921, 30, 323—328).—Stannic mercaptides can be prepared (a) by the action of tin and hydrochloric acid on organic disulphides with subsequent neutralisation, (b) from a thioalcohol and stannous chloride in presence of air, or (c) from a thioalcohol and stannic chloride. Attempts to prepare stannous mercaptides did not succeed, and the behaviour of tin in this respect is compared with that of its sulphides towards alkali sulphide solutions.

The *mercaptide*, $Sn(S \cdot C_6H_4 \cdot NMe_2)_4$, prepared from dimethylaniline-disulphide, is a red, crystalline substance, m. p. 159°; with benzoyl chloride in benzene solution, it forms the benzoate of the corresponding thioalcohol, m. p. about 136°; with methyl iodide, two reactions take place, one with the rupture of the sulphur-tin linking

and the combination of methyl and iodine with the elements respectively, the other with formation of the iodide of the quaternary ammonium base, $\text{NMe}_3\text{I}\cdot\text{C}_6\text{H}_4\cdot\text{SMe}$. Similarly, from di-*p*-aminophenyl disulphide, the *mercaptide*, $\text{Sn}(\text{S}\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2)_4$, red, leafy crystals, m. p. about 166° , was obtained. H. J. E.

Sulphobenzide [Diphenylsulphone]. EUG. GRANDMOUGIN (*Compt. rend.*, 1922, **174**, 168—170).—3:3'-Diaminodiphenylsulphone gives a bis-diazo-derivative which couples normally with the naphthols and their sulphonic derivatives. The dyes obtained have almost the same shades as the corresponding dyes from aniline itself, the chromophoric influence of the sulphone group in the meta-position to the two amino-groups being thus practically negligible. The dyes obtained dye only wool and not cotton.

New compounds mentioned are 3:3'-dichlorodiphenylsulphone, m. p. 108° ; 3:3'-dibromodiphenylsulphone, m. p. 119° ; and 3:3'-di-iododiphenylsulphone, m. p. 158° .

In view of the erroneous statements occurring in the literature, the correct melting points of certain of the 3:3'- and 4:4'-derivatives of diphenylsulphone are tabulated as follows.

	$(\text{NO}_2)_2$	$(\text{NH}_2)_2$	$(\text{NHAc})_2$	$(\text{OH})_2$	Cl_2	Br_2	I_2
3:3'	201°	168°	211°	$186\text{--}187^\circ$	108°	119°	158°
4:4'	282	174	280	239	147	172	197

W. G.

Cholesterol Dibromide. I. LIFSCHÜTZ (*Zeitsch. physiol. Chem.*, 1921, **114**, 286—289).—Cholesterol dibromide prepared by the ether method has m. p. $93\text{--}94^\circ$, whilst when the glacial acetic acid method is used it has m. p. $110\text{--}111^\circ$. The author brings forward evidence which suggests that a compound of the dibromide and acetic acid has been formed in the second case.

The author considers that the cholesterol dibromide, m. p. 122° , obtained by Windaus and Lüders is possibly an isomeride of the dibromide obtained by himself. S. S. Z.

The Replacement of Halogen in 4-Chloro-3-nitrobenzonitrile and in 4-Bromo-3-nitrobenzonitrile. TH. J. F. MATTAAR (*Rec. trav. chim.*, 1922, **41**, 24—37).—The reactions between 4-chloro-3-nitrobenzonitrile and/or 4-bromo-3-nitrobenzonitrile and sodium methoxide, sodium ethoxide, sodium phenoxide, methylamine, ethylamine, dimethylamine, aniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, methylaniline, *p*-phenylenediamine, hydrazine, phenylhydrazine, and phenylmethylhydrazine have been investigated. The following new substances have been prepared: 3-Nitro-4-methoxybenzonitrile, pale brown needles, m. p. 151° ; 3-nitro-4-ethoxybenzonitrile, white needles, m. p. 121° ; 3-nitro-4-phenoxybenzonitrile, colourless prisms, m. p. 138° ; 3-nitro-4-methylaminobenzonitrile, yellow needles, m. p. 169° ; 3-nitro-4-ethylaminobenzonitrile, yellow needles, m. p. 132° ; 3:5-dinitro-4-ethylnitroaminobenzonitrile, lustrous plates, m. p. $142\cdot5^\circ$; 3-nitro-4-dimethylaminobenzonitrile, yellow plates, m. p. 114° ; 3-nitro-4-*o*-toluidinobenzonitrile, brownish-yellow plates, m. p. 116° ; 3-nitro-4-*m*-toluidino-

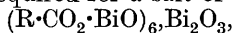
benzonitrile, orange needles, m. p. 149°; *3-nitro-4-p-toluidinobenzonitrile*, orange needles, m. p. 128°; *3-nitro-4-methylanilinobenzonitrile*, yellow, irregular plates, m. p. 144°; *3-nitro-4-p-aminobenzonitrile*, deep violet crystals, m. p. 158°; *benzaldehyde-2-nitro-4-cyanophenylhydrazine*, red plates which turn colourless on drying, m. p. 225°; *acetophenone-2-nitro-4-cyanophenylhydrazine*, lustrous, red needles, m. p. 232°; *3-nitro-4-phenylmethylhydrazinobenzonitrile*, red crystals, m. p. 132°. The reaction between phenylhydrazine and 4-chloro-3-nitrobenzonitrile (cf. Borsche, Stackmann, and Makaroff-Semljansky, A., 1917, i, 15) yields a substance which is considered to be converted on oxidation into 3-nitro-4-phenylhydrazinobenzonitrile, colourless needles, m. p. 181°.

H. J. E.

Preparation of Phenylglycine Compounds. BRITISH DYE-STUFFS CORPORATION, LTD., HERBERT LEVINSTEIN, and GEORGES IMBERT (Brit. Pat. 173540).—Phenylglycine compounds are obtained in one operation from trichloroethylene by heating it in aqueous suspension with aniline, and an alkali, preferably calcium hydroxide, in an autoclave at 140–190°, the treatment being continued until the intermediate products, for example, ethylenetriphenyltriamine, are completely transformed into phenylglycine compounds. For example, 132 parts of trichloroethylene, 100 parts of lime, 800 parts of water, and 280 parts of aniline, are heated in an autoclave with constant agitation for twenty-four hours at 180°. The excess of aniline is distilled off the calcium phenylglycine and excess of lime separated from the mother liquors, and converted into sodium phenylglycine by boiling with the requisite quantity of sodium carbonate.

G. F. M.

The Hydrolytic Decomposition of the Bismuth Salts of Phenolcarboxylic Acids. A. PERLING (*Ber. Deut. Pharm. Ges.*, 1921, **31**, 433–438).—The hydrolysis by water of the neutral and basic bismuth salts of benzoic, salicylic, protocatechuic, gallic, and cinnamic acids proceeds to a definite limit which is attained when they are heated at 100° with four consecutive quantities of water for a total of ten hours. Both the neutral and basic salts of the various acids eventually attain the same composition, the only salt remaining unchanged being the basic benzoate, having the composition $(\text{PhCO}_2 \cdot \text{BiO})_6 \cdot \text{Bi}_2\text{O}_3$. The experimentally-determined composition of the final hydrolytic product of all the other bismuth salts above mentioned was found to be in close agreement with the theoretical figure required for a salt of the composition



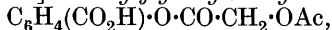
analogous to the basic benzoate (R =phenol residue), and it is therefore evident that hydrolysis proceeds to precisely the same point with all the salts. When shaken at 37° with 0.25% hydrochloric acid, conditions resembling those existing in the stomach, a slightly greater degree of hydrolysis was observed.

G. F. M.

Substituted Salicylic Acids. I. H. P. KAUFMANN and W. KAUFMANN (*Ber.*, 1922, **55**, [B], 282–288).—A number of

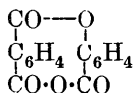
substances are described which were obtained during an investigation of the influence of different substituents on the physiological action of salicylic acid.

[With H. GÖTTING.]—*Acetylglycolylsalicylic acid*,

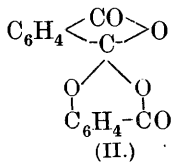


small, colourless needles, m. p. $103\text{--}104^\circ$, is prepared by the action of acetylglycolyl chloride on sodium salicylate in the presence of benzene at the atmospheric temperature. It is readily hydrolysed by warm water to acetylglycollic and salicylic acids.

The action of *s-o*-phthalyl chloride on sodium or disodium salicylate in the presence of boiling



(I.)



(II.)

dry benzene leads to the formation of a substance (annexed formulæ I or II), colourless needles, m. p. $158\cdot5^\circ$. It is slowly hydrolysed by alcoholic sodium hydroxide solution to phthalic and salicylic acids. It is

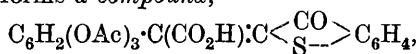
reduced by zinc dust and glacial acetic acid to phthalide and salicylic acid; the latter reaction appears to indicate the unsymmetrical constitution of the parent substance, but this point cannot yet be regarded as established with certainty. H. W.

Glucosides. X. The Action of *dl*-Acetobromoglucose on the Silver Salt of *dl*-Mandelic Acid. P. KARRER, C. NÄGELI, and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1922, 5, 141—146).—It has been shown previously (Karrer and Nägeli, A., 1919, i, 594) that acetobromoglucose reacts with silver *dl*-mandelate in the presence of toluene to form *d*-tetra-acetylglicosido-*dl*-mandelic acid, $\text{CO}_2\text{H}\cdot\text{CHPh}\cdot\text{O}\cdot\text{C}_6\text{H}_7\text{O}_5\text{Ac}_4$, *d*-tetra-acetylglucose *dl*-mandelate, and *d*-tetra-acetylglucose *d*-tetra-acetylglicosido-*l*-mandelate from which *l*-mandelic acid was isolated by hydrolysis. The similar action between *dl*-acetobromoglucose and silver *dl*-mandelate has been found to give products of the same three types, all of which are optically inactive. Since *d*-acetobromoglucose only combines with *l*-mandelic acid to form a corresponding compound (*loc. cit.*), it follows that the inactive tetra-acetylglucose tetra-acetylglicosidomandelate must be a racemate combined from *d*-tetra-acetylglucose *d*-tetra-acetylglicosido-*l*-mandelate and *l*-tetra-acetylglucose *l*-tetra-acetylglicosido-*d*-mandelate. Reaction thus appears to be unusually selective, the *d*-glucose derivative combining only with the *l*-acid in this manner, whereas the *l*-glucose compound unites with the *d*-acid. A satisfactory explanation of the unusually marked effect of configuration on the reaction cannot at present be given.

l-Acetobromoglucose, colourless needles, m. p. 88° , $[\alpha]_D^{25} -192\cdot7^\circ$, in ethereal solution, is prepared by the action of acetyl bromide and glacial acetic acid on *l*-glucose. When mixed in ethereal solution with an equal quantity of *d*-acetobromoglucose, it gives *dl*-acetobromoglucose, colourless needles, m. p. 85° . *dl*-Tetra-acetylglucose *dl*-mandelate and *dl*-tetra-acetylglucose *dl*-tetra-acetylglicosido-*dl*-mandelate have m. p. 146° and 227° , respectively. H. W.

New Synthesis of Hydroxylated Benzoylformic [Phenylglyoxylic] Acids. H. FINGER and LINA EIRICH (*J. pr. Chem.*, 1921, [ii], 103, 249—252).—Ethyl cyanoformate can be used instead of hydrocyanic acid in the Gattermann aldehyde synthesis, and hydroxylated phenylglyoxylic acids are produced. Pyrogallol and methyl cyanoformate, dissolved in ether, give with zinc chloride and gaseous hydrogen chloride 2:3:4-trihydroxyphenylglyoxylic acid, $C_6H_2(OH)_3 \cdot CO \cdot CO_2H$, m. p. 171° , which dyes chrome-mordanted wool. It gives a sodium salt, $C_6H_5O_6Na$; a normal aniline salt, m. p. 138° ; whilst on heating with aniline at 135° , 2:3:4-trihydroxybenzylideneaniline, $C_6H_2(OH)_3 \cdot CH:NPh$, is formed, thus proving the constitution of the acid.

The following derivatives of 2:3:4-trihydroxyphenylglyoxylic acid are also described: *nitrophenylhydrazone*, yellowish-red needles, m. p. 230 — 240° (decomp.); *semicarbazone*, decomp. 230° . With oxythionaphthen dissolved in acetic anhydride, trihydroxyphenylglyoxylic acid forms a compound,



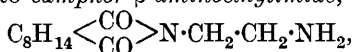
and it couples with benzenediazonium chloride to give an azo-dye.
W. O. K.

The Preparation of Chloro- and Bromo-tyrosine and the Analogous Tyramines. R. ZEYNEK (*Z. physiol. Chem.*, 1921, 114, 275—285).—3:5-Dibromotyrosine and 3:5-dichlorotyrosine are best prepared by the action of the respective halogens on *l*-tyrosine suspended in glacial acetic acid.

l-3:5-Dichlorotyrosine has m. p. 256 — 260° (decomp.), crystallises in rhombic platelets, and the anhydrous hydrochloride gives in 5% aqueous solution $[\alpha]_D^{20} -7.8^\circ$; in 4% hydrochloric acid, $[\alpha]_D^{20} -2.9^\circ$. A 5% solution of dichlorotyrosine containing $2H_2O$ dissolved in 4% hydrochloric acid gave $[\alpha]_D^{20} -2.8^\circ$. *p*-Hydroxyphenylethylamine, when suspended in glacial acetic acid and brominated, yields dibromotyramine hydrobromide, crystallising in monoclinic platelets, m. p. 270° . The free base crystallises in white, flat, rhombic rods, m. p. 210° . Dichlorotyramine hydrochloride, prepared similarly, crystallises in monoclinic plates, m. p. 284 — 286° ; the base has m. p. 219 — 222° . S. S. Z.

Preparation of Soluble Derivatives of Camphoric Acid. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 173063).—Soluble derivatives of camphor which retain the therapeutic properties of that substance but give stable solutions in water sterilisable by heat and therefore suitable for subcutaneous injection, are exemplified by certain *N*-substituted derivatives of camphorimide of the type $C_8H_{14} \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > N \cdot R \cdot N \begin{smallmatrix} R' \\ R'' \end{smallmatrix}$, where R is an alkyl or alkylene group, and R' and R'' are hydrogen, alkyl, or alkylene groups. These compounds are obtainable from camphorimide by the usual methods, as, for example, by causing its isolated dry salt or a solution to react with polyhalogenised saturated or unsaturated aliphatic hydrocarbons or with halogen hydrins, and

the *N*-halogen alkyl or *N*-halogen alkylene camphorimide thus obtained (after substituting halogen for hydroxyl if a halogen-hydrin has been used) is treated with ammonia or an alkylamine. Or, alternatively, camphoric acid or its anhydride may be caused to react with a diamine of the type $\text{NH}_2 \cdot \text{R} \cdot \text{NR}'\text{R}''$. The following substances are described: *Camphor-β-hydroxyethylimide*, a thick, colourless oil, b. p. $190^\circ/15$ mm., is prepared by the action of ethylene iodohydrin on sodiocamphorimide in absolute alcoholic solution. *Camphor-β-chloroethylimide*, prepared by the action of phosphorus pentachloride on the above, is a pale yellow oil, b. p. $168^\circ/10.5$ mm. By heating with ammonia at 100° under pressure, it is converted into *camphor-β-aminoethylimide*,



which can be isolated as its *hydrobromide* as an incompletely solidifying syrup which decomposes at 135 — 140° . The chloroethylimide, when similarly heated with 33% dimethylamine solution at 120 — 125° , gives *camphor-β-dimethylaminoethylimide*, b. p. $163^\circ/14$ mm. It forms a crystalline *hydrobromide*, m. p. 207° , soluble in both water and alcohol. *Camphor-β-bromoethylimide* is obtained by heating potassiocamphorimide with an excess of ethylene dibromide on an oil-bath. It boils at $186^\circ/12$ mm. When heated at 100° with diethylamine, it is converted into *camphor-β-diethylaminoethylimide*, a viscid oil, b. p. 183 — $185^\circ/12$ mm., which gives a crystalline *hydrobromide*, m. p. 157° . *Camphor-β-allylaminoethylimide* is similarly prepared from allylamine and the halogenethylimide. It boils at $187^\circ/12$ mm., and gives a *hydrobromide* crystallising in fine leaflets, m. p. 144° . Illustrative of the second general method of preparation, the above-mentioned β-diethylaminoethylimide may also be obtained by heating at 180 — 200° camphoric acid and *as-diethylethylenediamine*. The latter substance, obtained by the reduction of diethylaminoacetonitrile with sodium and alcohol, forms an oil, b. p. 140 — 145° , with strongly basic properties. In a similar way, from the reduction product of piperidine acetonitrile, by heating with camphoric acid, the corresponding imide *camphor-β-piperidylethylimide* is obtained. Its *hydrobromide* crystallises in fine, felted needles, m. p. 193.5° .
G. F. M.

The Bile Acids. III. Biloidanic Acid [Letsche's Acid].

W. BORSCHÉ, O. WEICKERT, and ROBERT MEYER (*Ber.*, 1921, **54**, [B], 3177—3182).—Biloidanic acid has been prepared by Letsche (*A.*, 1909, i, 697) by the action of a mixture of nitric and sulphuric acids on cholic acid, and examined subsequently by Schenck (*A.*, 1920, i, 847; 1921, i, 179), who concurs in ascribing to it the formula $\text{C}_{19}\text{H}_{28}\text{O}_{10}$. Specimens of the purified acid examined by the authors did not give analytical results in agreement with this formula. The acid was therefore esterified with methyl alcohol and hydrogen chloride, but the product, mainly a dimethyl trihydrogen ester, was not quite uniform. It was therefore converted by diazomethane into the pentamethyl ester (which

has also been prepared by Schenck from the silver salt and methyl iodide). The latter cannot be satisfactorily purified by crystallisation, but, after being distilled under diminished pressure gives analytical results in agreement with the formula $C_{23}H_{36}O_{10}$, thus indicating the formula $C_{18}H_{26}O_{10}$ for the parent acid. The pentamethyl ester has m. p. $91-92^\circ$ after softening at 87° , b. p. $321-322^\circ/18$ mm., $[\alpha]_D$ about $+20^\circ$ in absolute alcoholic solution. Direct analysis of the acid regenerated from the hydrogen ester leads to the same result. The pentamethyl ester has not yet been smoothly re-converted into the acid.

A modification of Letsche's method of preparing the acid is described which permits the isolation of biloidanic acid in the pure condition after a single crystallisation. H. W.

A Critical Examination of the Aromatic Aldehydes occurring in certain Eucalyptus Oils. ARTHUR RAMON PENFOLD (T., 1922, 121, 266-269).

The Reduction of Naphtholcarboxylic Acids to Aldehydes. HUGO WEIL and WALTER HEERDT (*Ber.*, 1922, 55, [B], 224-230).—A continuation of previous work (Weil and Ostermaier, this vol., i, 139).

Tetrahydronaphthaldehyde has been obtained previously (*loc. cit.*) by the reduction of β -naphthol-3-carboxylic acid by sodium amalgam in boric acid solution with the addition of a neutral mixture of sodium sulphite and sodium hydrogen sulphite. The same result is obtained when the action is effected at a temperature not exceeding -5° . The aldehyde is also obtained by the reduction of 2-acetoxynaphthalene-3-carboxylic acid, 1-amino- β -naphthol-3-carboxylic acid, and 1-bromo- β -naphthol-3-carboxylic acid, ammonia or hydrogen bromide respectively being eliminated from the compounds last named. Tetrahydronaphthaldehyde hydrazone, after being crystallised from alcohol containing a little glacial acetic acid, has m. p. 106.5° instead of 96.5° as previously recorded (*loc. cit.*). 1-Amino- β -naphthol-3-carboxylic acid is prepared conveniently by coupling β -naphthol-3-carboxylic acid with diazotised sulphanilic acid and reduction of the dye so formed with zinc dust and glacial acetic acid.

α -Naphthol-2-carboxylic acid does not appear to be reduced beyond the 1-hydroxynaphthal-2-aldehyde stage even by energetic treatment at 25° , 40° , or 55° .

4-Amino-1-hydroxynaphthalene-2-carboxylic acid is so feebly acidic that it is precipitated from solutions of its salts by boric acid and thus escapes reduction.

4-Sulpho-1-hydroxynaphthalene-2-carboxylic acid is reduced to α -naphthol-2-aldehyde, the sulphonic group being eliminated. On the other hand, the cautious reduction of 4-bromo-1-hydroxynaphthalene-2-carboxylic acid leads to the formation of 4-bromo-1-hydroxynaphthalene-2-aldehyde, which, however, could not be obtained in the homogeneous state. It gives the normal compounds with phenylhydrazine (yellow leaflets, m. p. 159°), aniline (orange-yellow needles, m. p. 161°), o-toluidine (yellowish-red

needles, m. p. 188°), *p*-toluidine (yellowish-red needles, m. p. 171°), benzidine ($C_{23}H_{17}ON_2Br$, red leaflets, m. p. 218°), α -naphthylamine (red needles, m. p. 196°), *o*-phenylenediamine ($C_{17}H_{13}ON_2Br$, m. p. 225°), *m*-phenylenediamine (m. p. 201°), *p*-phenylenediamine (m. p. 198°); with ammonia, it gives the compound, $C_{22}H_{18}O_3N_2Br_2$, yellow crystals, m. p. 126°.

4-Chloro-1-hydroxynaphthalene-2-carboxylic acid, m. p. 228°, prepared by the passage of chlorine into a solution of α -naphthol-2-carboxylic acid in glacial acetic acid, is reduced similarly to 4-chloro-1-hydroxynaphthalene-2-aldehyde. The latter gives the usual derivatives with hydroxylamine (colourless needles, m. p. 184°), hydrazine (yellow needles, m. p. 179°), phenylhydrazine (yellow leaflets, m. p. 153°), aniline (yellow needles, m. p. 157°), *o*-toluidine (orange-yellow crystals, m. p. 183°), *p*-toluidine (orange-yellow crystals, m. p. 164°), α -naphthylamine (reddish-yellow leaflets, m. p. 188°), benzidine ($C_{23}H_{17}ON_2Cl$, red crystals, m. p. 214°), *o*-phenylenediamine ($C_{17}H_{13}ON_2Cl$, leaflets, m. p. 221°), *m*-phenylenediamine (m. p. 250°), *p*-phenylenediamine (m. p. 244°); with ammonia it gives the compound, $C_{32}H_{18}O_3N_2Cl_2$. The sodium compound of 4-chloro-1-hydroxynaphthalene-2-aldehyde crystallises in yellow leaflets. H. W.

Preparation of Hydroxyaldehydes and their Derivatives.

SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Brit. Pat. 164715).—In the manufacture of aromatic hydroxyaldehydes by the process described in Brit. Pat. 161679 (A., 1921, i, 420) equally good results are obtained without the use of an organic solvent. Thus vanillin is obtained by adding a concentrated solution of 5·3 kilos. of sodium nitrite and, after some time, 4 kilos. of guaiacol and 8 kilos. of 40% formaldehyde solution to a solution of 8 kilos. of dimethylaniline in 33 kilos. of hydrochloric acid in presence of 33 kilos. of ice. A low temperature is maintained for some hours and the reaction is completed on a water-bath. G. F. M.

The Melting Points of certain Fatty-aromatic Ketones.

RIKO MAJIMA, KWANTO NAGAOKA, and KEISUKE TAMADA (*Ber.*, 1922, 55, [B], 215—217).—A number of ketones of the types $C_6H_3(OMe)_2 \cdot CO \cdot R$, $C_6H_4(OMe) \cdot CO \cdot R$, and $C_6H_5 \cdot CO \cdot R$ have been prepared. The melting points of a compound with an even number of carbon atoms in the side-chain is invariably higher than that of either of its immediate neighbours with an odd number of carbon atoms, as shown by the annexed table:

Side-chain.	M. p. of the compounds.		
	$C_6H_3(OMe)_2 \cdot CO \cdot R$	$C_6H_4(OMe) \cdot CO \cdot R$	$C_6H_5 \cdot CO \cdot R$
$\cdot CO \cdot C_{10}H_{21}$		49°	
$\cdot CO \cdot C_{11}H_{23}$	68—69°	62·5	45°
$\cdot CO \cdot C_{12}H_{25}$	59·5—60	59	41—42
$\cdot CO \cdot C_{13}H_{27}$	74—75	67	54—55
$\cdot CO \cdot C_{14}H_{29}$	64—65	65—66	50—51
$\cdot CO \cdot C_{15}H_{31}$	79—80	72—73	59—60
$\cdot CO \cdot C_{16}H_{33}$	67—68	70·5	56—56·5
$\cdot CO \cdot C_{17}H_{35}$	82—83	77—77·5	

H. W.

Elimination of Hydrogen from Aromatic Nuclei and Union of the Latter by means of Aluminium Chloride.

ROLAND SCHOLL and CHRISTIAN SEER (*Ber.*, 1922, **55**, [B], 109—117; cf. A., 1913, i, 56, 734).—Previous attempts to convert *o*-chlorophenyl α -naphthyl ketone into 5-chloro-1:9-benzanthrone were unsuccessful; this does not, however, appear to be a general characteristic of chlorophenyl ketones, since the corresponding meta- and para-compounds give substituted benzanthrone in rather poor yield.

[With JOSEF DAIMER.]—*o*-Chlorophenyl- α -naphthyl ketone crystallises in colourless needles, m. p. 82°.

m-Chlorophenyl- α -naphthyl ketone, small, pale yellow prisms, m. p. 77—79°, is obtained by the action of *m*-chlorobenzoyl chloride on naphthalene in the presence of carbon disulphide and aluminium chloride. It is converted by aluminium chloride at 145° into 6-chloro-1:9-benzanthrone, golden-yellow needles, m. p. 186—187°. The constitution of the latter follows from the observation that it is oxidised by chromic acid to 6-chloroanthraquinone 1-carboxylic acid, lustrous, golden needles, m. p. 295°, which loses carbon dioxide at 310—320° and yields 2-chloroanthraquinone, slender, yellow needles, m. p. 203—204°.

p-Chlorophenyl α -naphthyl ketone, colourless rods, m. p. 126—128°, is converted by aluminium chloride into 7-chloro-1:9-benzanthrone, yellow, microscopic crystals, m. p. 187—188°.

Anthraquinone-1-carboxyl chloride, pale yellow needles, m. p. 203—204° (cf. Schaarschmidt, A., 1915, i, 566), is conveniently prepared by boiling a solution of the carboxylic acid in phosphoryl chloride with a slight excess of phosphorus pentachloride. It is converted by naphthalene and aluminium chloride in the presence of nitrobenzene into α -naphthyl 1-anthraquinonyl ketone, m. p. 231—232°. Attempts to prepare a benzanthrone derivative from the latter were unsuccessful.

H. W.

Syntheses by means of Sodamide. IX. The Preparation of $\beta\beta$ -Dialkyl- α -hydrindones or 2:2-Dialkylindan-1-ones.

ALBIN HALLER and EDOUARD BAUER (*Ann. Chim.*, 1921, [ix], **16**, 340—354).—The chlorides of β -phenyl- $\alpha\alpha$ -dialkylpropionic acids, $\text{CH}_2\text{Ph}\cdot\text{CR}_2\cdot\text{CO}_2\text{H}$, behave like β -phenylpropionyl chloride (cf. Kipping, T., 1894, **65**, 480) in the presence of aluminium chloride, giving 2:2-dialkylindan-1-ones, which themselves react with sodamide to give the amide corresponding with the original acid chloride.

β -Phenyl- $\alpha\alpha$ -dimethylpropionic acid reacts with thionyl chloride, giving the acid chloride, m. p. 5°; b. p. 125—126°/15 mm., which when treated in the cold with aluminium chloride gives 2:2-dimethylindan-1-one, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CO}\end{smallmatrix}\rangle\text{CMe}_2$, m. p. 44—45°; b. p. 118—119°/15 mm., giving a semicarbazone, m. p. 209—210°. The indanone is decomposed by sodamide, giving β -phenyl- $\alpha\alpha$ -dimethylpropionamide, and since the alkylated indanone may be prepared from indanone itself by the action of methyl iodide on its sodium

derivative, this furnishes a new method for preparing β -phenyl- $\alpha\alpha$ -dialkylpropionamides.

Phenyl *n*-propyl ketone, when treated first with sodamide in anhydrous ether and subsequently with benzyl chloride, gives a mixture of *phenyl α -benzylpropyl ketone*, $\text{COPh}\cdot\text{CHEt}\cdot\text{CH}_2\text{Ph}$, b. p. $183\text{--}184^\circ/13$ mm., giving an *oxime*, m. p. 78° ; and *phenyl $\alpha\alpha$ -dibenzylpropyl ketone*, $\text{COPh}\cdot\text{C}(\text{CH}_2\text{Ph})_2$, m. p. $67\text{--}68^\circ$; b. p. $258^\circ/13$ mm. The former, when treated with sodamide in benzene and then with ethyl iodide, yields *phenyl α -benzyl- α -ethylpropyl ketone*, $\text{COPh}\cdot\text{C}(\text{Et})_2\cdot\text{CH}_2\text{Ph}$, m. p. $80\text{--}80.5^\circ$; b. p. $190\text{--}202^\circ/12\text{--}13$ mm., which can also be prepared by the benzylation of phenyl α -ethylpropyl ketone. Phenyl α -benzyl- α -ethylpropyl ketone reacts with sodamide to give *α -benzyl- α -ethylbutyramide*, which was not isolated in the free state, but was converted into *α -benzyl- α -ethylbutyric acid*, $\text{CH}_2\text{Ph}\cdot\text{C}(\text{Et})_2\cdot\text{CO}_2\text{H}$, b. p. $197\text{--}199^\circ/17$ mm., giving an *acid chloride*, b. p. $148^\circ/13$ mm. The acid chloride, in the presence of aluminium chloride in the cold, yielded *2:2-diethylindan-1-one*, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CO} \end{smallmatrix}\rangle\text{C}(\text{Et})_2$, m. p. 9° ; b. p. $138^\circ/13$ mm.

W. G.

Position of the Double Linking in Piperitone. I. A. R. PENFOLD (*Perf. Essent. Oil Rec.*, 1922, **13**, 19—20).—Piperitone gave on oxidation with cold permanganate a product from which diosphenol was isolated, and identified by its reaction as a keto-phenol and by the preparation of the oxime and the phenyl-urethane. It is probable therefore that the double bond occupies the same position in piperitone as in diosphenol, and the former substance would accordingly be Δ^1 -menthen-3-one. G. F. M.

Constitution of Quinonoid Organic Onium Salts. F. KEHRMANN (*Helv. Chim. Acta*, 1922, **5**, 69—71).—The recent criticisms of Hantzsch (this vol., i, 24) has led the author to state specifically that his formulæ (cf. A., 1918, i, 312; 1921, ii, 476) are applicable to carbonium salts. Further consideration, however, shows that it is unnecessary to indicate the particular union of the dissociable ion with the nitrogen atom, or, more generally, the basic point of attachment of the molecule by means of the dotted line as previously proposed. Nevertheless, it is advisable in writing the formulæ that the connexion between the dissociable ion and the basic group should be rendered sufficiently obvious either by placing them in close proximity or by marking the central atom in some particular manner, for example, by thickened type.

H. W.

Preparation of Intermediates [3-Chloro-2-aminoanthraquinone and 3-Chloro-1-bromo-2-aminoanthraquinone] and a Dyestuff of the Anthraquinone Series. FREDERICK WILLIAM ATTACK and CHARLES WILLIAM SOUTAR (Brit. Pat. 172682).—3-Chloro-2-aminoanthraquinone is obtained by the regulated chlorination at ordinary temperatures of 2-aminoanthraquinone in a suitable solvent such as glacial acetic acid or nitrobenzene until

the requisite increase in weight has taken place. It crystallises from acetic acid in orange-yellow needles, m. p. 221° . When 20 parts of the chloro-compound suspended with 10 parts of sodium carbonate in nitrobenzene are brominated at ordinary temperatures with 21 parts of bromine in 60 parts of nitrobenzene, 3-chloro-1-bromo-2-aminoanthraquinone is obtained as orange-coloured needles, m. p. 235° . This compound undergoes condensation on boiling in nitrobenzene solution with sodium and copper acetates with formation of a dyestuff having probably the constitution 3 : 3'-dichloroanthraquinone-1 : 2 : 1' : 2'-dihydroazine, but possibly the azine, as distinguished from the hydroazine, may be present. It dyes cotton bright blue shades from a hyposulphite vat. All the above reactions may be performed consecutively in the same liquid medium, for example, nitrobenzene, without isolation of the intermediate products. G. F. M.

Production of Dyestuff Intermediates [Aminoanthraquinones]. JOHN THOMAS, ARTHUR HUGH DAVIES, and SCOTTISH DYES, LTD. (Brit. Pat. 173006).—Higher yields of the corresponding aminoanthraquinones and products of better quality are obtained by heating 1-chloroanthraquinone or dichloroanthraquinones with aqueous ammonia in an autoclave than by the usual process with the sulphonic acids. The presence of small amounts of copper salts has a favourable influence on the course of the reaction. For example, a nearly theoretical yield of 1-aminoanthraquinone is obtained by heating 100 parts of 1-chloroanthraquinone with 700 parts of 26% ammonia at 170° for twelve hours in presence of 0.1 part of copper sulphate. G. F. M.

Preparation of 1-Chloro-2-aminoanthraquinone. ALEXANDER WALKER FYFE and BRITISH DYESTUFFS CORPORATION, LTD. (Brit. Pat. 173166).—1-Chloro-2-aminoanthraquinone is prepared, without previously protecting the amino-group by acetylation, by the direct chlorination at 15° of 2-aminoanthraquinone suspended in ten times its weight of nitrobenzene or other suitable solvent, such as acetic acid or chlorobenzene, until the requisite increase in weight has taken place. The yield amounts to 88% of the theoretical. G. F. M.

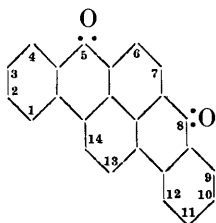
Some Products of the Reduction of 2-Hydroxyanthraquinone. ARTHUR GEORGE PERKIN and THOMAS WILLIAM WHATTAM (T., 1922, 121, 289—300).

Derivatives of β -Methylantraquinone. I. Syntheses of Chrysophanic Acid [1 : 8-Dihydroxy-3-methylantraquinone] and of 1 : 5-Dihydroxy-3-methylantraquinone. R. EDER and C. WIDMER (*Helv. Chim. Acta*, 1922, 5, 3—17).—The course of the reaction between α -nitrophthalic anhydride and *m*-cresol depends considerably on the condensing agent employed. In the presence of boric acid at 170 — 180° , 3'-(or 6')-nitro-3 : 6-dimethylfluoran, colourless, lustrous plates, m. p. 240 — 241° , a substance,

$C_{22}H_{15}O_6$, colourless needles, m. p. 210—211° (the constitution of which has not been elucidated), 6-nitro-*o*-2'-hydroxytoluoylbenzoic acid, $OH \cdot C_6H_3Me \cdot CO \cdot C_6H_3(NO_2) \cdot CO_2H$, coarse, pale green prisms, m. p. 227°, and 3-nitro-*o*-2'-hydroxy-*p*-toluoylbenzoic acid, prisms and needles, m. p. 239—240°, are formed. Attempts to convert the nitro-acids smoothly into anthraquinone derivatives by means of concentrated sulphuric acid were unsuccessful. In the presence of aluminium chloride, α -nitrophthalic anhydride and *m*-cresol give 3-nitro-*o*-2'-hydroxytoluoylbenzoic acid as the sole isolable product. The isomeric nitro-acids are reduced by ferrous hydroxide in boiling ammoniacal solution to 6-amino-*o*-2'-*p*-hydroxytoluoylbenzoic acid, almost colourless leaflets, m. p. 227—228°, and 3-amino-*o*-2'-hydroxytoluoylbenzoic acid, leaflets, m. p. 233—234°, respectively, which are converted in the usual manner into 6-hydroxy-*o*-2'-hydroxy-*p*-toluoylbenzoic acid, colourless, slender needles, m. p. 175—176°, and 3-hydroxy-*o*-2'-hydroxy-*p*-toluoylbenzoic acid, coarse, colourless needles, m. p. 229—230°. The 6-hydroxy-acid is transformed by concentrated sulphuric acid at 160—170° into 1:5-dihydroxy-3-methylantraquinone, golden-yellow leaflets, m. p. 190—191°, whereas the 3-hydroxy-acid is converted by a mixture of boric and sulphuric acids into 1:8-dihydroxy-3-methylantraquinone, yellow leaflets, m. p. 193—194°, which is identical in all respects with natural chrysophanic acid.

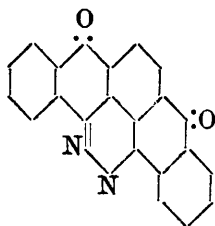
H. W.

Elimination of Hydrogen from Aromatic Nuclei, and Union of the Latter by means of Aluminium Chloride. IV. Ring Closure with Doubly Benzoylated Naphthalenes.



ROLAND SCHOLL and HEINRICH NEUMANN (*Ber.*, 1922, 55, [B], 118—126; cf. A., 1913, i, 56, 734, and this vol., i, 258).—1:4-Dibenzoylnaphthalene is convertible into dibenzopyrene-5:8-quinone (annexed formula), but the corresponding compound from 1:5-dibenzoylnaphthalene could not be prepared.

1:4-Dicyanonaphthalene, long, pale yellow needles, m. p. 206°, is prepared by distilling sodium naphthalene-1:4-disulphonate with potassium cyanide and is hydrolysed by boiling, moderately concentrated sulphuric acid to naphthalene-1:4-dicarboxylic acid, m. p. 309°. The latter is converted by phosphorus pentachloride into naphthalene-1:4-dicarboxyl chloride, slender needles, m. p. 80°, which is transformed by benzene and aluminium chloride in the presence of carbon disulphide into 1:4-dibenzoylnaphthalene, colourless needles, m. p. 106°. The ketone yields, after treatment with aluminium chloride at 130°, a small amount of dibenzopyrene-5:8-quinone, broad, reddish-brown needles, m. p. 365°, which is purified preferably by sublimation. The corresponding dibenzopyrene, greenish-yellow leaflets or prisms, m. p. 281·5—282°, is formed by reduction of the quinone with zinc dust in an atmosphere of hydrogen. The quinone is oxidised by chromic acid



and its chloride;

1:5-dibenzoylnaphthalene, colourless crystals, m. p. 185—186°, is obtained from the latter.

H. W.

Phenolcamphorein. SRI KRISHNA (T., 1922, **121**, 253—255).

Preparation of Terpeneol. ROBERT MARCHAND (Brit. Pat. 153605).—Terpeneol is obtained from terpin hydrate in nearly theoretical yield by distilling it with water and an organic sulphonic acid, preferably quinoline-8-sulphonic acid. The process may, if desired, be rendered continuous by adding further quantities of terpin hydrate as the terpeneol distils over.

G. F. M.

The Main Constituent of Japanese Lac. VIII. Position of the Double Bonds in the Side Chain of Urushiol and Demonstration that Urushiol is not Homogeneous. RIKO MAJIMA (*Ber.*, 1922, **55**, [B], 172—191; cf. A., 1920, i, 837, and previous abstracts).—Hydrourushiol is present to the extent of 10% in urushiol, the main constituent of Japanese lac. In addition, the following compounds are probably present: $C_6H_3(OH)_2 \cdot [CH_2]_7 \cdot CH:CH \cdot [CH_2]_5 \cdot CH_3$, which on oxidation gives rise to heptaldehyde and the acid, $C_6H_3(OH)_2 \cdot [CH_2]_7 \cdot CO_2H$, or its homologues and $C_6H_3(OH)_2 \cdot [CH_2]_7 \cdot CH:CH \cdot [CH_2]_4 \cdot CH:CH_2$, which yields, on oxidation, formic acid and the same aromatic substances as the preceding compound. The results of the analyses of the bromide and ozonide of the dimethyl ether and the volume of hydrogen absorbed during reduction indicate that it contains two double bonds in the molecule.

Urushiol is a mixture of compounds which differ from one another in the number and position of the double bonds present in the long, normal carbon chain. In this respect it exhibits a close similarity to the drying oils. It is difficult or almost impossible by the available methods to separate urushiol quantitatively into its components. Since, however, all the latter are converted by reduction into the same hydrourushiol, it appears desirable to retain the name urushiol for the original mixture, which is regarded as having a mean molecular formula, $C_{21}H_{32}O_2$ or $C_6H_3(OH)_2 \cdot C_{15}H_{27}$. The isolation of veratrol-*o*-carboxylic acid from the products of the oxidation of urushiol dimethyl ether by potassium permanganate affords valuable confirmation of the constitution of urushiol as deduced by other methods.

[With YOSHIHIDE TAHARA.]—Diacetylurushiol is conveniently prepared by acetylating crude urushiol and distilling the product in a high vacuum (b. p. 212—220°/0.3 mm.). It is ozonised in

chloroform solution and the crude ozonide is decomposed with steam. The volatile products contain acetaldehyde, heptaldehyde, and *n*-heptonic acid; the non-volatile portions consist of diacetylhydrourushiol, 2:3-diacetoxyphenyl-*n*-octaldehyde, a pale yellow liquid, b. p. 205—207°/1 mm., and azelaic acid.

[With GITARO TAKAYAMA.]—Acetylmethylurushiol is converted into its *diozonide*, and the latter is decomposed with steam. The products, isolated in the usual manner, are heptaldehyde, 2-acetoxy-3-methoxyphenyl-*n*-octaldehyde, $C_6H_5(OMe)(OAc) \cdot [CH_2]_7 \cdot CHO$, b. p. 190—210°/0.8 mm., and the corresponding acid, which could not be caused to crystallise and is characterised by conversion into 2-hydroxy-3-methoxyphenyloctonic acid, colourless needles, m. p. 49—50°. The presence of acetylhydrourushiol monomethyl ether is also established.

[With WATANABE.]—Urushiol dimethyl ether is emulsified with water by the aid of a little palmitic acid and sodium hydroxide and oxidised with aqueous potassium permanganate solution initially at the atmospheric temperature and finally at 60°, whereby a mixture of salts and an oil is obtained. The latter contains hydrourushiol dimethyl ether. The mixture of salts is decomposed by sulphuric acid, yielding carbon dioxide, formic acid, oxalic acid, adipic acid, sebacic acid, veratrol-*o*-carboxylic acid, 2:3-dimethoxyphenyl-*n*-octonic acid, and its higher homologues.

[With WATANABE.]—Acetaldehyde has been isolated from the products of the decomposition of the ozonides of dimethylurushiol and diacetylurushiol, but not from that of urushiol monomethyl ether. The difference in behaviour is probably due to the more careful fractional distillation of the latter. A series of experiments with various fractions obtained from urushiol dimethyl ether indicates that the parent substance of the acetaldehyde accumulates in the fractions of lower boiling point, and demonstrates that urushiol is a mixture of closely allied substances which can only be separated from one another with difficulty by fractional distillation.

[With TAKAYAMA.]—The distillation of large quantities of urushiol monomethyl and dimethyl ethers has disclosed the presence of small amounts of an unsaturated volatile hydrocarbon to which the name *urusene* is applied; analyses indicate that it is probably a mixture of $C_{15}H_{28}$ and $C_{15}H_{26}$.

[With OKAZAKI.]—Urushiol dimethyl ether absorbs approximately four atomic proportions of bromine in carbon disulphide solution; the product obtained is not homogeneous. H. W.

The Chief Constituent of Japanese Lac. IX. Chemical Investigation of the different, naturally-occurring Species of Lac which are closely allied to Japanese Lac. RIKO MAJIMA (*Ber.*, 1922, 55, [B], 191—214; cf. preceding abstract).—A Burmese lac (from the stems of *Melanorrhæa usitata*, Wall), to which the name "Thitsi" is applied, is shown to contain thitsiol, a homologue of isohydrourushiol with an unsaturated side chain. As judged by the amount of hydrothitsiol formed by

reduction, however, this substance cannot comprise more than the third part of the material investigated. In this respect, the Burmese variety differs markedly from the Japanese and Indo-Chinese products, since in the latter cases the crude material consists of substances which are reducible to hydrourushiol or hydrolaccol to an extent of at least 90%. Indo-Chinese lac, probably tapped from *Rhus succedanea*, L., contains mainly laccol, which is reduced readily to hydrolaccol; the latter is isomeric with hydrothitsiol, and is a higher homologue of hydrourushiol. Formosa lac from *Semeocarpus vernicifera* and a product from *Rhus ambigua*, Lav., or *Rhus orientalis*, Schn, are shown to contain laccol as main constituent, whereas two specimens of Chinese lac (probably from *Rhus vernicifera* or a closely allied species) contained mainly urushiol. A Siamese lac was found to be impure and to consist in all probability of a mixture of Indo-Chinese and Burmese lac.

[With CHOZO CHIBA.]—The Indo-Chinese lac is purified by solution in alcohol, filtration, and evaporation of the filtrate, treatment of the residue with saturated aqueous sodium chloride solution, and, finally, with light petroleum. It is thus obtained as a pale-brown, viscous liquid which resembles urushiol closely in appearance and in chemical behaviour. When treated with methyl iodide and sodium ethoxide, it is transformed into laccol dimethyl ether, $C_6H_3(OMe)_2 \cdot C_{17}H_{31}$, b. p. 206–208°/0.25 mm., d_4^{25} 0.92954. It is reduced by hydrogen in the presence of platinum black to hydrolaccol, $C_6H_3(OH)_2 \cdot C_{17}H_{35}$, m. p. 63–64°, which is oxidised by potassium permanganate in the presence of acetone to stearic acid. *Hydrolaccol dimethyl ether*, obtained by the catalytic hydrogenation of laccol dimethyl ether, crystallises in long prisms, m. p. 43–44°; with nitric acid it yields 5-nitrohydrolaccol dimethyl ether, m. p. 75–76°, and 5:6-dinitrohydrolaccol dimethyl ether, m. p. 86–87°.

[With YOSHIHIRO KUDO.]—A solution of laccol dimethyl ether in chloroform is converted by ozone into a *mono-ozonide*. The latter is decomposed by boiling water into heptaldehyde, acetaldehyde, formic acid, oxalic acid, an impure aldehyde of the composition $C_6H_3(OMe)_2 \cdot [CH_2]_5 \cdot CHO$, and nonane- ω : ω' -dicarboxylic acid, m. p. 109–111°.

Hydrolaccol is shown to be contained in the crude laccol, thus giving an analogy to the occurrence of hydrourushiol in urushiol (preceding abstract).

[With CHOZO CHIBA.]—The isolation of thitsiol from the black variety of "Thitsi" or Burmese lac is effected by means of alcohol and light petroleum. *Thitsiol dimethyl ether*, $C_{25}H_{40}O_2$, is a pale yellow, viscous liquid, b. p. 204–205°/0.2 mm., d 0.96390. *Hydrothitsiol*, $C_6H_3(OH)_2 \cdot C_{17}H_{35}$, has m. p. 94–96°. *Hydrothitsiol dimethyl ether* crystallises in leaflets, m. p. 56–57°; it is transformed by nitric acid in glacial acetic acid solution into 6-nitrohydrothitsiol dimethyl ether, pale yellow needles, m. p. 75–76°. Hydrothitsiol is shown to be identical with heptadecylcatechol by the direct synthesis of the latter; for this purpose, margaric acid is condensed with catechol in the presence of tin chloride and the

3 : 4-*dihydroxyphenyl hexadecyl ketone*, m. p. 100—103°, thus formed is reduced by Clemmensen's method to heptadecylcatechol.

The proximity to fresh lac juice or even to the lac tree is known to produce a painful but not dangerous skin disease in susceptible persons; this is now shown to be caused by urushiol, and is produced in order of decreasing intensity by distilled urushiol, ordinary urushiol, and crude Japanese lac. Similar effects are produced by other urushiol derivatives, and in this respect urushiol, hydro-urushiol, urushiol dimethyl ether, and hydrourushiol dimethyl ether are placed in order of diminishing activity. The action of urushiol is attributed to the conjoint effect of two contiguous hydroxyl groups and the unsaturated alkyl radicle. A series of experiments with catechol derivatives shows that the intensity of the action increases with increasing length of the alkyl chain, but is not noticeably affected by its position. Laccol of Indo-Chinese, Formosa, and Tsutaurushi lac is approximately as toxic as thitsiol of Burmah lac, but either substance attacks the skin much less violently than urushiol of Japanese or Chinese lac.

H. W.

Kawa-kawa Resin. YOSHIHARU MURAYAMA and KENJIRO MAYEDA (*J. Pharm. Soc. Japan*), 1921, No. 477, 959—968).—S. Murakami (*ibid.*, 1916, 393, and 1918, 563) isolated three compounds: *demethoxy-yanogonine*, $C_{14}H_{12}O_3$, m. p. 133—134°, *β -methylsticinic acid*, $C_{14}H_{14}O_3$, m. p. 175°, and *kawaic acid*, $C_{11}H_{10}O_4$ or $C_{17}H_{16}O_6$, m. p. 84—86°, from the kawa-kawa resin. The authors investigated kawaic acid and found that it corresponds with the empirical formula $C_{15}H_{16}O_5$, and contains one methoxyl group. When heated with alcoholic potash, it gives benzaldehyde and a compound, $C_{14}H_{16}O_3$, light yellow leaves, m. p. 164° (decomp.), which contains one methoxyl group. By oxidation with 2% potassium permanganate, it yields benzaldehyde and benzoic acid. From the mother-liquor from which kawaic acid was isolated a new acid, *β -kawaic acid*, $C_{14}H_{18}O_4$, colourless, slender needles, m. p. 101—103°, was isolated; it is moderately soluble in boiling water and ether, and very soluble in alcohol. It contains a methoxyl group and yields benzoic acid when oxidised with 5% potassium permanganate.

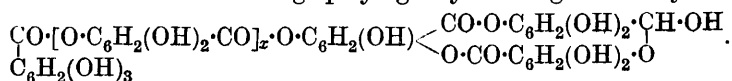
K. K.

The Tinctorial Properties of some Anthocyanins and certain Related Pigments. II. ARTHUR E. EVEREST and ARCHIBALD JOHN HALL (*J. Soc. Dyers and Col.*, 1922, **38**, 9—13; cf. A., 1921, i, 485).—An account of experiments carried out with a view to study the influence on the tinctorial properties of the introduction of acidic and basic radicles in the benzene nucleus of synthetic pigments related to anthocyanins.

Attempts to prepare amino-derivatives by nitration and reduction failed, for treatment of 2-phenylbenzopyroniumferrichloride with nitric acid, or nitric acid and sulphuric acid, resulted in oxidation, but satisfactory results were obtained by an indirect method. Diazotised amines, such as aniline, *o*- and *p*-toluidine,

sulphanilic acid, *p*-nitroaniline, α - and β -naphthylamine, couple with phenyl *o*-hydroxystyryl ketone, probably in the *p*-position with respect to the hydroxyl group, and on reduction yield an amino-derivative which is converted into the corresponding oxonium salt by alcoholic hydrochloric acid. The azo-compounds which were prepared from phenyl *o*-hydroxystyryl ketone possess an affinity for wool, but owing to their sparing solubility in water, their application is difficult, except in the case of the compound derived from sulphanilic acid. The corresponding azo-pyrylium compounds are to be dealt with subsequently. F. M. R.

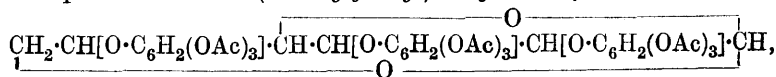
Gallotannin. M. NIERENSTEIN (*J. Soc. Chem. Ind.*, 1922, **41**, 29—30T; cf. Nierenstein, Spiers, and Geake, T., 1921, **119**, 275).—A critical discussion of the attempts to elucidate the constitution of gallotannin is given. It is considered that it is probably a glucoside of the following polydigalloylleucodigallic anhydride,



The formula explains the high molecular weight, the optical activity, and the low electrical conductivity of gallotannin. It is in accord with the observation that gallotannin is more acidic than pyrogallol towards diazoacetic ester. It accounts for the mutarotation of gallotannin and explains the different phases observed in the formation of ellagic acid from gallotannin. It is in accordance with the formation of tetramethylglucose from methylogallotannin. None of the four points last mentioned is explicable on the basis of Fischer's conception of gallotannin as pentadigalloylglucose.

H. W.

Crystalline Synthetic Tannins. I. P. KARRER and HARRY R. SALOMON (*Helv. Chim. Acta*, 1922, **5**, 108—123).—A solution of lævoglucosan in chloroform is converted by triacetylgalloyl chloride and quinoline into *tri-(triacetylgalloyl)lævoglucosan*,



m. p. (indefinite) 137°, after softening at 126°, $[\alpha]_D^{21}$ —10·45° in acetone solution, which has not been obtained in the crystalline condition. It is hydrolysed by an excess of sodium hydroxide in aqueous acetone solution at 0° and the solution, after neutralisation and removal of acetone in a vacuum, deposits successively two gelatinous precipitates (*A* and *B*) when preserved. The former dissolves freely in cold alcohol, but by allowing the alcoholic solution to evaporate slowly at the atmospheric temperature it gradually becomes crystalline and sparingly soluble in alcohol. It is subsequently readily crystallised from this solvent, and yields α -trigalloyllævoglucosan, long, six-sided crystals, decomp. 250—320°, $[\alpha]_D^{25}$ —18·02° in alcoholic solution. The ability of the substance (and others of this class) to give the typical tannin reactions cannot be investigated, since it is insoluble in water, but in 10% alcoholic

solution it readily causes gelatinisation with arsenic acid. It gives a *potassium* salt which is sparingly soluble in alcohol. The precipitate, *B* (see above), yields β -*trigalloyllævoglucosan*, broad needles, and flat, rectangular plates, decomp. $270\text{--}320^\circ$, $[\alpha]_D^{25} -21.00^\circ$ in alcoholic solution (the *potassium* salt is described). The α - and β -compounds are differentiated clearly by their behaviour towards ferric chloride in alcoholic solution, since the former gives a bluish-black, gelatinous precipitate, whereas, under similar conditions, the latter gives only a bluish-violet solution without a precipitate. *Digalloyllævoglucosan*, colourless needles, decomp. $220\text{--}270^\circ$, $[\alpha]_D^{25} -27.93^\circ$ in alcoholic solution, is prepared by extraction of the filtrate from the precipitates *A* and *B* with ethyl acetate, removal of the solvent, and treatment of the residue with aqueous acetone; the sparingly soluble *potassium* salt is described. The mother-liquors from the crystallisation of the digalloyl derivative contain gallic acid and *monogalloyllævoglucosan*, decomp. 240° after darkening at 220° .

It is remarkable that the trigalloyllævoglucosans, when impure, are freely soluble in acetone or alcohol, in which they dissolve but sparingly after being recrystallised; similarly, crude digalloyllævoglucosan dissolves with great ease in water, whereas the pure product is very sparingly soluble. It appears probable, therefore, that the natural and synthetic tannins which are freely soluble in water and alcohol are all mixtures the components of which in the pure condition are characterised by sparing solubility.

The typical tannin reactions, such as the gelatinisation of alcoholic arsenic acid solution, are not exhibited by monogalloyllævoglucosan, which in this respect behaves similarly to Fischer's monogalloylglucose; the presence of at least two galloyl residues in the sugar molecule appears essential to the development of tannin characteristics.

H. W.

Synthesis of α -Benzopyrone Derivatives and the Rupture of the Pyrone Ring in these Compounds. J. TRÖGER and FR. BOLTE (*J. pr. Chem.*, 1921, [ii], 103, 163—187; cf. Tröger and Lux, A., 1910, i, 161).—Coumarin derivatives of the type

$\text{C}_6\text{H}_4 \begin{smallmatrix} \diagup \text{CH} \diagdown \\ \diagdown \text{O} \diagup \end{smallmatrix} \cdot \text{SO}_2\text{R}$ are obtained by the action of acetic anhydride

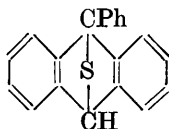
at water-bath temperature on a mixture of salicylaldehyde and the requisite arylsulphonylacetic acid. From benzenesulphonylacetic acid is obtained 3-benzenesulphonylcoumarin, m. p. $217\text{--}217.5^\circ$ (*loc. cit.*), from *p*-toluenesulphonylacetic acid, 3-*p*-toluenesulphonylcoumarin, colourless, tabular crystals, m. p. 221° , and from *p*-chlorobenzenesulphonylacetic acid, 3-*p*-chlorobenzenesulphonylcoumarin, m. p. 242° (*loc. cit.*). 3-Benzenesulphonylcoumarin is changed by alcoholic sodium ethoxide at water-bath temperature into *phenyl-o-hydroxystyrylsulphone*, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_5$, colourless plates, m. p. 166° ; the corresponding *acetoxy*-compound has m. p. 123° and the *benzoyloxy*-derivative, m. p. 135° . The following compounds were prepared in similar manner. *p*-Tolyl-*o*-hydroxystyrylsulphone, $\text{OH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_4\text{Me}$, colourless

plates, m. p. 154°; the *acetoxy*-derivative, m. p. 109°; and *benzoyloxy*-derivative, m. p. 98°; *p*-chlorophenyl-*o*-hydroxystyrylsulphone, m. p. 168—169°; *acetoxy*-derivative, m. p. 126°; and *benzoyloxy*-derivative, m. p. 96°.

* Benzenesulphonylacetic acid and resorcyaldehyde ($\text{CHO}:\text{OH}:\text{OH} = 1:2:4$) with acetic anhydride gives 7-*acetoxy*-3-benzenesulphonylcoumarin, colourless needles, m. p. 237°, but only if there be some sodium benzenesulphonylacetate in the free acid. With sulphuric acid, 7-*acetoxy*-3-benzenesulphonocoumarin yields 7-*hydroxy*-3-benzenesulphonylcoumarin. On alkaline hydrolysis, the acetyl compound yields phenyl-2:4-dihydroxystyrylsulphone, $\text{C}_6\text{H}_5(\text{OH})_2\text{CH}:\text{CH}:\text{SO}_2\text{Ph}$, yellow crystals, m. p. 209—210°, of which the following derivatives are described: *dimethyl ether*, a pale yellow powder, m. p. 108°; *diacetoxy*-derivative, leafy crystals, m. p. 112°; *dibenzoyloxy*-derivative, colourless needles, m. p. 77°. Similarly, 7-*acetoxy*-3-*p*-toluenesulphonylcoumarin, m. p. 234°; 7-*hydroxy*-3-*p*-toluenesulphonocoumarin, m. p. 239°; *tolyl*-2:4-dihydroxystyrylsulphone, m. p. 184°, and its *dimethyl ether*, m. p. 108°; *diacetoxy*-derivative, m. p. 108°; and *dibenzoyloxy*-derivative, m. p. 132°, and 7-*acetoxy*-3-*p*-chlorobenzenesulphonylcoumarin, rhombic crystals, m. p. 224°; 7-*hydroxy*-3-*p*-chlorobenzenesulphonylcoumarin, small, transparent needles, m. p. 226°; *p*-chlorophenyl-2:4-dihydroxystyrylsulphone, transparent crystals, m. p. 193°, and its *dimethyl ether*, m. p. 77°, *diacetoxy*-derivative, m. p. 112°; *dibenzoyloxy*-derivative, m. p. 164°, were prepared. No derivatives of coumarinic or coumaric acid could be isolated on attempting to rupture the pyrone ring, but they are to be assumed as intermediate stages in some of the hydrolyses.

W. O. K.

Sulphur as the Bridge Atom in the Middle Ring of a Derivative of Anthracene. A. BISTRZYCKI and B. BRENNEN (*Helv. Chim. Acta*, 1922, 5, 20—28; cf. A., 1915, i, 245; 1920, i, 629).—The action of concentrated sulphuric acid on 2:4:4-triphenyl-1:3-oxthiophan-5-one, $\text{CPh}_2\text{S}(\text{CHPh})\text{CO}\cdot\text{O}$, has been ex-



amined further and is shown to yield 9-phenyl-9:10-dihydromesothioanthracene.

2:4:4-Triphenyl-1:3-oxthiophan-5-one dissolves gradually in sulphuric acid (d 1.84) with brisk evolution of carbon monoxide and formation of a yellow solution which rapidly becomes dark violet-red. The solution is neutralised with aqueous ammonia and boiled until the precipitate becomes flocculent, thus yielding 9-phenyl-9:10-dihydromesothioanthracene, slender, yellow needles, m. p. 117—118°. The latter is converted by distillation with zinc dust into 9-phenylanthracene, m. p. 152°, the production of which suggests the possibility that the parent substance is in reality the thioketone, $\text{C}_6\text{H}_4\text{CS}(\text{CHPh})\text{C}_6\text{H}_4$. This hypothesis, however, is negated by its stability towards phenylhydrazine, alcoholic sodium hydroxide solution, and aniline, as well as by

its reduction by zinc and hydrochloric acid in the presence of glacial acetic acid to 1:3-*diphenylthiophthalan*, $C_6H_4\langle\begin{smallmatrix} CHPh \\ CHPh \end{smallmatrix}\rangle S$, colourless, silky needles, m. p. 106·5—107·5°, the constitution of which follows from its conversion by more drastic treatment with the same reagents into *o*-dibenzylbenzene, m. p. 78°. Oxidation of phenyldihydromesoanthracene with hydrogen peroxide in glacial acetic acid solution gives *o*-dibenzoylbenzene, m. p. 145—146°, which is shown by direct comparison to be identical with the product prepared by Simonis and Remmert (A., 1915, i, 136).

4:4-Diphenyl-2-*p*-chlorophenyl-1:3-oxthiophan-5-one (A., 1920, i, 631) is similarly converted by sulphuric acid into 2-*chloro-9-phenyl-9:10-dihydromesoanthracene*, microscopic aggregates of yellow prisms, m. p. 124—126° after softening at 120°. H. W.

Constitution of Matrine. II. HEIZABURŌ KONDŌ, NICHIRŌ KISHI, and CHŪRŌ ARAKI (*J. Pharm. Soc. Japan*, 1921, 1047—1069; cf. A., 1921, i, 882).—By reducing matrine with sodium and amyl alcohol, *deoxymatrine*, $(C_{15}H_{24}N_2)_2$, rhombic prisms, m. p. 162° (*aurichloride*, yellow, amorphous precipitate; *platinichloride*, orange-yellow plates, decomposes at 284°. The *dimethiodide*, colourless needles, m. p. 178°, and its *aurichloride*, yellow needles, m. p. 180°; *platinichloride*, an orange-yellow, crystalline precipitates, decomposing at 282°; *picrate*, yellow, slender crystals, m. p. 109°; *mercurichloride*, white prisms, m. p. 175—180°), and *desoxymatrine oxide*, $(C_{15}H_{24}N_2)_2O$, a yellow, amorphous base, were obtained. To reduce the products further, *deoxymatrine* was heated with hydrogen iodide (*d* 1·7) and red phosphorus at above 250° for five hours, when *dimatridine*, $(C_{15}H_{25}N_2)_2$, long, colourless needles, m. p. 160° (*platinichloride*, orange-yellow needles, decomposing at 275°; *aurichloride*, yellow needles, m. p. 215°; *dimethiodide*, an amorphous precipitate; and its *aurichloride*, a yellow, crystalline powder, decomposing at 193°; *platinichloride*, a light reddish-yellow, crystalline powder, decomposing at 279°; *mercurichloride*, a white powder, m. p. about 150°; *picrate*, a yellow powder, m. p. about 92°), and a crystalline *base*, m. p. 75—76°, isomeric with the former, were produced. *Dimatridine* was formed also by the catalytic reduction of *deoxymatrine* with hydrogen in the presence of platinum black. *Deoxymatrine oxide*, when subjected to reduction with hydrogen iodide and red phosphorus, yielded the base, $C_{10}H_{16}N$, described in the former paper. The electrolytic reduction of matrine did not give a satisfactory result, but a small quantity of an unsaponifiable crystalline *base*, m. p. 72—76°, was formed (*platinichloride*, decomposing at 254°, and *aurichloride*, m. p. 206—208°). K. K.

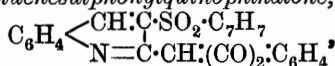
Synthesis of β -Arylsulphonylquinolines containing a Side Chain in the 2-Position. J. TRÖGER and W. MENZEL (*J. pr. Chem.*, 1921, [ii], 103, 188—215).—3-*p*-Toluenesulphonyl-2-methylquinoline, $C_6H_3\langle\begin{smallmatrix} C:C\cdot SO_2\cdot C_6H_4\cdot CH_3 \\ N:C\cdot CH_3 \end{smallmatrix}\rangle$, obtained by heating an

alcoholic solution of *o*-aminobenzaldehyde with *p*-toluenesulphonylacetone, and a small amount of sodium hydroxide, forms lustrous, broad needles, m. p. 152°, and on distillation with zinc dust yields 2-methylquinoline, thus proving its constitution. The following derivatives are described: *hydrochloride*, $C_{17}H_{15}O_2NS \cdot HCl$, m. p. 150°; *nitrate*, m. p. 138°; *sulphate*, $C_{17}H_{15}O_2NS \cdot H_2SO_4$; *oxalate*, $C_{17}H_{15}O_2NS \cdot C_2O_4H_2$, decomp. 145°; *platinichloride*,



m. p. 216°; *aurichloride*, $C_{17}H_{15}O_2NS \cdot HAuCl_4$, m. p. 194°; *mercurichloride*, m. p. 148°; *stannochloride*, $(C_{17}H_{15}O_2NS)_2 \cdot H_2SnCl_4$, m. p. 235°; *methiodide*, $C_{17}H_{15}NSO_2 \cdot MeI$, m. p. 146°; *methochloride*,

m. p. 156°; the *benzylidene* derivative, $C_6H_4 \begin{smallmatrix} <CH:C \cdot SO_2 \cdot C_7H_7 \\ N=C \cdot CH:CH \cdot C_6H_5 \end{smallmatrix}$, yellowish-white needles, m. p. 204° (*hydrochloride*, m. p. 202°); the corresponding *ethylidene* derivative, m. p. 165° (*hydrochloride*, m. p. 160°), and β -*p*-toluenesulphonylquinophthalone,



small, brittle prisms, m. p. 147°.

In the same way, from benzenesulphonylacetone and *o*-aminobenzaldehyde is obtained 3-benzenesulphonyl-2-methylquinoline, yellowish-white, thin needles, m. p. 144°, and the following derivatives: *hydrochloride*, $C_{16}H_{13}O_2NS \cdot HCl$, m. p. 105°; *nitrate*, m. p. 126°; *sulphate*, decomp. 150°; *oxalate*; *platinichloride*; *aurichloride*, m. p. 186° (decomp.); *mercurichloride*, m. p. 95°; *stannochloride*, m. p. 245°; *methiodide*, $C_{16}H_{13}O_2NS \cdot CH_3I$, m. p. 135°; *methochloride*, m. p. 149°; the *benzylidene* derivative, $C_{23}H_{17}O_2NS$, slender needles, m. p. 195° (*hydrochloride*, m. p. 198°); the *ethylidene* derivative, $C_{18}H_{15}NSO_2$, small, nodular crystals, m. p. 154° (*hydrochloride*); and 3-benzenesulphonylquinophthalone, $C_{24}H_{15}O_4NS$, yellow needles, m. p. 140°. Similarly, from *p*-chlorobenzenesulphonylacetone is obtained 3-*p*-chlorobenzenesulphonyl-2-methylquinoline, lustrous, colourless, long, slender needles, m. p. 155°, and the following derivatives: *hydrochloride*, $C_{16}H_{12}O_2NSCl \cdot HCl$, m. p. 200°; *nitrate*, m. p. 132°; *sulphate*, *oxalate*, *platinichloride*, *aurichloride*, m. p. 180°; *mercurichloride*, m. p. 195–198°; *stannochloride*, m. p. 235°; *methiodide*, $C_{16}H_{12}O_2NSCl \cdot CH_3I$, m. p. 150°; *methochloride*, m. p. 160°; the *benzylidene* derivative, $C_{23}H_{16}O_2NSCl$, a yellowish-green, microcrystalline powder, m. p. 200° (*hydrochloride*); the *ethylidene* derivative, $C_{18}H_{14}O_2NSCl$, slender, yellowish-white needles, m. p. 185° (*hydrochloride*); and 3-*p*-chlorobenzenesulphonylquinophthalone, $C_{24}H_{14}O_4NSCl$, small, rhombic crystals, m. p. 150°. In no case could the benzylidene or ethylidene derivative be oxidised to the corresponding carboxylic acid.

From β -naphthalenesulphonylacetone and *o*-aminobenzaldehyde 3- β -naphthalenesulphonyl-2-methylquinoline, $C_{26}H_{20}O_2NS \cdot C_{10}H_7$, $N \cdot CMe$

is obtained as greyish-white, prismatic needles, m. p. 160°; *platinichloride*, $(C_{26}H_{20}O_2NS)_2 \cdot H_2PtCl_6$, m. p. 228°. By using benzenesulphonylacetophenone derivatives, corresponding phenylquinolines are obtained and will be described later.

W. O. K.

Extension of the Kishner-Wolff Method of Reduction. I. ERNST THIELEPAPE (*Ber.*, 1922, **55**, [B], 136—138).—The replacement of the oxygen atom of ketones and aldehydes by hydrogen has been effected by Wolff (A., 1912, i, 988) through the corresponding hydrazones. The extension of the reaction to carbonyl groups in general is now being investigated together with the decomposition of substituted hydrazine or hydrazone groups with the elimination of nitrogen in the cases of substances which are not derived from true ketones or aldehydes.

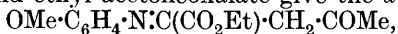
4-Methylquinoline-2-hydrazone, $C_6H_4 \begin{matrix} \text{CMe} \cdot \text{CH} \\ | \\ \text{NH} \cdot \text{C} \cdot \text{N} \cdot \text{NH}_2 \end{matrix}$, m. p. 148°,

is prepared from 2-chloro-4-methylquinoline, more conveniently from 4-methylquinoline and hydrazine hydrate. The hydrazone is converted into 4-methylquinoline when heated during seventy-two hours at 150—180° with potassium hydroxide, or by treatment of its solution in boiling water with copper sulphate or in cold water with iron chloride. H. W.

The Quinoline Series. I. Synthesis of 4-Substituted Quinolines and of Quinoline-4-carboxylic Acids. ERNST THIELEPAPE (*Ber.*, 1922, **55**, [B], 127—135).—Attempts are described to synthesise 4-substituted quinolines or 2:4-disubstituted quinolines in which the substituent in position 2 is easily removable.

Aniline hydrochloride and sodium formylacetone yield the *anil*, $NPh \cdot CH \cdot CH_2 \cdot CO \cdot CH_3$, colourless crystals, m. p. 91·5°; after being distilled in a high vacuum (b. p. 128—134°/2·5—5 mm.), the product has m. p. about 61° and then passes into the modification, m. p. 91·5°, which is also produced when attempts are made to crystallise the variety, m. p. 61°. The nature of the isomerism has not been elucidated. All attempts to effect ring closure with formation of a quinolyl derivative were unsuccessful.

p-Anisidine and ethyl acetoneoxalate give the *anil*,



yellow crystals, m. p. 68°, which could not be converted into a substituted quinoline.

α -Ethoxalyl-*N*-methylacetanilide, $NMePh \cdot CO \cdot CH_2 \cdot CO \cdot CO_2Et$, colourless crystals, m. p. 84·5°, is prepared by the condensation of *N*-methylacetanilide with ethyl oxalate in ethereal solution in the presence of sodium ethoxide. It is converted by concentrated sulphuric acid at -15° into ethyl 1-methyl-2-quinolone-4-carboxylate,

$C_6H_4 \begin{matrix} C(CO_2Et) \cdot CH \\ | \\ NMe \text{---} CO \end{matrix}$, m. p. 134—135°, which is hydrolysed by

boiling aqueous sodium hydroxide to the corresponding acid, m. p. 251—252°. The ester is converted by phosphorus pentachloride in the presence of phosphoryl chloride into ethyl 2-chloro-quinoline-4-carboxylate, yellow crystals, m. p. 64·5° (2-chloro-quinoline-4-carboxylic acid may be obtained similarly from 2-hydroxyquinoline-4-carboxylic acid). 2-Hydrazinoquinoline-4-carboxylic acid, unstable, yellow crystals which do not melt below 305°, is obtained from the chloro-acid and hydrazine; the corresponding

hydrazide, colourless, unstable crystals, m. p. 228—229° (decomp.) after darkening and softening above 190°, is prepared from ethyl 2-chloroquinoline-4-carboxylate. Quinoline-4-carboxylic ester is converted similarly into *quinoline-4-carboxyhydrazide*, colourless crystals, m. p. 154·5°. *2-Iodoquinoline-4-carboxylic acid*, almost colourless crystals, m. p. 195—196°, after darkening at 180° and softening at 190°, is prepared from the 2-chloro-acid by the action of potassium iodide and red phosphorus in the presence of hydriodic acid (*d* 1·50). H. W.

Arylated Pyridines. III. Quinodihydropyridines. W. DILTHEY (*Ber.*, 1922, 55, [B], 57—59; cf. A., 1920, i, 448; 1921, i, 735).—The pyridine analogues of the deeply coloured anhydro-bases obtained by the action of dilute alkali on *p*-hydroxyarylp-*pyrylium* salts are readily prepared when the pyridine nitrogen atom is united to an aromatic residue. Thus 1 : 2 : 6-*triphenyl-4-p-hydroxyphenylpyridinium chloride*, pale yellow crystals which do not melt below 340° (obtained from 2 : 6-diphenyl-4-*p*-hydroxyphenylpyrylium chloride and aniline), is converted by ammonia in alcoholic solution into 1 : 2 : 6-*triphenyl-4-quinopyridan*, $\text{O}:\text{C}_6\text{H}_4:\text{C}_5\text{NH}_2\text{Ph}_3$, yellowish-red needles, m. p. 302°. Solutions of the substance or its salts are not fluorescent. H. W.

New Method for the Preparation of Alkamines. II. JIRÔ TAKEDA and SAJÛRÔ KURODA (*J. Pharm. Soc. Japan*, 1921, 1—76).—The authors have shown (A., 1920, i, 228) that styrene dibromide, anethole dibromide, and the like reacting with carbamide produce substituted dihydro-oxazoles, which are changed to the corresponding alkamines by the action of alkali hydroxides. By the decomposition of the methyl derivatives of these dihydro-oxazoles, *N*-methylalkamines are, however, obtained, so that the imino-oxazolidine formula,
$$\begin{array}{c} \text{R} \cdot \text{CH} \cdot \text{NH} \\ | \\ \text{R}' \cdot \text{CH} - \text{O} \end{array} > \text{C} : \text{NH},$$
 must replace the

constitution,
$$\begin{array}{c} \text{R} \cdot \text{CH} \cdot \text{N} \\ | \\ \text{R}' \cdot \text{CH} - \text{O} \end{array} \gg \text{C} : \text{NH}_2,$$
 given earlier. By the action of acetic anhydride and sodium acetate, these compounds are converted mainly into acetyl derivatives,
$$\begin{array}{c} \text{R} \cdot \text{CH} \cdot \text{N} \cdot \text{Ac} \\ | \\ \text{R}' \cdot \text{CH} - \text{O} \end{array} > \text{C} : \text{NH}, \text{CH}_3 \cdot \text{CO}_2\text{H},$$

but to a small extent into the acetyloxazolidones,
$$\begin{array}{c} \text{R} \cdot \text{CH} \cdot \text{N} \cdot \text{Ac} \\ | \\ \text{R}' \cdot \text{CH} - \text{O} \end{array} > \text{CO};$$

the hydrolysis of the former by alkali hydroxides produces the corresponding alkamine through the oxazolidone more easily than imino-oxazolidines themselves. In these reactions, an isomeric β -alkamine is produced in small quantity with the α -alkamine; the *isoadrenaline* base of Mannich (A., 1910, i, 411) corresponds with the former. The method was applied to dihydronaphthalene dibromide, which with carbamide yields the corresponding imino-oxazolidine; this is converted into the corresponding alkamine by way of the acetyl derivative. The bases are not identical with those described by Bamberger and Lodter (A., 1893, i, 591;

1896, i, 99), but are stereoisomerides. The following substances were prepared.

I. Anetholealkamine group. 4-*p*-Anisyl-5-methyloxazolidone, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{NH} > \text{CO}$, rhombic plates, m. p. 110—112°, is



prepared by heating anethole-2-imino-oxazolidine with water at 140—150° in a sealed tube with a small quantity of anethole-alkamine; *acetyl* derivative, hexagonal plates, m. p. 111—112°.

4-*p*-Anisyl-5-methyloxazoline mercaptan, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N} > \text{C}\cdot\text{SH}$,
 $\text{Me}\cdot\text{CH}-\text{O}$

white plates, m. p. 86—88°, from anetholealkamine, carbon disulphide, and potassium hydroxide; *acetyl* derivative, colourless plates, m. p. 79—81°. α -*p*-Hydroxyphenyl- β -hydroxypropylamine, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{NH}_2)\cdot\text{CHMe}\cdot\text{OH}$, colourless, hexagonal plates, m. p. 173°, from anetholealkamine and hydrogen iodide (*hydrochloride*, m. p. 187°; *dibenzoate*, m. p. 173°), which yields α -*p*-hydroxyphenyl-methyl- β -hydroxypropylamine, with methyl iodide; *hydrochloride*, m. p. 184—186°. β -Anetholealkamine, thin plates, m. p. 80°, is prepared by heating anethole oxide with alcoholic ammonia at 130° (*copper salt*, m. p. 161°). By acetylation of the bromo-anethole-2-imino-oxazolidine with acetic anhydride and sodium acetate, its *N-acetyl* derivative, plates, m. p. 190—192°, and the *acetyloxazolidone*, m. p. 134°, are prepared; the former gives bromoanetholealkamine (α -*p*-methoxybromophenyl- β -hydroxypropylamine), thin plates, m. p. 118° (*hydrochloride*, m. p. 247°; *copper derivative*, m. p. 168°).

II. *iso*Safrolealkamine group. 4-Methylenedioxyphenyl-5-methyloxazolidone, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}\cdot\text{NH} > \text{CO}$, plates, m. p. 170—171°,
 $\text{Me}\cdot\text{CH}-\text{O}$

is prepared by heating *isosafole*-2-imino-oxazolidine with water at 140° in a sealed tube, *isosafole*alkamine and ammonia being simultaneously formed. By acetylation of *isosafole*-2-imino-oxazolidine with acetic anhydride and sodium acetate, the *N-acetyl-acetate*, m. p. 208°, and the *acetyloxazolidone*, colourless prisms, m. p. 116—119°, are formed, the former, when heated at 205°, is changed first into the latter, and then into β -*isosafole*alkamine (*copper salt*, m. p. 171—173°). Benzoylation of *isosafole*-2-imino-oxazolidine by Schotten-Baumann's method yields only the *N-benzoyloxazolidone*, m. p. 180—182°. When boiled with 30% sodium hydroxide, the *acetyl-acetate* yields *isosafole*alkamine, $\text{CH}_2\cdot\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{NH}_2)\cdot\text{CHMe}\cdot\text{OH}$, slender needles, m. p. 79° (*hydrochloride*, m. p. 210—215°; *platinichloride*, orange-yellow crystals, m. p. 200—202°; *copper derivative*, $(\text{C}_{10}\text{H}_{13}\text{O}_3\text{N})_2\text{CuO} + 2\text{H}_2\text{O}$, deep violet crystals, m. p. 185—186°), whilst with very dilute alkali the free *N-acetyl* derivative, m. p. 153°, is formed. By acetylation with acetic anhydride, *isosafole*alkamine gives the *N-acetyl* derivative, prisms, m. p. 156°, which change to *isosafole*alkamine acetate (*hydrochloride*, needles, m. p. 198—200°, when treated, in benzene suspension, with hydrogen chloride; *platinichloride*, orange-yellow crystals, m. p. 200°). In the same way,

N-benzoylisosafrolealkamine, needles, m. p. 139°, suffers rearrangement to isosafrolealkamine benzoate (hydrochloride, m. p. 203°; platinichloride, m. p. 201°). By heating with carbon disulphide and potassium hydroxide, isosafrolealkamine produces the mercaptan,

$$\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\underset{\text{MeCH}\cdot\text{O}}{\text{CH}\cdot\text{N}}\text{>C}\cdot\text{SH}, \text{ granules, m. p. 160°; the}$$

acetyl-mercaptan forms white, hexagonal plates, m. p. 93°. Methylisosafrole-2-imino-oxazolidine,

$$\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\underset{\text{Me}\cdot\text{CH}\text{---}\text{O}}{\text{CH}\cdot\text{NMe}}\text{>C}\cdot\text{NH}, \text{ a light}$$

yellow syrup, is prepared from isosafrole-2-imino-oxazolidine and methyl iodide (hydrochloride, m. p. 205°), the hydrolysis of which by alcoholic sodium hydroxide produces *N*-methylisosafrolealkamine (α -methylenedioxyphenylmethyl- β -hydroxypropylamine),

$\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{NHMe})\cdot\text{CHMe}\cdot\text{OH}$,
m. p. 89—90° (hydrochloride, m. p. 142—144°; platinichloride, m. p. 196°; copper derivative, deep violet crystals, m. p. 151°). Dimethylisosafrole-2-imino-oxazolidine is prepared from the monomethyl compound and methyl iodide (hydriodide, thin plates, m. p. 181°), the hydrolysis of which by alcoholic sodium hydroxide produces *N*-methylisosafrolealkamine and methylamine. *N*-Acetylmethylisosafrolealkamine, white crystals, m. p. 111—113°, and the *N*-benzoyl compound, prisms, m. p. 145—148°, are prepared from the methylalkamine. They are converted into *O*-acetyl-*N*-methylisosafrolealkamine hydrochloride, m. p. 182° (platinichloride, m. p. 163—169°), and the *O*-benzoyl compound, prisms, m. p. 215° (platinichloride, m. p. 170°), by passing hydrogen chloride into their ethereal solutions. *N*-Dimethylisosafrolealkamine, m. p. 71—73°, is prepared from the monomethyl compound and methyl iodide (hydrochloride, m. p. 173°; platinichloride, m. p. 190—200°); benzoyl chloride produces *O*-benzoyl-*N*-dimethylisosafrolealkamine hydrochloride, m. p. 224—226° (platinichloride, m. p. 140°). Bromoisosafrole-2-imino-oxazolidine, thin plates, m. p. 197°, is prepared by heating bromoisosafrole dibromide and carbamide at 150° (hydrochloride, m. p. 197°); on acetylation, it yields *N*-acetylbromoisosafrole-2-imino-oxazolidine acetate, long needles, m. p. 173—176°, which gives bromoisosafrolealkamine, prisms, m. p. 126—128°, by hydrolysis (hydrochloride, m. p. 231°; copper derivative, m. p. 158°).

III. Methylisoeugenolalkamine group. Methylisoeugenol dibromide and carbamide react to form methylisoeugenol-2-imino-oxazolidine, m. p. 153—155° (hydrochloride, m. p. 166—168°; platinichloride, m. p. 195°), which is converted into the *N*-acetylacetate, m. p. 155—157°, by heating with acetic anhydride; hydrolysis of the acetyl compound with 30% sodium hydroxide produces α :3:4-dimethoxyphenyl- β -hydroxypropylamine (methylisoeugenolalkamine), $(\text{OMe})_2\text{C}_6\text{H}_3\cdot\underset{\text{MeCH}\cdot\text{OH}}{\text{CH}\cdot\text{NH}_2}$, thin plates, m. p. 95—96° [hydro-

chloride, m. p. 222°; platinichloride, m. p. 201°; copper compound (base)₂CuO+2H₂O, m. p. 166—167°]. *O*-*N*-Dimethylisoeugenol-2-imino-oxazolidine, a pale yellow oil, is prepared from the imino-

oxazolidine and methyl iodide (*hydrochloride*, m. p. 144°); hydrolysis produces α -3:4-dimethoxyphenylmethyl- β -hydroxypropylamine (*dimethylisoeugenolalkamine*), hexagonal plates, m. p. 90—91° (*hydrochloride*, m. p. 190—193°; *platinichloride*, m. p. 172—174°; *copper* derivative, m. p. 138°), which gives the *hydrochloride* of the O-benzoyl derivative, m. p. 198°; the latter suffers rearrangement to the N-benzoyl derivative, m. p. 140°. α -3:4-Dimethoxyphenyl- β -hydroxypropyldimethylamine (*trimethylisoeugenolalkamine*), is a light yellow oil; the *hydrochloride* forms white nodular crystals, m. p. 149—150°.

IV. Dihydronaphthalenealkamine group. Dihydronaphthalene dibromide and carbamide react at 140° to form *dihydronaphthalene-2-imino-oxazolidine*, thin plates, m. p. 158—159° (*hydrochloride*, prismatic plates, m. p. 198°; *platinichloride*, m. p. 224°), which is converted to the N-acetyl-acetate, plates, m. p. 123—124°, and then into β -hydroxytetrahydro- β -naphthylamine (*dihydronaphthalenealkamine*), thin plates, m. p. 107—108° (*hydrochloride*, m. p. 215°; *platinichloride*, m. p. 220°; *picrate*, yellow needles, m. p. 191°; *copper* derivative, (base)₂CuO + 2H₂O, violet-red needles, m. p. 176°). *Methyldihydronaphthalene-2-imino-oxazolidine*, prepared from the above compound and methyl iodide, forms thin plates, m. p. 66—68°; *hydriodide*, m. p. 203° [*hydrochloride* (+1H₂O), m. p. 254°, anhydrous]. As by-product, an oily *isomeride* is obtained; *hydrochloride*, m. p. 235°. β -Hydroxytetrahydro- β -naphthylmethylamine, needles, m. p. 85°, is prepared from the above imino-oxazolidine derivative by hydrolysis with 20% sodium hydroxide [*hydrochloride*, m. p. 214°; *copper* derivative, (base)₂CuO, light reddish-brown crystals, m. p. 218°], which by methyl iodide is converted into β -hydroxytetrahydro- β -naphthylldimethylamine, an oil; *hydrochloride*, m. p. 224°; *picrate*, yellow plates, m. p. 160°.

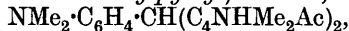
K. K.

Nitro-derivatives of Alkylated Benzdines. G. VAN ROMBURGH (*Rec. trav. chim.*, 1922, **41**, 38—43; cf. Mertens, A., 1877, 605; A., 1886, 1022; and van Romburgh, A., 1887, 245).—One of the substances obtained by the action of dilute nitric acid on dimethylaniline, at first known as *isodinitrodimethylaniline*, was shown to be a tetranitrotetramethylbenzidine, but the positions of the nitro-groups were not determined. The author considered it probable that the 3:3':5:5'-positions were occupied by these groups, and prepared the 3:3':5:5'-tetranitrotetramethylbenzidine. Tetranitro-4:4'-dimethoxydiphenyl (cf. Hirsch, A., 1889, i, 511), was treated with dimethylamine, nitrated, and boiled with phenol, the resulting product being found to be identical with the tetranitrotetramethylbenzidine first obtained. The reactions involved serve as a means for the preparation of alkylated tetranitrobenzidines. The following were prepared: 3:3':5:5'-tetranitro-diethylbenzidine, m. p. 248°, which, on treatment with concentrated nitric acid yields 3:3':5:5'-tetranitrodiphenyl-4:4'-diethyldinitroamine, long needles, m. p. 230° (decomp.); 3:3':5:5'-tetranitro-dipropylbenzidine, dark red needles, m. p. 200°, which with nitric

acid (*d* 1.49) yields 3:3':5:5'-*tetranitrodiphenyl-4:4'-dipropyl-dinitroamine*, small, yellow plates, exploding at 213°; 3:3':5:5'-*tetranitrodiisopropylbenzidine*, deep red needles, decomp. 250°, yielding with nitric acid 3:3':5:5'-*tetranitrodiphenyl-4:4'-diisopropyl-dinitroamine*, colourless, decomp. 209°; 3:3':5:5'-*tetranitrodiisobutylbenzidine*, deep red crystals, *m. p.* 194°, yielding with concentrated nitric acid 3:3':5:5'-*tetranitrodiphenyl-4:4'-diisobutyl-dinitroamine*, colourless needles, decomp. 205°; 3:3':5:5'-*tetranitrodiallylbenzidine*, orange-red needles, *m. p.* 205°, yielding on nitration 3:3':5:5'-*tetranitrodiphenyl-4:4'-diallyl-dinitroamine*, decomp. 100°. All the above nitroamines are converted into the corresponding dialkylbenzidines on treatment with boiling phenol.

H. J. E.

The Iron Salts of Dipyrrolyphenylmethane Dyes. Triphenylpyrrolymethane. I. HANS FISCHER and VIKTORIA LUCKMANN (*Z. physiol. Chem.*, 1921, **115**, 77—93).—*p*-Dimethylaminophenyl-bis(3-acetyl-2:4-dimethylpyrroly)methane,



is prepared by heating on the water-bath an alcoholic solution of 3-acetyl-2:4-dimethylpyrrole with *p*-dimethylaminobenzaldehyde in the presence of potassium hydrogen sulphate, and precipitated with sodium carbonate. It crystallises from ethyl acetate in tufts of slender, colourless needles, *m. p.* 165—166°. The *ferrichloride* forms brown prisms, *m. p.* 255° (decomp.).

Dimethylaminophenyl-bis(-3-carbethoxy-2:4-dimethylpyrroly)methane, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{C}_4\text{NHMe}_2\cdot\text{CO}_2\text{Et})_2$, prepared from ethyl 2:4-dimethylpyrrole-3-carboxylate and *p*-dimethylaminobenzaldehyde in presence of potassium hydrogen sulphate, forms colourless, irregular leaflets, *m. p.* 204—205°. The *ferrichloride* crystallises in fine needles. *p*-Dimethylaminophenyl-bis(-3-carbethoxy-2:5-dimethylpyrroly)methane prepared from ethyl 2:5-dimethylpyrrole-3-carboxylate and *p*-dimethylaminobenzaldehyde in presence of concentrated sulphuric acid, has *m. p.* 240°, and its *ferrichloride* has *m. p.* 228°. *Triphenyl-3-acetyl-2:4-dimethylpyrrolymethane*, prepared from triphenylcarbinol and 3-acetyldimethylpyrrole by heating in glacial acetic acid, forms slender, colourless needles, *m. p.* 156°. *Triphenyl-3-carbethoxy-2:4-dimethylpyrrolymethane*, obtained from triphenylcarbinol and ethyl 2:4-dimethylpyrrole-3-carboxylate crystallises in prisms, *m. p.* 170°. *Triphenyl-p-dimethylaminophenylmethane*, prepared from triphenylcarbinol and dimethylaniline, crystallises in slender needles, *m. p.* 208°.

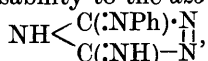
S. S. Z.

Preparation of a New Acridine Compound. LEOPOLD CASSELLA & Co., G.m.b.H. (Swiss Pat. 89241; from *Chem. Zentr.*, iv, 1010).—Formaldehyde is allowed to react with a 3:6-diamino-10-methylacridinium salt. For example, 3:6-diamino-10-methylacridinium chloride is dissolved in water and mixed with *N*-hydrochloric acid. On addition of 30% formaldehyde, a bright orange-coloured suspension is obtained. After agitation, the condens-

ation product is separated, washed with *N*-hydrochloric acid and water, and dried; it is a brick-red powder with antiseptic properties.
G. W. R.

Certain Triazoles. F. ARNDT [with E. MILDE, F. TSCHENSCHER, (FRL.) F. BRELICH, and G. ECKERT] (*Ber.*, 1922, **55**, [B], 12—18; cf. A., 1921, i, 813).—An arrangement has been reached between the author and Fromm (cf. this vol., i, 62) concerning publication in this field. The present communication is due to the fact that, in some respects, certain triazoles prepared by the authors do not harmonise in their properties with those described by Fromm in his forthcoming paper in the *Annalen*.

An alcoholic suspension of phenyldithiobiuret is converted by hydrazine hydrate and subsequent acidification with hydrochloric acid into *anilothiourazole*, $\text{NH} \begin{smallmatrix} \text{C}(\text{NPh}) \cdot \text{NH} \\ \text{CS} \text{---} \text{NH} \end{smallmatrix}$, colourless, lustrous leaflets, m. p. 275° or somewhat higher when rapidly heated (Fromm, m. p. 268°), which is oxidised by potassium ferricyanide in alkaline solution to the *disulphide*, $(\text{NHPh} \cdot \text{C} \begin{smallmatrix} \text{N} \cdot \text{H} \\ \text{N} \text{H} \end{smallmatrix} \text{>} \text{C})_2 \text{S}_2$, yellow crystals, m. p. 233° (Fromm, m. p. 225°). *Anilothiourazole methyl ether*, $\text{NH} \begin{smallmatrix} \text{C}(\text{NPh}) \cdot \text{NH} \\ \text{C}(\text{SMe}) \text{---} \text{N} \end{smallmatrix}$, a matt, crystalline powder, has m. p. 187—188°; the corresponding *nitrate*, m. p. 110° (decomp.), is described. *Iminoanilourazole*, $\text{NH} \begin{smallmatrix} \text{C}(\text{NPh}) \cdot \text{NH} \\ \text{C}(\text{NH}) \text{---} \text{NH} \end{smallmatrix}$, colourless leaflets, m. p. 157° (the *monohydrate* is also described), is obtained by the addition of ammonia to the acidic mother-liquors from the preparation of anilothiourazole. The constitution of the compound is deduced from its analysis, its mode of formation, amphoteric nature, convertibility into a sparingly soluble nitrate, decomp. 118°, and oxidisability to the *azo*-compound,



a pale, brownish-red powder, violent decomp., 138°. The same constitution is assigned by Fromm to a substance, m. p. 70°, prepared by the action of hydrazine on phenylthiuret; this product, however, appears to be a salt containing anilothiourazole as acidic component and two basic components, one of which, m. p. 149°, is possibly identical with aminoguanylphenylthiocarbamide, whereas the other is iminoanilourazole.
H. W.

The Significance of the Second Dissociation Constant of Uric Acid in the Equilibrium of Monourate Solutions. ARISTIDES KANITZ (*Z. physiol. Chem.*, 1921, **116**, 96—106).—A theoretical paper. Salts of uric acid formed by the action of monoacidic bases on the acid dissociate in accordance with its two stages of dissociation partly into the normal diurate salt and free uric acid as follows:

$$\frac{\text{Monourate}}{\text{Diurate} \times \text{free uric acid}} = \frac{k_1}{k_2}$$

(k_1 = constant for first stage of dissociation of the acid, k_2 = constant for second stage of dissociation of the acid). Calculated from results previously obtained by various workers $k_1/k_2 = 775$, or 2350. From which there is derived $k_2 = 2.6 \times 10^{-9}$ or 8.5×10^{-10} .

S. S. Z.

The Azo-dyes of Bilirubin. I. HANS FISCHER and HERMANN BARRENSCHEEN (*Z. physiol. Chem.*, 1921, **115**, 94—104).—A monoazo- and a diazo-product were obtained by treating bilirubin with benzenediazonium chloride. The two compounds were separated by crystallising the mixture from alcohol—the monoazo-derivative being soluble in this solvent. The *monoazo*-compounds, $\text{C}_{33}\text{H}_{35}\text{O}_6\text{N}_4 \cdot \text{N}:\text{NPh}$, crystallised in small, brownish-red prisms, the *diazo*-compound, $\text{C}_{33}\text{H}_{34}\text{O}_6\text{N}_4(\text{N}:\text{NPh})_2$, in monoclinic crystals.

S. S. Z.

Colouring Matters of the Isatin-yellow Series. JH. MARTINET (*Rev. Gén. Mat. Col.*, 1921, **26**, 177—179).—When a solution of a diazonium compound is added to a solution of isatin-6-sulphonic acid in presence of sodium acetate, a hydrazone is formed, and not an azo-compound, as is shown by the stability of these compounds towards reducing agents, and by the fact that identical compounds are formed by the action of the corresponding hydrazine on isatin-6-sulphonic acid. The following hydrazones of sodium isatin-6-sulphonate in this series are described:—*Phenylhydrazone*, slender, lemon-yellow needles soluble in sulphuric acid with an orange-yellow colour, isomeric with isatin-yellow (the *p*-sulphophenylhydrazone of isatin). *p*-*Chlorophenylhydrazone* forms yellow needles soluble in sulphuric acid with an orange-yellow colour. *o*-*Tolylhydrazone* crystallises in orange-yellow needles soluble in sulphuric acid with a dark orange-yellow colour. *m*-*Tolylhydrazone*, an orange-yellow, crystalline powder soluble in sulphuric acid with an orange-yellow colour. *p*-*Tolylhydrazone*, rosettes of golden-yellow needles, coloured bright red by sulphuric acid and soluble with an orange-yellow colour. *m*-*Xylylhydrazone* forms an orange-red powder soluble in sulphuric acid with a dark brownish-red colour. ψ -*Cumylhydrazone*, a reddish-brown powder soluble in sulphuric acid with a dark brownish-red colour. *p*-*Ethoxyphenylhydrazone*, dark yellow, felted needles soluble in sulphuric acid with a red colour. *o*-*Methoxyphenylhydrazone*, dark yellow needles soluble in sulphuric acid with a red colour. *p*-*Chloro-o-methoxyphenylhydrazone*, a dark yellow, crystalline powder soluble in sulphuric acid with a scarlet-red colour. *o*-*Carboxyphenylhydrazone*, a lemon-yellow, crystalline powder soluble in sulphuric acid with a golden-yellow colour; the aqueous solution forms a brick-red precipitate with silver nitrate. *Diphenyl-4:4'-dihydrazone*, a brown, crystalline powder with a brownish-red reflex soluble in perchloric acid with a violet-red colour. *3:3'-Dimethoxydiphenyl-4:4'-dihydrazone*, a brown powder

soluble in perchloric acid with a violet colour. All these hydrazones are soluble in water and acetic acid, crystallise from alcohol, and their aqueous solutions are darkened slightly by alkalis. They dye wool and silk in bright yellow, orange, or red shades, and all possess a direct affinity for cotton from an alkaline bath, the affinity increasing with the molecular weight. The fastness is not great, but these colouring matters possess an interest on account of their tinctorial power, brightness, and level-dyeing properties.

In a parallel series of experiments some derivatives of isatin-5-sulphonic acid were prepared by the action of various hydrazines. *Potassium isatin-5-sulphonate phenylhydrazone*, lemon-yellow needles very soluble in water, dyes wool and silk greenish-yellow shades of low fastness. *Sodium isatin-5-sulphonate p-tolylhydrazone* forms long, golden-yellow needles. *Isatin-5-sulphonic acid phenylmethyl hydrazone* forms yellow, felted needles.

F. M. R.

The Free Amino-groups of the Proteins. R. ENGELAND (*Z. physiol. Chem.*, 1921, **116**, 226—227); S. EDLBACHER (*ibid.*, 228; cf. A., 1921, i, 199).—Polemical.

S. S. Z.

The Optical Rotatory Power of Crystalline Ovalbumin and Serum-albumin. ELRID GORDON YOUNG (*Proc. Roy. Soc.*, 1922, [B], **93**, 15—35).—The specific rotation of crystalline ovalbumin is constant if recrystallisation is made at the isoelectric point, but varies with changes in the hydrogen-ion concentration of the solution. The constant values obtained by the author are: $[\alpha]_D^{25} - 30.81^\circ$ and $[\alpha]_E^{15} - 37.53^\circ$. The variations produced by the addition of small quantities of acid or alkali are explained on the basis of a tautomeric change of the lactam-lactim type. Crystalline horse serum-albumin was prepared by two methods. In each case the preparation had $[\alpha]_D^{18} - 62.8^\circ$ and $[\alpha]_E^{18} - 78.4^\circ$.

E. S.

The Action of Nitrous Acid on Casein. MAX S. DUNN and HOWARD B. LEWIS (*J. Biol. Chem.*, 1921, **49**, 327—341).—The distribution of nitrogen in casein and deaminised casein was determined. In agreement with the current view as to the nature of the free amino-groups in proteins, lysine was found to be absent from the hydrolysate of deaminised casein, whilst the amount of monoamino-nitrogen was correspondingly increased. Some destruction of tyrosine occurs during the deamination of casein.

E. S.

Yeast-nucleic Acid. II. H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1921, **114**, 201—203; cf. A., 1921, i, 66).—By utilising the method of precipitating sodium guanylate with a concentrated solution of sodium acetate, it is found that a certain sample of yeast-nucleic acid contained 12—14% of this salt.

S. S. Z.

The Influence of β -Naphthalenesulphonyl Chloride on the Proteins. S. EDLBACHER and BERTHOLD FUCHS (*Z. physiol. Chem.*, 1921, **114**, 133—136).—Clupeine, salmine, sturine, thymus-

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histone, gelatin, casein, and edestin were treated with β -naphthalene-sulphonyl chloride and the amount which combined with the respective proteins was ascertained. The basic protamines and the histone showed a relatively higher figure than the other proteins. The difference was, however, rather insignificant. The lysine content of the protein seems to have no influence on this reaction. S. S. Z.

The Titration Curve of Gelatin. DOROTHY JORDAN LLOYD and CHARLES MAYES (*Proc. Roy. Soc.*, 1922, [B], **93**, 69—85).—Determinations were made of the hydrogen-ion concentrations of solutions of gelatin in known concentrations of acid and alkali hydroxide, and the amount of combined acid or alkali hydroxide was calculated in each case. It is concluded from the results that for concentrations of acid not exceeding 0.02*N* combination occurs at the free amino-groups of the gelatin molecule; for greater concentrations of acid, however, there is probably also combination at the nitrogen of the peptide linkings. No conclusion was drawn as to the mode of attachment of alkalis. E. S.

Equilibrium: Gelatin-Hydrochloric Acid. II. ROBERT WINTGEN and HEINZ VOGEL (*Kolloid Z.*, 1922, **30**, 45—53; cf. A., 1921, ii, 247).—The hydrogen-ion concentration of mixtures of gelatin and hydrochloric acid has been determined electrometrically at 25° and the values have been compared with those calculated by means of the equilibrium formula previously published (*loc. cit.*). The acid concentration varied between 0.05*N* and 0.004*N*, and the gelatin concentration between 0° and 7%. The two sets of results agree astonishingly well, and indicate that dilute hydrochloric acid and concentrated acid combine with the same number of basic groups in gelatin, and if it is assumed that gelatin is a uniform substance, only one amino-group reacts with hydrochloric acid. It behaves therefore as a monacid base toward hydrochloric acid and has a molecular weight of 885 for the anhydrous material or 1070 for the air-dried material and an ionisation constant 5.74×10^{-11} . Turbidity and precipitation occur in the neighbourhood of the isoelectric point, and at this point solutions of 0.2% and 0.5% gelatin with *N*/3000- and *N*/1300-hydrochloric acid are seen in the ultramicroscope to contain numerous rapidly moving particles. The electrical conductivity of solutions of gelatin of concentrations up to 7% in 0.05*N*- and 0.025*N*-hydrochloric acid has been measured at 25° and from the results it is shown that $\Delta_{\infty} = 88.5$ for gelatin chloride at 25° and that the ionic conductivity of the gelatin ion is 13. Comparative measurements with β -glutinin show that the power of this substance to combine with hydrochloric acid does not differ essentially from that of gelatin and that β -glutinin has a molecular weight of about one-half that of gelatin. J. F. S.

Vitamins from the Point of View of Structural Chemistry. R. R. WILLIAMS (*J. Ind. Eng. Chem.*, 1921, **13**, 1107).—3-Hydroxy-

pyridine, which exists in two crystalline modifications, is shown by titration with bromine to be non-enolic in neutral solution, like the 2- and 4-compounds. It forms a 1-methyl ether which is a viscous oil miscible with water in all proportions and not volatile in steam. Its physiological action is not established. Three modifications of 4-phenylisocytosine were obtained, two of which had identical melting points and crystallographic properties, but differed greatly in their solubility in alcohol. Two freshly prepared modifications, which seemed to be Johnson and Hill's β - and δ -forms, were fed to pigeons and all the birds receiving the β -form lost weight less rapidly than those receiving the δ -form. After being kept for two months, however, the same two preparations showed no physiological difference. The author considers that vitamin-*B* will eventually be found to be a cyclic nitrogen compound in some ways analogous to the above. H. C. R.

Vitamins from the Point of View of Physical Chemistry.

VICTOR LAMER (*J. Ind. Eng. Chem.*, 1922, **13**, 1108—1110).—The amount of vitamin-*A* in skim milk is roughly equal to that contained in the fat layer. The water-soluble vitamin-*B* is also somewhat soluble in fatty oils. Vitamin-*B* is absorbed by Fuller's earth and by dialysed iron, and blood charcoal removes a measurable amount of vitamin-*C* from orange juice; the extent of adsorption is very sensitive to changes in the hydrogen-ion concentration. Vitamin-*C* is partly retained on filtration through Chamberland candles. The destruction of the antiscorbutic vitamin by heat is a chemical reaction the velocity of which is accelerated by increase of temperature according to the equation $X = K\sqrt[4]{t}$, where X is the per cent. of destruction, t the time in hours, and values of K are 0.26, 0.39, and 0.49 for 60°, 80°, and 100°, respectively. These data exclude the possibility that vitamin-*C* is of a protein- or enzyme-like nature. Heating at a reduced hydrogen-ion concentration results in an increased velocity of destruction. Bubbling oxygen through the solution at 100° results in the complete destruction of the vitamin in one hour, both in acid and weakly alkaline solution. Bubbling hydrogen through causes somewhat greater destruction than when no gas was used.

H. C. R.

Chloroform and Pepsic Digestion. A. ASTRUC and E. RENAUD (*J. Pharm. Chim.*, 1922, [vii], **25**, 81—87).—Chloroform has only a very slow destructive influence on the diastatic activity of pepsin, whilst chloroform vapours have no appreciable action. Chloroform water is a suitable solvent for pharmaceutical preparations of pepsin, and exerts a distinct preservative action, although after two months a small decrease in the fermentative activity can be detected. Chloroform water is, however, a bad digestive medium, and considerably retards digestion in vitro, but it would not be correct to deduce therefrom that in the stomach it also exerts an opposing influence on digestion and the activity of the pepsin.

G. F. M.

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The Influence of Reaction on the Action of Trypsin. I. W. E. RINGER (*Z. physiol. Chem.*, 1921, **116**, 107—128).—The optimum H-ion concentration for the action of trypsin at 37° was under certain conditions found to be P_H 11.3. It was also found that strongly acid solutions inactivated the enzyme. At a H-ion concentration of P_H 3.15 trypsin could be kept at 37°. As the H-ion concentration diminished the inactivation became more marked. At P_H = 12 the enzyme was almost instantaneously destroyed. The maximum imbibition of fibrin took place at a reaction which had an instantaneous inactivating action on trypsin.
S. S. Z.

The Inactivation of Trypsin. I. II. The Equilibrium between Trypsin and the Inhibiting Substance formed by its Action on Proteins. III. Spontaneous Inactivation. JOHN H. NORTHROP (*J. Gen. Physiol.*, 1921, **4**, 227—244, 245—260, 261—274).—The decomposition of gelatin by trypsin was investigated quantitatively by conductivity determinations and also by formal titration. Inactivation of trypsin is not effected by amino-acids or by the products of the hydrolysis of proteins by acid or alkali. The inhibiting substance occurs in the products of trypsin digestion and is dialysable. The equilibrium between the inhibitor and trypsin is found to agree with the scheme, trypsin+inhibitor \rightleftharpoons trypsin—inhibitor; it is reached instantaneously and is independent of the substrate concentration. On the assumption that hydrolysis is proportional to the concentration of free trypsin, it is shown that the laws of mass action are applicable. There is no evidence for any appreciable combination of trypsin with gelatin. Spontaneous inactivation of trypsin is also shown to occur independently of the influence of hydrolytic products. The rate of this inactivation approximates closely to that demanded by a unimolecular reaction. Trypsin digestion products in excess exert a protective effect by inhibiting spontaneous inactivation.

G. W. R.

Maltase. III. The Non-identity of Maltase and α -Glucosidase. RICHARD WILLSTÄTTER and WERNER STEIBELT (*Z. physiol. Chem.*, 1921, **115**, 199—210; cf. A., 1920, i, 795; 1921, ii, 72).—A number of preparations and yeasts have given quotients for the time value for glucosidate/time value for maltase, of varying magnitudes. The two enzymes are therefore not identical.
S. S. Z.

Effect of certain Antiseptics on the Activity of Amylases. H. C. SHERMAN and MARGUERITE WAYMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 2454—2461).—Low concentrations of chloroform did not affect the activity of commercial pancreatin or malt extract, but did affect the purified preparations of these amylases. Toluene had very little influence on the activities of the amylases either in their commercial or purified condition. All the preparations studied, either commercial or purified, were injured by formaldehyde even in low concentrations, and they were all very sensitive to copper sulphate. The percentage loss of enzyme action due to

these two antiseptics did not depend on the ratio of antiseptic to enzyme or to substrate, but on the concentration of the antiseptic in the system. The sensitiveness of the amylases to formaldehyde or copper sulphate as compared with their sensitiveness to toluene is possibly connected with the protein nature of the enzymes.

W. G.

The Influence of certain Amino-acids on the Enzymic Hydrolyses of Starch. H. C. SHERMAN and FLORENCE WALKER (*J. Amer. Chem. Soc.*, 1921, **43**, 2461—2469).—Previous work (cf. this vol., i, 66) has been extended to a study of glycine, alanine, tyrosine, and phenylalanine, using, however, Lintner's soluble starch as the substrate. Addition of any of these amino-acids caused an increase in the rate of hydrolysis of starch by purified pancreatic amylase, commercial pancreatin, saliva, or purified malt amylase, but less marked results were obtained with malt extract, taka-diastrase, or an aspergillus amylase. The addition of two of these amino-acids produced no greater effect than would result from the same concentration of one of them. The favourable effect of the added amino-acid was not due to any alteration in hydrogen-ion concentration of the medium or to the combination of the amino-acid with the product of the enzyme action. It is probably due, in part at least, to a protection of the enzyme from deterioration in the aqueous dispersion in which it acts. The addition of these amino-acids is a very effective means of protecting the enzyme from the deleterious action of copper sulphate (cf. preceding abstract) and may even serve to restore to full activity an enzyme which has been partly inactivated by copper sulphate.

W. G.

The Influence of Arginine, Histidine, Tryptophan, and Cystine on the Hydrolysis of Starch by Purified Pancreatic Amylase. H. C. SHERMAN and MARY L. CALDWELL (*J. Amer. Chem. Soc.*, 1921, **43**, 2469—2476).—The amylolytic power of purified pancreatic amylase on soluble starch was measured in the presence of these amino-acids, using glycine and phenylalanine as control amino-acids (cf. preceding abstract). Arginine and cystine favourably influence the digestion of starch, but histidine and tryptophan do not. It is again shown (*loc. cit.*) that the results obtained were not due to any variation in the hydrogen-ion concentration of the medium. There are thus apparently specific effects due to the amino-acids studied, which may depend on the structure of these acids and thus discriminate their action from that of the monoamino-acids originally studied.

W. G.

Remarks on the Elution of Saccharase and Maltase from Adsorbed Substances. RICHARD WILSTÄTTER and RICHARD KUHN (*Z. physiol. Chem.*, 1921, **116**, 53—66).—Monosodium phosphate accelerates the elution of adsorbed saccharase from alumina with a solution of sucrose. A phosphate mixture of $P_H=7$ has the same effect. This is not due either to the definite H-ion concentration or to the specific action of the phosphate,

as a citrate buffer of $P_H=4.5$ produces a similar acceleration but not an acetate buffer of this H-ion concentration. Primary phosphate has also an influence on the elution. Very low concentrations of glycerol sometimes raise the extracting power of primary phosphates. Maltase solutions do not remove adsorbed saccharase from alumina, but they can do so in the presence of monosodium phosphate. Maltase is not extracted by maltose alone, but is extracted by maltose in the presence of a buffer mixture. S. S. Z.

The Specific Nature of Saccharase and Raffinase. RICHARD WILLSTÄTTER and RICHARD KUHN (*Z. physiol. Chem.*, 1921, **115**, 180—198).—The quotient for time value for raffinase/time value for saccharase for several preparations of inverting enzymes was found to be 11.3. Similar quotients were also worked out for a number of yeasts. It is therefore concluded that saccharase and raffinase are two different enzymes. From the constant quotient obtained with the various inverting preparations it may be assumed that the two enzymes show a great similarity in some of their physical properties and are therefore not amenable to fractionation. S. S. Z.

The Regeneration of Inactivated Saccharase by Dialysis. HANS V. EULER and OLOF SVANBERG (*Z. physiol. Chem.*, 1921, **114**, 137—148).—Saccharase inactivated by silver nitrate, mercuric chloride, or aniline can be regenerated by dialysis. Whilst in the case of the metal salts the total regeneration of the enzyme cannot be accomplished, saccharase inactivated by the action of aniline can have its entire activity restored by dialysis. The saccharase of an active dry preparation could not be extracted with aniline. S. S. Z.

Rennet Coagulation of Milk as a Stimulated Process. EMIL BAUR and EUGEN HERZFELD (*Z. physikal. Chem.*, 1921, **98**, 460—473).—The velocity of coagulation of milk by rennet of various concentrations has been determined at 37° with the object of ascertaining whether the process is stimulated, and whether the rennet concentration is augmented by rennet contained in the milk. The results show that the coagulation is accompanied by an autocatalytic formation of new rennet in the milk. Experiments have been made to ascertain the rate at which the reaction is transmitted through milk in which no rennet has been placed. The reactions were carried out in a capillary tube which was connected with a large tube containing milk and rennet. The rate of transmission of the reaction is found to be 0.8 cm./hour. A control experiment shows that diffusion would have occasioned only a transmission of 1.0 ± 0.5 cm. in hours. J. F. S.

Oxydases. A. W. VAN DER HAAR (*Chem. Weekblad*, 1922, **19**, 33—34).—The failure of Wester (*ibid.*, 1921, **18**, 700—703) to detect a blue coloration with guaiacol in alcohol may be due to the presence of reducing saccharides; after removal of these by dialysis, the blue colour is readily obtained. Priority is claimed for the

author (A., 1910, i, 604; 1917, i, 301) for observations as to the chemical nature of the oxydase molecule advanced by Willstätter and Stoll. S. I. L.

Tannase. KARL FREUDENBERG and ERICH VOLLBRECHT (*Z. physiol. Chem.*, 1921, **116**, 277—292).—For the preparation of tannase the mould (*Aspergillus niger*?) was grown on a medium consisting of myrobalan extract, dipotassium phosphate, ammonium sulphate, and magnesium sulphate. After about four days' growth it was extracted with water, care being taken that the acid was neutralised with barium hydroxide during the extraction. The extract was then concentrated in a vacuum and the enzyme precipitated with absolute alcohol. The conditions under which tannase can be estimated quantitatively, using methyl gallate as the substrate, were also worked out. S. S. Z.

Reactions of the Phosphazines. WALTER THEODORE KARL BRAUNHOLTZ (T., 1922, **121**, 300—305).

Action of Arsenious Chloride on Aniline. JOHN H. SCHMIDT (*J. Amer. Chem. Soc.*, 1921, **43**, 2449—2454).—Aniline reacts with arsenious chloride in solution in *n*-heptane to give a yellow compound, *trianilinesarsine hydrochloride*, $\text{As}(\text{NHPh}, \text{HCl})_3$, m. p. 148—150°, which is probably identical with the compound described by Schiff (*Compt. rend.*, 1863, **56**, 268, 1095). This compound is readily transformed by heating it, either alone or preferably with an excess of aniline, into cyclic arsenic compounds. The first product is chlorophenarsazine, which with alkalis gives *phenarsazine oxide*, $\text{O}(\text{As} \langle \text{C}_6\text{H}_4 \rangle \text{NH})_2$, and this on oxidation with hydrogen peroxide

in alkaline solution yields *phenazarsinic acid*, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{AsO} \cdot \text{OH}$.

From this acid, on nitration, *dinitrophenazarsinic acid* was obtained, giving a *disodium* salt. *Aniline arsenate*, m. p. 147—148°, and *dianiline arsenate*, m. p. 143°, were obtained by the interaction of aniline and syrupy arsenic acid in alcoholic solution, using excess of aniline or acid according to the salt required.

A simple arrangement for sublimation in a vacuum, using a Beckmann boiling apparatus, is described. W. G.

Organo-derivatives of Thallium. IV. Action of Thallium Chlorides on the Grignard Reagent and on Organo-derivatives of Tin, Lead, and Bismuth. DOROTHY GODDARD and ARCHIBALD EDWIN GODDARD (T., 1922, **121**, 256—261).

Physiological Chemistry.

Physiology of the Respiration of Fishes in Relation to the Hydrogen-ion Concentration of the Medium. EDWIN B. POWERS (*J. Gen. Physiol.*, 1921, 4, 305—317).—The absorption by marine fishes of oxygen at low tension is dependent on the hydrogen-ion concentration of sea-water. It is suggested that variations in the ability of individuals of a species to absorb oxygen at a given hydrogen-ion concentration depend on the alkaline reserve of the blood. G. W. R.

The Respiratory Processes in *Mya arenaria* and other Marine Mollusca. J. B. COLLIP (*J. Biol. Chem.*, 1921, 49, 297—310).—From experiments on the survival of *Mya arenaria* under anærobic conditions, it is concluded that this, and other calcareous shelled molluscs, have in their tissues a store of oxygen which suffices temporarily to replace the external supply of the latter. Under anærobic conditions the normal acid-base balance is maintained by the mobilisation of the reserves of calcium in the liver and the shell. C. R. H.

The Action of Intravenous Injections of Hypertonic Solutions of Various Sugars on the Respiratory Metabolism of the Dog. MAX BÜRGER (*Biochem. Z.*, 1921, 124, 1—24).—Within half an hour of the intravenous injection of hypertonic solutions of dextrose and lævulose, the respiratory quotient rises to a value above 0.9 with simultaneous increased heat production. The relatively greater heat production after lævulose points to direct utilisation of the sugar without previous conversion into glycogen. The considerably smaller effects of intravenous injection of hypertonic lactose and sucrose solutions is an indirect effect, and is attributed to an increased kidney and heart activity produced by flow of tissue fluids into the blood owing to the action of the hypertonic carbohydrate solutions. H. K.

The Influence of Lack of Calcium in the Diet on the Respiratory Basal Metabolism. FAUSTO PEDOTTI (*Biochem. Z.*, 1921, 123, 272—283).—Rats fed on a diet deficient in calcium show a diminished respiratory basal metabolism. H. K.

The Physiology of the Glands. XLVIII. Experiments on the Respiratory Metabolism of the Dog with Extirpated Spleen. LEON ASHER and CHU KODA (*Biochem. Z.*, 1921, 122, 154—160).—The gaseous metabolism on a normal diet of dogs which have had their spleens removed is normal. This differs from the results of others on rats and rabbits. H. K.

The Physiology of the Glands. XLIX. The Respiratory Interchange of the Dog with Extirpated Spleen and Diet Deficient in Iron. LEON ASHER and FRANCIS H. DOUBLER (*Biochem. Z.*, 1921, 122, 161—167).—Extirpation of the spleen

coupled with an iron-free diet has no action on the respiratory gaseous metabolism or the coagulation time of the blood of the dog. The hæmoglobin content of the blood falls off very slowly.

H. K.

The Action of Carbon Dioxide on Salt and Water Distribution in Blood. G. MUKAI (*J. Physiol.*, 1921, **55**, 356—370; from *Physiol. Abstr.*, 1922, **6**, 568).—On treatment with carbon dioxide, the chlorine and water content of the corpuscles increases, the former by anion interchange, the latter by osmosis consequent on the increased carbon dioxide and chlorine in the corpuscles. Corpuscles always contain more carbon dioxide than the corresponding serum; the carbon dioxide is carried partly by increased alkali and partly by proteins. There is presumptive evidence that the corpuscles were alive for more than six hours in these experiments.

E. S.

The Distribution of Chlorine in the Blood. S. VAN CREVELD (*Biochem. Z.*, 1921, **123**, 304—314).—The results of recent workers on the distribution of chloride in the blood are criticised. Direct estimation on the circulating blood shows that the corpuscles are permeable; the percentage of chloride in the corpuscles relative to that of the plasma is greater in venous than in arterial blood. There is no evidence of a fixation of chloride as a fibrinogen chloride compound.

H. K.

Relation between the Chloride Content of the Blood and its Volume per cent. of Cells. A. NORGAARD and H. C. GRAM (*J. Biol. Chem.*, 1921, **49**, 263—278).—Estimations were made of the chloride content of whole blood and plasma in normal and pathological cases. Nearly constant values were obtained for the plasma in all cases, whilst the values for whole blood were found to be dependent on the cell volume percentage, the smaller the latter the greater being the chloride content of the blood. Calculations of the chloride content of the corpuscles yielded, with one exception, constant values.

E. S.

The Fate of Sulphides in the Blood. HOWARD W. HAGGARD and THOMAS J. CHARLTON (*J. Biol. Chem.*, 1921, **49**, 519—529).—The toxic properties of hydrogen sulphide are due neither to the formation of a compound with the hæmoglobin of the blood nor to the production of sodium sulphide in the plasma. On the contrary, in vitro and in vivo experiments show that sodium sulphide is rapidly and completely hydrolysed by blood, the resulting hydrogen sulphide being quickly oxidised in the presence of oxygen. The toxic effects of hydrogen sulphide, and consequently of sodium sulphide, are not cumulative.

E. S.

The Isolation of Amino-acids in Blood. EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1921, **114**, 250—254).—The presence of all the known amino-acids was established in the serum and in the plasma of cattle and horses by examining the dialysates of these fluids. Substances, on the other hand, giving the biuret reaction

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or substances consisting of more than one amino-acid could not be found in the dialysate of these plasmas and serums. S. S. Z.

Blood Acetone Substances after the Injection of Small Amounts of Adrenaline Chloride. ROGER S. HUBBARD and FLOYD R. WRIGHT (*J. Biol. Chem.*, 1921, **49**, 385—388).—After injection of adrenaline there is a rise in the concentration of acetone substances in the blood, which, however, bears no apparent relation to changes in the blood-sugar concentration or carbon dioxide-combining power. C. R. H.

Fibrinogen Content of Human Blood. H. C. GRAM (Pamphlet, Copenhagen, 1921, pp. 276; from *Physiol. Abstr.*, 1922, **6**, 566; cf. this vol., ii, 240).—A method of estimating fibrinogen in 2 c.c. of citrated blood after adding calcium chloride is described. In normal adults the plasma yields 0.2 to 0.38%; in whole blood the figures are 0.11 to 0.19. A number of diseases are mentioned in which variations occur. E. S.

Animal Calorimetry. XIX. The Influence of Acids on the Carbon Dioxide-combining Power of the Blood Plasma. SOPHIA A. TAISTRA (*J. Biol. Chem.*, 1921, **49**, 479—483).—Measurements of the carbon dioxide-combining power of the blood indicate that the specific dynamic action of foodstuffs is not dependent on neutralisation of the alkaline reserve of the blood. E. S.

Animal Calorimetry. XX. The Influence of the Ingestion of Meat and of Glycine and Alanine on the Carbon Dioxide-combining Power of Blood Plasma. ALFRED CHANUTIN (*J. Biol. Chem.*, 1921, **49**, 485—486).—The ingestion of meat, glycine, or alanine in a dog increases the alkali reserve of the blood plasma as measured by its carbon dioxide-combining power. E. S.

The Flocculating Capacity of Human Blood-plasma. WILHELM STARLINGER (*Biochem. Z.*, 1921, **123**, 215—224).—Flocculation in blood-plasma, produced, for example, by saturated sodium chloride solution, can be used as a measure of fibrinogen content. Inhibition of flocculation is produced by acid, alkali, neutral salts, increase of temperature, pepsin, and Witte peptone, whilst agar, gum-arabic, gelatin, and glycine increase flocculation. H. K.

The Influence of Potassium and of Radioactivity on the Oxidation Velocity of the Red Corpuscles. PHILIPP ELLINGER (*Z. physiol. Chem.*, 1921, **116**, 266—276).—The presence of potassium in the surrounding medium is indispensable for the respiratory function of the red blood-corpuscles. It can be replaced by rubidium, but not by caesium. Radioactive substances emitting α -rays cannot replace potassium in the respiratory function of the corpuscles. Eosin has a stimulating action in low and an injurious action in high concentrations. Fluorescein has an injurious action even in very low concentrations. The stimulating influence of eosin is independent of the action of potassium. S. S. Z.

Permeability of the Red Blood-corpuscles. E. WIECHMANN (*Deuts. med. Woch.*, 1921, 47, 824—825; from *Physiol. Abstr.*, 1922, 6, 565; cf. this vol., i, 80).—The rapidity with which the exchange of ions occurs depends on specific properties of the ions themselves. E. S.

The Analysis of a Volume Curve of Blood-corpuscles in Hypertonic Solutions, which renders possible the Simultaneous Differentiation of Osmotic and Colloido-chemical Changes in Volume. TAKEO TAKEI (*Biochem. Z.*, 1921, 123, 104—127).—Blood-corpuscles of men, rabbits, and oxen shrink in hypertonic solution proportionally to the external osmotic pressure, when this pressure does not exceed four times the normal pressure, quite independently of the nature of the medium. Beyond this point there is a sudden increase of corpuscular volume which may almost reach the initial normal volume. This is ascribed to a swelling of the erythrocyte colloids. The shrinkage is a reversible process, but the swelling is irreversible, as hæmolysis takes place on dilution. In serum rendered hypertonic by dextrose there is no swelling of the corpuscles. H. K.

The Biochemistry of the Phosphatides and Sterols. IV. The Importance of the Proportion of Cholesterol-Lecithin of the Erythrocyte Surface for the Stability of Suspensions of Blood-corpuscles and for Natural Hæmolysis. R. BRINKMAN and (FRL.) H. WASTL (*Biochem. Z.*, 1921, 124, 25—36).—In salt solutions, corpuscles lose their distinctive velocity of sedimentation owing to a washing away of constituents of the surface of the corpuscles. These constituents may be recovered as a cholesterol (light petroleum soluble) fraction and a phosphatide (alcohol-soluble) fraction. If both be added to the washed corpuscles, they recover their property of agglutination, whereas if only phosphatides be added there is hæmolysis. H. K.

Agglutination and Velocity of Sedimentation of Corpuscles. II. WILHELM STARLINGER (*Biochem. Z.*, 1921, 122, 105—119).—The addition of kaolin, bolus alba, or animal charcoal retards the sedimentation of corpuscles by adsorbing the fibrinogen. Gelatin, agar, and gum, however, accelerate the flocculation and sedimentation. This is attributed to a diminution of the suspension stability of the corpuscles, due partly to abstraction by adsorption by these substances of the break-down products of the corpuscles and partly to withdrawal of water. H. K.

The Action of some Electrolytes and Non-Electrolytes on the Velocity of Sedimentation of the Red Blood-corpuscles of the Horse. J. RUNNSTRÖM (*Biochem. Z.*, 1921, 123, 1—26).—The velocity of sedimentation of horse corpuscles was determined in presence of various salts, hydrochloric acid, serum, gelatin, and narcotics. The results obtained show great variation, and are interpreted on the hypothesis that the action of ions is due to adsorption on the surface of the corpuscle, the presence of colloids

modifying the adsorption of the ions through competition for the erythrocyte surface.

H. K.

The Distribution of Chloride between Corpuscles and Plasma. AUGUSTIN MURESANU (*Biochem. Z.*, 1921, **124**, 114—118).—In agreement with other observers, the corpuscles were found to be practically free from chloride. The contrary statements of Siebeck (*Arch. exp. Path. Pharm.*, 1920, **85**, 214), even employing Siebeck's method, could not be substantiated. In some pathological cases, for instance, nephritis, the corpuscles contain appreciable quantities of chloride.

H. K.

Permeability of Cells and Tissues. VIII. The Question of the Distribution of Hormones and Drugs in the Blood. HANS SCHAEPI (*Biochem. Z.*, 1921, **122**, 232—250).—The distribution of barium chloride, choline bromide, and nicotine between corpuscles and plasma or serum was determined by a physiological method—using Fuhner's nerve-free leech preparation. The corpuscles are impermeable to barium, but nicotine and choline both distribute themselves equally in plasma or serum and corpuscles.

H. K.

The Fixation of Quinine by Red Blood-corpuscles and the Distribution of Quinine in Blood. P. RONA and E. BLOCH (*Biochem. Z.*, 1921, **121**, 235—258).—By making use of the relation, that when the toxic concentration of quinine on the activity of serum lipase is increased in geometrical progression the velocity constants of the hydrolysis of tributyrin by lipase fall off in arithmetical progression, the authors find that 80 to 90% of the quinine added to blood is fixed by the corpuscles. The method is applicable to fractions of a mg. of quinine. After intravenous injection of quinine, only 1 to 4% of the quinine could be found in the blood.

H. K.

The Distribution of Cinchona Alkaloids in the Organism. II. ALFRED SCHNABEL (*Biochem. Z.*, 1921, **122**, 285—294).—Further experiments with kidney and brain suspensions and optochin show the same behaviour as earlier experiments with corpuscles. The optochin is taken up by the cells and slowly given up to the surrounding fluid. Parallel with this behaviour in vitro, it is found that freshly defibrinated blood of a rabbit injected with optochin has a lower concentration of optochin in the serum when examined immediately than when kept for some time. The fixation of optochin by corpuscles is an adsorption phenomenon. Quinine, which can also be estimated by its inhibitory action on the reducing capacity of pneumococci to methylene-blue, but is about one-twentieth as active as optochin, is likewise taken up by the corpuscles and slowly given off to the surrounding fluid, producing an actual increased concentration of quinine in the surrounding fluid.

H. K.

The Theory of Blood-clotting. ALBERT FUNCK (*Biochem. Z.*, 1921, **124**, 148—155).—Flocculation of fresh undialysed

fibrinogen only takes place between P_H 4 and P_H 9. At an acidity greater than P_H 4, fibrinogen wanders to the cathode and at an alkalinity greater than P_H 9 to the anode. Purified solutions of serum-albumin, serum-globulin, and egg-albumin cause clotting of fibrinogen but fibrino-globulin is without action. H. K.

The Quantitative Action of some Factors in the Clotting of Blood. LUDWIG HELLER (*Biochem. Z.*, 1921, **123**, 90—103).—At a lower concentration than about 10%, normal blood does not clot. At a blood-dilution of 1 : 200, the minimum concentration of calcium chloride necessary for clotting is 0.005 to 0.006%; at higher dilutions, the minimal calcium chloride concentration is higher, and at lower dilutions of the blood, lower. The concentration of sodium chloride is also of influence. The results are applied to the blood of pathological cases. H. K.

The Free and Esterified Sulphuric Acid in Normal and in Pathological Body-fluids. WOLFGANG HEUBNER and ROBERT MEYER-BISCH (*Biochem. Z.*, 1921, **122**, 120—127).—Normal serum contains about 0.02% of sulphate which can be dialysed out with the chlorides, but is adsorbed by the proteins when these are precipitated. In pathological exudates there was one-third less sulphuric acid than in serum and a small proportion of sulphuric acid in ester form. The latter shows an increase after sulphur injections in diseases of the joints. H. K.

Fixation of Lime by Animal Tissues. VI. E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1921, **124**, 299—310).—A number of bases and basic substances inhibit the fixation of calcium by cartilage or serum. The action of anions on the fixation of calcium by serum and brain-matter has also been examined. H. K.

Physico-chemical Investigations on Body-fluids. IV. The State of Sugar in Serum. STEFAN RUSZNYÁK and GÉZA HETÉNYI (*Biochem. Z.*, 1921, **121**, 125—126).—The reducing substances present in serum are greater in amount than in the ultra-filtrate. After fermentation with yeast, the residual reducing substances in the serum are equal in amount to those in the ultra-filtrate. A portion of the original sugar of the serum is therefore in a colloidal, non-ultra-filtrable state. H. K.

"Double-nitrogen," a Diagnostic for Endogenous Protein-breakdown, especially for Hidden Suppuration. ARNOLD HAHN (*Biochem. Z.*, 1921, **121**, 262—272).—The difference between the nitrogen content of serum after removal of proteins and breakdown products by precipitation with phosphotungstic acid and the nitrogen content of serum after removal of proteins alone by trichloroacetic acid, gives a measure of the protein degradation products present. This value the author terms "double-nitrogen" (Doppelstickstoff). H. K.

The Action of Kaolin on the Terminal Component and on the Tributyrin Hydrolytic Capacity of Guinea Pig's Serum. O. OLSEN (*Biochem. Z.*, 1921, **124**, 119—129).—Previous experiments (*ibid.*, **112**, 188) showed an analogy between the final portion of the complement and the tributyrinase, rather than with the middle portion, or the third component of the complement. By gentle agitation of sera with kaolin, it is now shown that the final portion of the complement is inactivated before the tributyrinase. It is thought that the final portion of the complement may be complex, the tributyrinase constituting one component. H. K.

Hæmolytic Action of Sodium Glycocholate. ERIC PONDER (*Proc. Roy. Soc.*, 1922, [B], **93**, 86—103).—Serum-albumin, peptone, adrenaline, pituitrin, histamine, and histidine accelerate or retard the hæmolytic activity of sodium glycocholate according as they are added after or before the latter to the suspension of blood cells. The author is unable to explain these results on the theory that the bile salt dissolves the corpuscle envelope, but suggests that they are due to a disturbance of surface tension at the surface of the corpuscle. Blood-serum inhibits the hæmolytic action of both sodium taurocholate and sodium glycocholate. E. S.

Animal Calorimetry. XVIII. The Behaviour of Various Intermediary Metabolites on the Heat Production. GRAHAM LUSK [with JAMES EVENDEN] (*J. Biol. Chem.*, 1921, **49**, 453—478; cf. A., 1919, i, 105).—No change in metabolism was produced by the administration of sodium hydrogen carbonate to a dog. Increased heat production was, however, observed in each case after administration of the following substances: acetic acid, lactic acid, sodium lactate, glycollic acid, sodium glycollate, hydrochloric acid, sodium salt of glycine. There was no relation between the potential hydrogen-ion concentration and the specific dynamic action of the substances administered. E. S.

The Hydrolysis of Casein and Deaminised Casein by Proteolytic Enzymes. MAX S. DUNN and HOWARD B. LEWIS (*J. Biol. Chem.*, 1921, **49**, 343—350).—Deaminised casein is hydrolysed by pepsin and trypsin, but is unattacked by erepsin except after the preliminary action of either of the first-named enzymes. In each case, the action proceeds at a slower rate than in the corresponding case of casein. Experiments on a dog indicate that it is metabolised in the animal body, although repeated ingestion produces vomiting and loss of appetite. E. S.

The Problem of Nuclein Metabolism. II. The Influence of Human Fæces on Yeast-nucleic Acid. JULIUS ROTHER (*Z. physiol. Chem.*, 1921, **114**, 149—160; cf. A., 1920, i, 784).—Approximately one-half of the purine bases of yeast-nucleic acid have their purine rings ruptured when the acid is digested for forty to forty-eight hours at 37° with a suspension of human fæces. In a metabolic experiment with a human being, it was found that the purine ring of the bases given to the patient per os in the form

of yeast-nucleic acid was ruptured in the lower portion of the intestine. The reaction depends on the time of sojourn of the nucleic acid in the large intestine. S. S. Z.

Synthesis of Uric Acid in the Human Organism. GUSTAV KOLLMANN (*Biochem. Z.*, 1921, **123**, 235—244).—Observations on a twenty-six year old girl for fifty days on a standard diet poor in purines resulted in an increase of weight of 4 kilograms and an excretion of 15 grams of uric acid in excess of the quantity furnished by the food. A purine synthesis is postulated, but requires further confirmation. H. K.

The Formation of Mercapturic Acid during the Ingestion of a Protein Minimum. JOSEPH KAPFHAMMER (*Z. physiol. Chem.*, 1921, **116**, 302—307).—During the ingestion of a protein minimum, added bromobenzene is converted into *p*-bromophenyl-mercapturic acid if at the same time cystine is introduced subcutaneously. S. S. Z.

The Action of the Thyroid Gland Hormone in Phloridzin Diabetes. XLVI. LEON ASHER and WALTER HARRISBERGER (*Biochem. Z.*, 1921, **121**, 64—75).—Phloridzinised rats show an increased basal metabolism on administration of desiccated thyroid. H. K.

Vitamin-B and Co-enzymes. II. H. v. EULER and KARL MYRBACK (*Z. physiol. Chem.*, 1921, **115**, 155—169).—A method is described by means of which vitamin-B ("Biocatalyst") is estimated quantitatively by its stimulating power on alcoholic fermentation. A maximum is reached by the addition of the stimulating substance after which any further addition inhibits the fermentation. Utilising this method, it is found that a considerable quantity of the vitamin is used up in the human body per day. S. S. Z.

Increase of Nitrogen after Fleshy and Meal Diets. L. DIENES (*Biochem. Z.*, 1921, **123**, 128—143).—After emaciation, more nitrogen is fixed from fleshy foods than from wheaten flour. H. K.

Replacement of Protein by Urea in Rations. A. MORGEN, G. SCHÖLER, K. WINDHEUSER, and ELSA ÖHLMER (*Landw. Versuchs.-Stat.*, 1921, **99**, 1—26).—Experiments with sheep and milch animals showed that in rations containing a normal amount of protein, replacement by urea is possible up to 30—40%. A slight depression in milk production in the case of milch sheep and goats receiving a portion of their nitrogen in the form of urea was balanced by an improvement in the quality of the milk. G. W. R.

Colorimetric Experiments on Tryptophan. VI. The Tryptophan Content of some Foods and the Tryptophan Requirement of Men. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Z.*, 1921, **122**, 58—85; cf. A., 1921, i, 64, 74; ii, 71).—For the purpose of this investigation, the tryptophan content of a large

number of foodstuffs had to be determined colorimetrically (Voisenet's test). As the presence of a large proportion of fats or starch interferes with the reaction, the proteins had to be isolated in some cases. On an average, the tryptophan content of nutritive protein is between 2% and 2.4%. By making use of the large numbers of metabolic experiments described in the literature, the authors show that a man weighing 70 kilos. consumes 2.5 to 3.2 grams of tryptophan per diem, and no harm ensues if the tryptophan content is only one-half of this. H. K.

Histochemistry of Spermatozoa. IV. Chemical Composition of the Spermatozoa of the Shad (*Clupea alosa*). H. STEUDEL (*Z. physiol. Chem.*, 1921, **114**, 161—166; cf. A., 1911, ii, 626, 905; 1913, i, 216).—The nucleic acid of the spermatozoa of the shad was prepared by the sodium acetate and alcohol method as the copper salt, $C_{43}H_{57}O_{34}N_{15}P_4Cu_2$. The amount of the salt obtained was equal to 41.47% of the total matter. The phosphorus-nitrogen ratio of the spermatozoa of the shad was found to be identical with that of the spermatozoa of the herring.

S. S. Z.

Sugar Content of the Hen's Egg. J. S. HEPBURN and E. Q. ST. JOHN (*J. Amer. Inst. Homeopathy*, 1921, **14**, 339—343).—A modification of the method of Folin and Wu (A., 1919, ii, 308; 1920, ii, 337) yielded the following results for the minimum, maximum, and average percentage content of dextrose respectively: whole egg, 0.36—0.49, 0.45%; white free from yolk, 0.29—0.57, 0.47%; yolk free from white, 0.11—0.15, 0.14%; yolk commercially separated, 0.16—0.35, 0.25%. Results obtained from eggs after preservation in sodium silicate solution, and from frozen white of egg, were within the above limits, but putrid white of egg contained no dextrose. CHEMICAL ABSTRACTS.

Lipoids. XVIII. The Preparation of Phosphosulphatides from Brain. SIGMUND FRÄNKEL and OSKAR GILBERT (*Biochem. Z.*, 1921, **124**, 206—215).—The portion of protagon from human brains which forms a barium salt insoluble in alcohol is known to be free from galactosides. It contains, however, sulphur and phosphorus. A portion of the barium salts soluble in benzene was prepared and the fraction of this soluble in light petroleum is a phosphosulphatide, the ratio P : S : N : Ba being 1 : 1 : 3 : 2. On hydrolysis, the barium salt gave aminoethyl alcohol and cerebronic acid. H. K.

Lipoids. XIX. A Lecithin from Human Brain. SIGMUND FRÄNKEL and ARTUR KÄSZ (*Biochem. Z.*, 1921, **124**, 216—227).—Linnert's sahidin from human brain has been re-examined. At one stage of the purification the phosphorus nitrogen ratio was 3 : 2, in agreement with Linnert's values, but further purification by solution in toluene and precipitation with alcohol gave finally a sparingly soluble product which proved to be pure lecithin (N : P = 1 : 1). The hydrolytic products were glycerylphosphoric acids, choline, stearic, and oleic acids. H. K.

Sugar of Cerebrospinal Fluid. R. COOPE (*Quart. J. Med.*, 1921, **15**, 1—8; from *Physiol. Abstr.*, 1922, **6**, 564).—A low sugar content is found in tubercular meningitis, and certainly not a high one in encephalitis lethargica, which some French writers claim.

E. S.

The Relation between Blood-plasma and Tissue Fluids, especially the Aqueous Humour and the Cerebrospinal Fluid. I. The Sugar Content and the Question of the Combined Sugar. J. DE HAAN and S. VAN CREVELD (*Biochem. Z.*, 1921, **123**, 190—214).—The dextrose content of the aqueous humour and of the cerebrospinal fluid of the rabbit is less than that of the blood-plasma. In hyperglycemia produced by adrenaline, the diffusion of dextrose into the two fluids is moderately rapid and of the same order in both. The excess of dextrose in normal blood-plasma over that in the aqueous humour is attributed to the non-dialysable bound sugar, whilst the difference in the cerebrospinal fluid is augmented by the greater consumption of dextrose by the brain.

H. K.

Comparative Study of the Sugar Content of the Spinal Fluid in Diseases of the Nervous System. L. D. STEVENSON (*Arch. Neurol. Psychiatry*, 1921, **6**, 292—294).—Benedict's method led to distinctly higher results than those given by Shaffer's method. Four cases of encephalitis gave an average of 60 mg. of sugar per 100 c.c. by Shaffer's method. Former values with Folin's method were much higher. It is suggested that some other reducing substance may be present in cases of encephalitis, which may not interfere with the Shaffer method.

CHEMICAL ABSTRACTS.

Chemical and Biochemical Investigations of the Nervous System under Normal and Pathological Conditions. IX. GIACOMO PIGHINI (*Biochem. Z.*, 1921, **122**, 144—151).—A review of the previous results of the author and of others.

H. K.

The Thermolability of the Sucrose-splitting Enzyme of the Human Jejunum. H. VON EULER and KARL MYRBÄCK (*Z. physiol. Chem.*, 1921, **115**, 68—76).—The sucrose-splitting enzyme of the human jejunum is much more thermolabile than the corresponding yeast enzyme. The two enzymes are therefore not identical.

S. S. Z.

A Basic Protein Derivative. K. FELIX (*Z. physiol. Chem.*, 1921, **116**, 150—165).—Basic protein derivatives were obtained from the mucous membrane of the intestine, from the lymphatic glands, and from the thymus. They were prepared by extracting the tissues with dilute hydrochloric acid, precipitating the histone by saturating the solution with sodium chloride, and finally precipitating the basic derivative with phosphotungstic acid. The distribution of nitrogen in these derivatives has been worked out. Trypsin did not digest these substances.

S. S. Z.

The Saccharase of the Intestine. H. VON EULER and O. SVANBERG (*Z. physiol. Chem.*, 1921, **115**, 43—67).—Quantitative determinations of the enzymic activity of the intestinal saccharase in various sections of the intestine are given. S. S. Z.

Action of Potassium, Calcium, and Magnesium Ions on the Sympathetic Nerve of the Heart. J. TEN CATE (*Arch. Néerland. physiol.*, 1921, **6**, 269—288).—Frogs' hearts perfused with Ringer solution containing magnesium, or excess of potassium or calcium, or from which potassium is omitted, respond to excitation of the accelerator nerve or to the action of adrenaline after they have ceased to beat. The same holds if the Ringer solution is replaced by an isotonic solution of common salt, but there is no response when calcium-free Ringer is used. The possible explanation is discussed. E. S.

Potassium and Radioactivity. S. G. ZONDEK (*Biochem. Z.*, 1921, **121**, 76—86).—Using a Straub's heart preparation, the author failed to confirm any of Zwaardemaker's observations (A., 1918, i, 326). Zwaardemaker's success is attributed to the use of antiquated methods. H. K.

The Ionic Equilibrium of Cells. The Physiology of Sodium. S. G. ZONDEK (*Biochem. Z.*, 1921, **121**, 87—108).—Hearts were perfused with various concentrations of solutions containing sodium, potassium, and calcium ions. The heart can adjust itself to other concentrations of the ions mentioned than the normal. The antagonistic action of calcium to potassium and to sodium is thought to be related to the atomic number of these elements, for whereas the difference of atomic number of potassium and calcium is unity, and their relative intensity is approximately equal, sodium has an atomic number nine less than calcium, and its antagonistic action is much less. H. K.

The Creatine Content of the Human Heart Muscle in Various Illnesses. FR. CONSTABEL (*Biochem. Z.*, 1921, **122**, 152—153).—Heart muscle in a braced condition contains a higher percentage of creatine than when in a relaxed condition as in fatty degeneration. H. K.

The Chemistry of the Lungs. I. UBALDO SAMMARTINO (*Biochem. Z.*, 1921, **124**, 234—243).—Lung tissue contains much cholesterol, cholesteryl esters, glyceryl palmitate, and unsaturated phosphatides. There is relatively little lecithin and cephalin, but a much larger proportion of cerebrosides and phosphosulphatides. H. K.

The Action of Pilocarpine on the Glycogen Content of Organs. CURT HORNE MANN (*Biochem. Z.*, 1921, **122**, 269—273).—The hyperglycemia produced by pilocarpine was not influenced by administration of oxygen through the vena femoralis. The glycogen of the liver is used up, but that of the muscles shows but a slight decrease. H. K.

The Steric Transformation of the Hexoses through the Agency of Organs and Cells (the so-called Stereokinases). S. ISAAC and E. ADLER (*Z. physiol. Chem.*, 1921, **115**, 105—129).—The surviving liver was the only organ which was found to be able to transform lævulose into dextrose. This organ fulfilled this function only when it was intact and irrigated. Other tissues, such as muscle or blood corpuscles, as well as the pulp and extracts of various organs failed to bring about this transformation.

S. S. Z.

Higher Alcohols in the Unsaponifiable Matter from Shark and Ray-fish Liver Oils. MITSUMARU TSUJIMOTO and YOSHIYUKI TOYAMA (*Chem. Umschau*, 1922, **29**, 27—29, 35—37, 43—45).—Kagurazame oil (from the liver of *Hexanchus corinus*, Jordan and Gilbert) has the following characters: d_{40}^{25} 0.9146, acid number 0.49, saponification number 163.0, iodine number (Wijs) 124.5, n_D^{20} 1.4740, Hehner number 97.70, unsaponifiable matter 15.24%, glycerol 5.43%, acid number of the fatty acids 192.5, polybromide number of the fatty acids 26.30%. The oil does not contain squalene. The unsaponifiable matter consists chiefly of two new dihydric alcohols, one saturated and the other unsaturated. The saturated alcohol, *batyl alcohol*, $C_{10}H_{42}O_3$, is obtained by the hydrogenation of the unsaturated one in alcoholic solution at the ordinary temperature in the presence of platinum black. It crystallises in colourless, rectangular laminae with silvery lustre, m. p. 69°. The unsaturated *selachyl alcohol*, $C_{20}H_{40}O_3$, is a yellow liquid, $d_4^{25} = 0.9206$, $n_D^{25} = 1.4690$, iodine number 78.9. It is uncertain whether one of the three oxygen atoms of these alcohols is in the form of a hydroxyl group which cannot be acetylated or is part of an ether-like structure.

These alcohols also form the principal constituents of the unsaponifiable matter of the liver oils from the following species: *Cirrhitigaleus barbifer*, *Somniosus microcephalus*, *Narcacion tokionis*, *Chimæra owstoni*, *Chimæra mitsukurii*. They also occur together with large quantities of squalene in the unsaponifiable matter from the liver oils of *Lepidorhinus kimbei* and *Zameus squamulosus*. The liver oil from *Chlamydoselachus anguineus* probably contains another alcohol as the principal constituent of the unsaponifiable matter. The principal constituent of the unsaponifiable matter of Doran-ei oil is cholesterol.

H. C. R.

The Stimulatory Action of Amino-acid Hydrochlorides on the Pancreatic Secretion. M. ARAI (*Biochem. Z.*, 1921, **121**, 175—179).—The hydrochlorides of glycine, *d*-alanine, *d*-glutamic acid, and glycylglycine injected into the duodenum of a dog with a temporary pancreatic fistula cause a vigorous pancreatic secretion. Histidine hydrochloride and glucosamine hydrochloride had no action. Intravenous or subcutaneous administration of any of these salts was without result. Adrenaline inhibits such a pancreatic secretion, but atropine is without action.

H. K.

The Nucleic Acids of the Spleen of Cattle. H. STEUDEL (*Z. physiol. Chem.*, 1921, **114**, 255—261).—As in the case of the

pancreas it is possible to obtain from the spleen of cattle guanylic acid and a real nucleic acid. The former was obtained from a protein isolated from the spleen by boiling the minced organ with water, filtering, and precipitating the filtrate with 50% acetic acid and alcohol. Guanylic acid was prepared from this protein by treating it with 2% sodium hydroxide on the water-bath, acidifying with acetic acid, and filtering. The guanylic acid separated from the filtrate on keeping. The nucleic acid was prepared from the residue of the spleen obtained after the aqueous extraction in the preparation of the protein by digesting it with 33% sodium hydroxide and precipitating with alcohol. Ten grams of the nucleic acid yielded 0.9 gram of guanine (calculated 0.8668) and 0.68 gram of adenine (calculated 0.7698). S. S. Z.

The Physiology of the Glands. XLVII. The Relations between the Thymus, Spleen, and Bone-marrow. LEON ASHER and GENGU MATSUMO (*Biochem. Z.*, 1921, **123**, 27—50).—The hæmoglobin and white corpuscular content of blood were examined after extirpation of the thymus and spleen. Stimulation of the bone-marrow of normal rabbits by hydrocyanic acid or by bleeding leads to a fall in the hæmoglobin, an increase of lymphocytes, but a decrease in the number of leucocytes. Extirpation of the thymus inhibits this response almost completely. Extirpation of the spleen, however, has little effect. H. K.

The Degradation of Carbohydrates in Transversely Striated Muscles. I. FRITZ LAQUER (*Z. physiol. Chem.*, 1921, **116**, 169—222).—The formation of lactic acid from various sugars by frog muscle has been studied under different physiological conditions. S. S. Z.

Reduction of the Aromatic Nitro-group as Indicator of Partial Processes of Respiration and of Fermentation. A Method for the Comparative Estimation of Biological Oxidoreduction. I. Experiments with Respiring Cells. II. Experiments with Fermenting Cells. W. LIPSCHITZ and A. GOTTSCHALK (*Pflüger's Archiv*, 1921, **191**, 1, 32—50; from *Physiol. Abstr.*, 1922, **6**, 589—590).—I. The *m*-nitrophenylhydroxylamine produced by the reducing action of tissues on *m*-dinitrobenzene can be estimated colorimetrically after filtration, and a quantitative measure of hydrogen activation thus obtained. Experiments on frog muscle show that the rate of reduction depends on the concentration of co-ferment in the sense in which that term was used by Meyerhof; the falling-off of the rate of reduction with time resembles that of the oxygen respiration rate. Reduction is destroyed by temperatures above 80°, is dependent on intact cell structure, is diminished with increase of oxygen pressure and by narcotics. Whilst combinations of narcotics have an additive effect on the reduction, a combination of a narcotic with hydrogen cyanide always shows less inhibition than the sum of the effects of the two substances separately, and not infrequently less than one alone. The curve relating inhibition to reduction of con-

centration of hydrogen cyanide is, unlike the oxygen respiration curve, a diphasic one, with a maximum at 0.05% and a new minimum at 0.5% potassium cyanide (neutralised). Reduction is lost after extraction of the muscle with water, but is restored again by muscle or yeast juice, or by succinic, fumaric, citric, glutamic, and α -glycerophosphoric acids; after partial extraction, it is restored to some extent by lactic acid, but never by maleic, glutaric, pyruvic, hydroxybutyric, or tartaric acid, or by glycerol, glyceric acid, dextrose, lævulose, or glycogen. In unextracted muscle reduction is accelerated by succinic and fumaric acids, but inhibited by maleic acid, also by saponin (cf. Hopkins, A., 1921, i, 635).

II. The musculatures of *Ascaris* and *Lumbricus* were studied as examples of facultative anærobic tissues. *Ascaris* reduced powerfully; the reduction was independent of intact cell structure, was thermolabile, dependent on the presence of co-ferment, not inhibited by oxygen, and never inhibited more than 30% by hydrogen cyanide, the curve being also not diphasic. *Lumbricus* reduced less powerfully, the reduction being dependent on intact cell structure, and being inhibited up to 80% by hydrogen cyanide (uniphasic). The reduction by *Bacillus proteus* and *B. butyricus* is also (incompletely) inhibited by potassium cyanide (0.25%). E. S.

Fixation of Calcium by Animal Tissues. IV and V. E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1921, **121**, 131—141, 142—149).—IV. Natural cartilage rich in sodium, swells better than cartilage artificially enriched with calcium or magnesium. In all three cases there is a minimum of swelling at P_H 4.7, the isoelectric point of the cartilage protein.

V. Calcium is only taken up by cartilage at concentrations above 0.01*N*. Tryptic and autolytic processes, or the presence of urea, and ammonium chloride inhibit its fixation. H. K.

I. The Composition of Chinese Edible Birds' Nests and the Nature of their Proteins. II. The Isolation and the Nature of the Amino-sugar of Chinese Edible Birds' Nests. CHI CHE WANG (*J. Biol. Chem.*, 1921, **49**, 429—439, 441—452).—The edible birds' nests contain a glucoprotein which is digested by both pepsin and trypsin. From the product of hydrolysis with hydrochloric acid a hexosamine hydrochloride was isolated which appears to be different from both glucosamine and chondrosamine hydrochlorides. It has $[\alpha]_D +70.6^\circ$ (equilibrium), the initial rotation depending on the method of crystallisation, and becomes black at 250° after darkening at a much lower temperature. With phenylhydrazine and acetic acid, it forms an osazone which melts at 214° with rapid heating, and at a considerably lower temperature after remaining over sulphuric acid. The birds' nests contain inadequate protein for the growth of rats. E. S.

Bioluminescence. XIV. The Specificity of Luciferin and Luciferase. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1921, **4**, 285—295).—The luciferin-luciferase reaction was obtained in a

few cases only out of a number of luminous organisms investigated. The luciferin of one species will not luminesce with the luciferase of another species unless closely related. Specificity is consequently indicated.
G. W. R.

The Identification of the Aldehyde-like Substance in the Urine of Diabetics as Acetaldehyde. W. STEPP and R. FEULGEN (*Z. physiol. Chem.*, 1921, **114**, 301—306).—The aldehyde-like substance in the urine of diabetic patients was concentrated by fractional distillation of the urine and was precipitated by dimethylcyclohexanedione as a substance of m. p. 138—140°. Comparison with ethyldenebisdimethylcyclohexanedione, prepared in similar manner from acetaldehyde, showed complete identity; it is therefore concluded that the volatile reducing substance found in the urine of some diabetics is acetaldehyde.
S. S. Z.

The Analytical Detection and Differentiation of Acetaldehyde, Aldol, Glyoxylic Acid, and their Presence in the Urine of Diabetic Patients. ROBERT FRICKE (*Z. physiol. Chem.*, 1921, **116**, 129—149).—Aldol forms a complex with "dimedon" [dimethyldihydroresorcinol] which can be differentiated from the analogous acetaldehyde complex by its insolubility in light petroleum. The presence of small quantities of crotonaldehyde was established in the urine in serious cases of diabetes. Furfuraldehyde and glyoxylic acid, on the other hand, were not found. The author confirms Stepp's observation concerning the presence of acetaldehyde in the urine of diabetic patients.
S. S. Z.

Excretion of Ammonia following Experimental Administration of Acids via the Stomach and Peripheral Vein. ROBERT W. KEETON (*J. Biol. Chem.*, 1921, **49**, 411—427).—Administration of hydrochloric acid to dogs by stomach tubes causes increased excretion of ammonia in the urine without affecting the total nitrogen excreted. If injected intravenously, however, there is an increased excretion both of ammonia and of total nitrogen.
E. S.

Creatine Formation in a Case of Progressive Pseudo-hypertrophic Muscular Dystrophy. R. B. GIBSON and FRANCES T. MARTIN (*J. Biol. Chem.*, 1921, **49**, 319—326).—In a case of this type ingested creatine was completely eliminated as creatine and creatinine, chiefly the former. The excretion of creatine and creatinine was increased by ingestion of protein and of glyco-cyamine, but was unaffected by sarcosine, asparagine, or cystine. The increase after administration of large amounts of protein was derived from the portion of the latter which was katabolised exogenously.
C. R. H.

First Results of the Treatment of Syphilis by Sodium *p*-Hydroxy-*m*-aminophenylarsinate or "189." L. FOURNIER, L. GUÉNOT, and A. SCHWARTZ (*Ann. Inst. Pasteur*, 1922, **36**, 53—62).—This salt, described by Fourneau (*ibid.*, 1921, **35**, 571) as No. 189, has a favourable action on human syphilis, although

it is not so powerful or constant in its results as salvarsan. It is relatively slightly toxic and is supported by patients who do not tolerate other arsenical preparations. G. B.

Treatment of Syphilis by Bismuth. L. FOURNIER and L. GUÉNOT (*Ann. Inst. Pasteur*, 1922, **36**, 14—33; cf. A., 1921, i, 908, and this vol., i, 89).—Sodium bismuthyl tartrate and other bismuth salts were administered, suspended in oil, by intramuscular injection (ten to twelve times 0.2—0.3 gram). Bismuth is an extremely powerful antisymphilitic agent; it is, however, apt to cause stomatitis. The bismuth is principally eliminated by the urine and, on keeping the latter, is deposited as sulphide as the result of a fermentative process. G. B.

The Distribution Coefficients of Diuretics and Narcotics and the Theory of Narcosis. GIUSEPPE AIELLO (*Biochem. Z.*, 1921, **124**, 192—205).—The distribution coefficients of caffeine, theobromine, ethoxycaine, and theophylline were determined between water and olive oil and between serum and olive oil. In each case the amount retained by serum is greater than that retained by water. The distribution coefficients of trional and sulphonal were determined between oil and serum. The failures of theories of narcosis is due to a lack of solvents exactly analogous to the tissue fluids concerned. H. K.

Pharmacological Action of Colloidal Arsenious Sulphide. E. MENEGHETTI (*Biochem. Z.*, 1921, **121**, 1—39).—Colloidal arsenious sulphide, in whatsoever way it is administered to rabbits, dogs, or guinea-pigs, changes its state of dispersion and becomes granular. When given intravenously, this may cause embolism of the lung capillaries, but if the animal survives, the after-effects are those of a metabolite, probably arsenious oxide. H. K.

The Behaviour of Inactive Malic Acid in the Organisms of the Dog and Rabbit. M. TOMITA (*Biochem. Z.*, 1921, **123**, 231—234).—Subcutaneous administration of *l*-malic acid to a rabbit resulted in the excretion of about 11% in the urine. When, however, the *dl*-malic acid was similarly administered to rabbits or dogs, the acid excreted was dextrorotatory. H. K.

Barium Compounds in the Viscera. K. KRAFFT (*Z. Unters. Nahr. Genussm.*, 1921, **42**, 390—391).—In a case of poisoning, a number of yellowish-white nodules were found adhering to the walls of the stomach. An analysis of these gave barium carbonate 64.7%, barium sulphate 35.3%. The quantity of barium remaining in the stomach was 0.2478 gram assuming equal distribution, but a large quantity had presumably been ejected by vomiting. Barium salts are converted into barium chloride in the stomach, with the exception of the insoluble barium sulphate. The minimum fatal dose of barium chloride is 0.09 gram per kilo of body-weight. H. C. R.

Protein Intoxication. F. PENTIMALLI. **I. Introduction** (*Riforma med.*, 1921, **37**, 532—536). **II. Toxicity of Egg-albumin and its Derivatives** (*Gazz. intern. med. chir. igiene*, 1921, **29**, 65—72). **III. Toxicity of Peptones** (*Rass. intern. clin. terap.*, 1921, **2**, 185—192). **IV. Toxicity of Milk and its Derivatives** (*La pediatria*, 1921, **29**, 481—494). **V. Behaviour of Blood Pressure and of Respiration** (*Folia med.*, 1921, **7**, 321—330). **VI. Behaviour of Body Temperature** (*Arch. sci. biol.*, 1921, **2**, 44—58). **VII. Nystagmus** (*Riforma med.*, 1921, **27**, 573—578). **VIII. Morphological Changes of the Blood** (*Hæmatologica*, 1921, **2**, 527—578). (From *Physiol. Abstr.*, 1922, **6**, 595—596.)—The physiological action of injections of proteins and protein products was studied under the various headings indicated in the titles. E. S.

Chemistry of Vegetable Physiology and Agriculture.

The Importance of Sequence in Biology. I. KARCZAG (*Biochem. Z.*, 1921, **122**, 43—51).—Provided the number of bacteria used is not too large, the author shows that the addition of chloroform or toluene, first, to a dextrose bouillon and subsequent addition of *Bacillus coli*, has a greater inhibiting influence than the addition of *B. coli* to a dextrose bouillon, first, and then addition of the antiseptic. In both cases there is inhibition compared with the control.

H. K.

The Importance of Sequence in Biology. II. L. KARCZAG and K. HAJÓS (*Biochem. Z.*, 1921, **122**, 52—57).—That the order of mixing the components is of influence, the authors show by a study of the systems (a) the antitryptic action of serum (trypsin+casein+serum), (b) the hæmolytic system (corpuscles+complement+hæmolysin), (c) the bacteriolytic action of immune serum on *Paratyphosus-B* (Pfeiffer's experiment).

H. K.

The Importance of the Amino-acids of Hæmoglobin for the Cultivation of the Influenza Bacilli. MARTIN JACOBY and KÁTE FRANKENTHAL (*Biochem. Z.*, 1921, **122**, 100—104).—The influenza bacillus can be caused to grow on agar if histidine be added. A less favourable growth is obtained on addition of leucine.

H. K.

The Degradation of *l*-Tryptophan by *Bacillus proteus*. TAKAOKI SASAKI and ICHIRO OTSUKA (*Biochem. Z.*, 1921, **121**, 167—170).—*l*-Tryptophan, in a suitable medium containing glycerol is converted by *B. proteus* into *l*-indole-lactic acid. The isolation of this acid is simplified by its quantitative precipitation by basic copper acetate solution.

H. K.

The Degradation of *dl*- α -Naphthylalanine by *Bacillus proteus*. TAKAOKI SASAKI and JIRO KINOSE (*Biochem. Z.*, 1921, **121**, 171—174).—Glycine anhydride when condensed with α -naphthaldehyde by Sasaki's reaction gives 2 : 5-diketo-3 : 6-dinaphthylidenepiperazine, unmolten at 320°. Reduction with hydriodic acid and red phosphorus leads to *dl*- α -naphthylalanine, m. p. 240°. On submitting the latter amino-acid to the action of *B. proteus*, *d*-naphthylalanine was isolated, m. p. 142° (corr.) and $[\alpha]_D +24.31^\circ$ in alcohol.
H. K.

The Bacterial Degradation of *l*-Leucine. MINORU ARAI (*Biochem. Z.*, 1921, **122**, 251—257).—*l*-Leucine submitted to *Proteus vulgaris* on a suitable medium gave the corresponding nitrogen-free *d*-hydroxy-acid, but *Bacillus subtilis* gave the lævo-acid. By varying the nutrient medium, *P. vulgaris* gave isoamylamine.
H. K.

Influence of the Hydrogen-ion Concentration on the Growth and Formation of Toxin of Tetanus Bacilli. K. G. DERNBY and B. ALLANDER (*Biochem. Z.*, 1921, **123**, 245—271).—Growth of tetanus bacilli takes place between P_H 5 and 8.5, the optimum range being between 7 and 7.6. The stability zone, however, of tetanus toxin is between P_H 5.8 and 8, the optimum range being 6.0 to 7.5. For large-scale preparation of tetanus toxin, the initial P_H should be 8 and when more acidity develops than P_H 6.8, fresh neutralisation is necessary.
H. K.

Microchemistry of a New Group of Purple Bacteria. JOS. GICKLHORN (*Ber. Deut. bot. Ges.*, 1921, **39**, 312—319).—Two new species of purple bacteria, namely, *Chromatium Linsbaueri* and *Rhabdochromatium Linsbaueri*, are shown to contain, in addition to sulphur, considerable quantities of amorphous calcium carbonate.
G. W. R.

The Oxidation of Sulphur by Soil Organisms. JACOB G. LIPMAN, SELMAN A. WAKSMAN, and JACOB S. JOFFE (*Soil. Sci.*, 1921, **12**, 475—490).—A study of the chemical changes occurring during the growth of *Thiobacillus thio-oxidans* in artificial media is reported. The hydrogen-ion concentration and titratable acidity of the medium increase with the age of the culture, as also does the amount of sulphate produced. There appears to be a period of marked activity after four and again after eight days. Sulphate production is followed by the conversion of insoluble into soluble phosphates; 94% of the total insoluble phosphate was rendered soluble in fifteen days, but no further increases occurred. Old cultures (one hundred and twenty days) were found to have P_H 0.8 and their acidity was 0.68*N*. Optimum growth of the organism occurs in media with P_H 2.8—2.0, although the organism can exist in a medium of P_H 0.58. Acidity less than that corresponding with P_H 5.6 is unfavourable. The possible uses of sulphur manuring to combat potato scab, to reclaim black alkali soils, and increase the availability of phosphates and potassium, are indicated.
A. G. P.

The Formation of Acetaldehyde and the Realisation of the Second Form of Fermentation with Various Fungi. CARL NEUBERG and CLARA COHEN (*Biochem. Z.*, 1921, **122**, 204—224).—A large number of micro-organisms can ferment dextrose with production of acetaldehyde and glycerol. The acetaldehyde was fixed by addition of sodium hydrogen sulphite or calcium sulphite. When the proportion of acetaldehyde was large, the production of an equivalent proportion of glycerol was demonstrated.
H. K.

A Biological Method for the Estimation of Substances which Injure the Cell and the Embryo. II. ALFRED SCHNABEL (*Biochem. Z.*, 1921, **122**, 295—300; cf. A., 1921, ii, 788).—A graphic modification of the author's previously described method for determining the concentration of substances which inhibit the methylene-blue reducing capacity of bacteria.
H. K.

Comparative Experiments on the Antiseptic Action of some Chloro-derivatives of Methane, Ethane, and Ethylene. GEORG JOACHIMOGLU (*Biochem. Z.*, 1921, **124**, 130—136).—The antiseptic action of aqueous solutions of chloro-derivatives of methane, ethane, and ethylene on *Vibrio Metschnikoff* falls off in the order hexachloroethane, tetrachloroethylene, pentachloroethane, tetrachloromethane, trichloroethylene, dichloroethylene, α -dichloroethane, tetrachloroethane, $\alpha\beta$ -dichloroethane, chloroform, dichloromethane.
H. K.

Bactericidal Action of Pyromucic Acid. H. P. KAUFMANN (*Ber.*, 1922, **55**, [B], 289—290).—Pyromucic acid in 0.5% and 1% solution kills *Bacillus coli* within five minutes, in 0.25% solution within thirty minutes, and in 0.1% solution within seven hours; development is arrested in 0.05% solutions. *Staphylococcus aureus* is rather more resistant to pyromucic acid. The salts of the latter have only slight bactericidal action. In its effect, pyromucic acid is very similar to benzoic acid, but the latter is much superior in practical application to products such as fruit and meat.
H. W.

Nature of Yeast Fats. IDA SMEDLEY MACLEAN (*Z. physiol. Chem.*, 1921, **113**, 199—200).—Polemical. A reply to Hinsberg and Roos (A., 1921, i, 148).
S. S. Z.

Yeast Gum and Saccharase. E. SALKOWSKI (*Z. physiol. Chem.*, 1921, **114**, 307—308).—A reply to Svanberg (A., 1921, i, 202). Saccharase is not always associated with gum in yeast.
S. S. Z.

The Nitrogenous Constituents of Yeast. II. The Purine Bases and the Diamino-acids. Results. JACOB MEISENHEIMER (*Z. physiol. Chem.*, 1921, **114**, 205—249).—Top and bottom fermentation yeasts show no marked differences in the composition of their products of degradation. Ammonia forms 8% of the total nitrogen. Twelve per cent. of the total nitrogen can be

accounted for in the purine and pyrimidine bases as follows: guanine 4%, adenine 4%, cytosine (?) 2.4%, and uracil (?) 1.6%. Ten per cent. is present as histidine and arginine, and 10% as lysine. Of the 60% of the total nitrogen found to be associated with the monoamino-acids, 0.5% was traced to glycine, 10–15% to alanine, 10–15% to valine, 5–10% to leucine, 2% to proline, 8% to phenylalanine, 3.5% to aspartic acid, 6% to glutamic acid, 2% to tyrosine, 0.5% to tryptophan, 2% to cystine and other sulphur compounds, 4.5% to oxyproline (?), 0.5% to choline, and 0.5% to glucosamine. The ratio of amino- to nonamino-nitrogen as obtained by Van Slyke's method was always found to be lower than the figures calculated from the above data. S. S. Z.

The Nitrogenous Constituents of Yeast. MARTIN SCHENCK (*Z. physiol. Chem.*, 1921, **116**, 308–309).—Polemical, in reply to Meisenheimer (A., 1919, i, 370; preceding abstract). S. S. Z.

Carboligase. II. CARL NEUBERG and LUDWIG LIEBERMANN (*Biochem. Z.*, 1921, **121**, 311–325; cf. A., 1921, i, 480).—*o*-Chlorobenzaldehyde was added to yeast undergoing fermentation. *o*-Chlorobenzyl alcohol and *o*-chlorobenzoic acid were isolated. The enzyme carboligase causes a condensation of another portion of the aldehyde with acetaldehyde with formation of the ketone-alcohol, $C_6H_4Cl \cdot CH(OH) \cdot COMe$, which exhibits optical activity but gives an inactive *p*-nitrophenylosazone, m. p. 302–303°, *thio-semicarbazone*, m. p. 216–218°. Anisaldehyde reacts less smoothly. The *p*-nitrophenylosazone of the corresponding ketone-alcohol was isolated, m. p. 266°. The ketone alcohols will be described later.

H. K.

The Thermostability of the Co-enzyme and its Separation from Vitamin-B from Yeast. TH. THOLIN (*Z. physiol. Chem.*, 1921, **115**, 235–256).—One half of the co-enzyme of alcoholic fermentation is destroyed by heating at 96° for one hour, or at 100° for thirty-seven minutes at P_H 5.6. The vitamins from yeast and cabbage which accelerate alcoholic fermentation differ in their thermostability from the co-enzyme and are therefore not identical with it. It is thus possible to separate the two substances.

S. S. Z.

The Dismutation of Various Aldehydes by Yeast. H. KUMAGAWA (*Biochem. Z.*, 1921, **123**, 225–230).—*iso*Valeraldehyde, *isobutaldehyde*, heptaldehyde, and benzaldehyde when submitted to the action of yeast in a 1% sodium hydrogen carbonate solution undergo the Cannizzaro reaction and yield the corresponding acids and alcohols. The proportion of the alcohol is usually somewhat greater than that of the acid, owing to a simultaneous phytochemical reduction of the original aldehyde.

H. K.

The Course of Alcoholic Fermentation in Presence of Calcium Carbonate. JOHANNES KERB and KURT ZECKENDORF (*Biochem. Z.*, 1921, **122**, 307–314).—The authors are unable to confirm the experiments of Fernbach and Schoen (A., 1920, i, 406)

on the production of considerable quantities of pyruvic acid by fermentation in presence of calcium carbonate. Its production in Fernbach and Schoen's experiments must be as a by-product due to oxidation of lactic acid by use of an atypical yeast.

H. K.

Pyruvic Acid as an Intermediary in the Alcoholic Fission of Dextrose. MAX VON GRAB (*Biochem. Z.*, 1921, **123**, 69—89).—Apart from the experiments of Fernbach and Schoen (*A.*, 1920, i, 406) with an atypical yeast, pyruvic acid has never been isolated as an intermediate product in a typical yeast fermentation. By use of a new fixative, β -naphthylamine, the author has isolated the condensation product of pyruvic acid and β -naphthylamine—namely, α -methyl- β -naphthacinchoninic acid—from the interaction of press juice and dextrose.

H. K.

The Enzymic Synthesis of Fructosediphosphate (Hexose-phosphate). HANS V. EULER and FOLKE NORDLUND (*Z. physiol. Chem.*, 1921, **116**, 229—244).—The optimum H-ion concentration for the formation of fructose diphosphate by a bottom fermentation yeast was found to be P_H 6.2—6.6. This reaction is about the optimum for all sugars; levulose, however, showed a somewhat different reaction curve.

S. S. Z.

Maltase. IV. The Fermenting Activity of Yeasts Poor in Maltase. RICHARD WILLSTÄTTER and WERNER STEIBELT (*Z. physiol. Chem.*, 1921, **115**, 211—234; cf. this vol., i, 282).—The approximate figure for the quotient (time value for maltase/time value for saccharase) for brewer's yeasts was found to be 20. The time values for saccharase in the brewer's yeast strains did not show great variations; on the other hand, those in some of the distiller's yeast strains differed within very wide limits, as also did the time values for maltase in the different strains. The fermenting capacity of the various yeasts was studied. From the observations made it was concluded that maltose can also be fermented without being previously hydrolysed, as the hydrolysis by some strains proceeded much more slowly than the actual fermentation by those strains. No dextrose could be established in the fermenting medium when the fermentation of maltose carried out with maltase-free yeasts was interrupted.

S. S. Z.

The Action of Salts on the Bleaching of Methylene-blue by Various Species of Yeast. H. KUMAGAWA (*Biochem. Z.*, 1921, **121**, 150—163).—The reducing capacity of various species of yeast for methylene-blue is very variable. Metallic salts inhibit or retard the reduction, but not invariably. The somewhat anomalous results are attributed to the influence of the physiological state of the yeast-cells at the moment of the experiment.

H. K.

New Classes of Stimulants of Alcoholic Sugar-fission. VII. CARL NEUBERG, ELSA REINFURTH, and MARTA SANDBERG (*Biochem. Z.*, 1921, **121**, 215—234).—A large number of purine derivatives have been tested and found without exception to have a stimulating

effect on the process of cell-free fermentation of dextrose by means of yeast press juice. The nucleosides adenosine and guanosine were also beneficial and the nucleic acids to a lesser extent. Degradation products of purines had a distinctly favourable influence. The authors hesitate to class the above substances as hydrogen acceptors. H. K.

The Action of Silver Compounds on Yeast. ERNEST ZERNER and ROBERT HAMBURGER (*Biochem. Z.*, 1921, **122**, 315—318).—Silver nitrate, chloride, and carbonate have a toxic action on yeast. H. K.

Nature of Alcoholic Fermentation. C. C. WARDEN (*Amer. J. Physiol.*, 1921, **57**, 454—469; from *Physiol. Abstr.*, 1922, **6**, 600).—The conclusion is drawn from experiments described, more especially as to the effect of the addition of surfaces of various kinds, that alcoholic fermentation is a catalytic process occurring at the surface of yeast-cells, on the colloidal surfaces of yeast juice, and at artificial surfaces composed of fat complexes similar to those found in yeast-cells. Further, it is held that the enzyme of yeast belongs to the cellular antigens. Interesting considerations as to the nature of enzyme action on anti- and co-enzymes will be found in the paper. E. S.

The Decomposition of *d*-Galactose according to the Second Mode of Fermentation. M. TOMITA (*Biochem. Z.*, 1921, **121**, 164—166).—*d*-Galactose, like *d*-glucose, *d*-mannose, and *d*-fructose, when fermented in the presence of disodium sulphite gives an equimolecular proportion of acetaldehyde and glycerol. H. K.

Fermentation without Yeast. A. BAU (*Biochem. Z.*, 1921, **122**, 303—306).—A criticism of the claims of Baur and Herzfeld (*A.*, 1922, i, 93). H. K.

Photosynthesis and the Functions of Pigments in the Living Plant. E. C. C. BALY (*J. Soc. Dyers and Col.*, 1922, **38**, 4—9).—The author deals with photochemical reactions, and, in particular, the conversion of carbon dioxide and water into formaldehyde and oxygen as the first step in the synthetic growth of the vegetable organism. In the laboratory, the oxygen tends to oxidise the formaldehyde to formic acid, but in the living plant it is quantitatively evolved as oxygen. Suggestions as to the mechanism whereby gaseous oxygen is transpired are outlined. F. M. R.

Photosynthesis. I. The Ratio of Carbon Dioxide to Oxygen in Carbon Assimilation. S. KOSTYTSHEV (*Ber. Deut. bot. Ges.*, 1921, **39**, 319—328).—The ratio CO_2/O_2 may depart from unity in the case of leaves exposed to artificial atmospheres containing abnormally large amounts of carbon dioxide. The assimilation of carbon dioxide is at first in excess of the oxygen liberated, but after a short time this relation is reversed. Eventually the ratio becomes normal. Similar results are obtained with algae. It is unlikely that under normal conditions variations

in the ratio of carbon dioxide absorbed to oxygen liberated occur. Assimilation should be measured by the amount of carbon dioxide absorbed, and not by the amount of oxygen liberated. G. W. R.

Photosynthesis. II. Does Injury Stimulate Photosynthesis? S. KOSTYTSHEV (*Ber. Deut. bot. Ges.*, 1921, 39, 328—333).—Injury to leaves was found to be without any stimulating effect on carbon assimilation. A slight depression of assimilation observed was attributed to restriction of the assimilating area consequent on the method of experiment. G. W. R.

Photosynthesis. III. Does Carbon Assimilation take place during Summer Night in Subarctic Regions? S. KOSTYTSHEV (*Ber. Deut. bot. Ges.*, 1921, 39, 334—338).—Carbon assimilation generally ceases at sunset, even although the twilight in latitude 60° N. furnishes sufficient light for the process to go on. This may be due to the effect of the fall in temperature in closing the stomata. A certain amount of carbon assimilation was found to take place after sunset in the case of coniferous trees. G. W. R.

The Chemical Constitution of Protoplasm. HEINRICH WALTER (*Biochem. Z.*, 1921, 122, 86—99).—The protoplasm of myxomycetes behaves like that of the higher plants. When extracted from the cells with absolute alcohol, ether, and chloroform, it is only partly digested by pepsin, but completely by trypsin. The plasma consists of a phospho-protein-like substance, plastin, which is digested by trypsin, and a lipid component. H. K.

Direct and Indirect Determinations of Permeability. W. J. V. OSTERHOUT (*J. Gen. Physiol.*, 1921, 4, 275—283).—A method is described for determining the electrical conductivity of the cell sap of a species of *Nitella*. The results obtained by tests of the sap isolated from cells show that, whilst in pure sodium nitrate solution rapid penetration of the nitrate ion takes place accompanied by injury to the cell, in the case of a balanced solution of calcium nitrate and sodium nitrate penetration is slow and the cell remains uninjured. Direct evidence was obtained for the supposition that both penetration and also recovery from plasmolysis are more rapid in the case of injurious solutions than in the case of non-toxic solutions. G. W. R.

Penetration of Kations into Living Cells. MATILDA MOLDENHAUER BROOKS (*J. Gen. Physiol.*, 1921, 4, 347—349).—The permeability of the protoplasm of a species of *Nitella* was investigated by examination of the cell sap. The protoplasm is normally permeable to lithium, caesium, and strontium ions, penetration being more rapid in unbalanced than in balanced solutions. G. W. R.

The Permeability of Plant-plasma for Neutral Salts. IV. HUGO KAHHO (*Biochem. Z.*, 1921, 123, 284—303; cf. A., 1922, i, 94).—Micrometer observations were made on the first root of yellow

lupin (1 to 1.5 cm. long) when placed in isotonic salt solutions, which were, however, hypertonic to the plant plasma. The initial contraction is followed by a relatively slower and smaller expansion. This latter is used as a measure of the penetrability of various salts. The permeability of the ions follows the sequence $\text{NO}_3, \text{I}, \text{Br} > \text{Cl} > \text{tartrate} > \text{SO}_4 > \text{citrate}$ and $\text{K} > \text{Na} > \text{Li} > \text{Mg} > \text{Ba} > \text{Ca}$. Moreover, the permeability of an ion is inhibited by a second ion the further it lies to the right in this series. The results accord with the view that the toxicity of neutral salts stands in close relation to the permeability of plasma for these salts.

H. K.

The Green Respiratory Pigment and its Importance in the Oxidation of Protein Substances in the Sprouting Seeds of *Helianthus annuus*. ALEXANDER OPARIN (*Biochem. Z.*, 1921, 124, 90—96).—Gorter's chlorogenic acid absorbs two molecules of oxygen in alkaline solution. Analysis points to a removal of four atoms of hydrogen by the oxygen. This formation of a green oxidation product is accelerated twenty-fold by addition of phenolase from sunflower seeds. Experiments were carried out on the oxidation of amino-acids, peptides, and proteins in the presence of chlorogenic acid, use being chiefly made of the Van Slyke methods of analysis. The results are held to support the view that the amino-acids and proteins become oxidised with liberation of ammonia. In the living plant, the latter is used for the synthesis of asparagine and glutamine.

H. K.

Effect of Transpiration on the Disappearance of Starch from Leaves. HANS MOLISCH (*Ber. Deut. bot. Ges.*, 1921, 39, 339—344).—The disappearance of starch from leaves placed in darkness is more rapid in a dry than in a moist atmosphere. Leaves kept in a moist atmosphere, although little of their starch had been altered, contained more reducing sugars than leaves kept in a dry atmosphere which had lost all their starch. It is supposed that substances other than sugars, probably dextrins and similar substances, are formed from the decomposition of starch. It is not necessary to assume translocation, as the starch reaction disappears even in stalkless leaves.

G. W. R.

The Oxalic Acid Content of Early Spring Leaves, and some Observations concerning this Acid. A. BAU (*Z. tech. Biol.*, 1921, 8, 151—155; from *Physiol. Abstr.*, 1922, 6, 599).—Oxalic acid was found in the young leaves of elder, hawthorn, and horse-chestnut, and in those of young barley plants.

E. S.

The Manganese Content of Flowers. D. H. WESTER (*Pharm. Weekblad*, 1922, 59, 51—55).—Various carefully selected flowers were gathered from dry dust-free localities in dry weather, and transferred at once to closed tared flasks. Moisture, ash, and manganese were determined in the samples. The average moisture content was between 80 and 90% (minimum 75.6, maximum 94.5%). Ash averaged 1% (minimum 0.31%, maximum 1.93%). All species examined contained manganese, varying from 11.2 to 222.1 mg.

per 100 grams of ash, but no regularity was observed in its distribution between families. Only small differences were observed between individuals of the same species plucked at different times and places.

S. I. L.

The Occurrence of Calcium Oxalate in the Gidgee Wattle (*Acacia cambagei*, Baker). THOS. STEEL (*Chem. News*, 1921, **123**, 315—316).—Both the outer and inner bark of *A. cambagei* contain 18.82% of calcium oxalate, calculated as $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ on the dry weight, whilst the outer white wood contains 5.81% and the inner dark wood 3.81%. Samples of bark from other species of *Acacia* contained amounts varying from 1.36 to 8.92% of the oxalate.

W. G.

Chemical Constituents of a Chinese Drug "Hsiung Ch'uang." I. YOSHIHARU MURAYAMA (*J. Pharm. Soc. Japan*, 1921, No. 477, 951—959).—From a Chinese drug "Hsiung Ch'uang" or "Ch'uang Hsiang," the dried root of *Cnidium officinale*, Makino, Sakai (*Tokyo Igakukai Zasshi*, 1916, 935) isolated a phenol; an ester, $\text{C}_{22}\text{H}_{36}\text{O}_3$ (which when saponified gave cnidic acid, $\text{C}_{12}\text{H}_{20}\text{O}_3$, and an alcohol, $\text{C}_{10}\text{H}_{18}\text{O}$), and cnidiolactone, $\text{C}_{12}\text{H}_{18}\text{O}_2$, b. p. 177—178°/15 mm. By distilling the powdered drug with steam and extracting with ether, the author has obtained a brownish-yellow, viscous oil of characteristic odour, from which *cnidiolactone*, $\text{C}_{12}\text{H}_{18}\text{O}_2$, was separated as an oil, b. p. 178—180°/13 mm., d 1.047, α_D -65.0°, n_D^{17} 1.5061. By reduction with sodium and alcohol, followed by treatment with 1% potassium permanganate, the lactone gave a compound, $\text{C}_{12}\text{H}_{22}\text{O}_3$, crystallising in white needles, m. p. 50°, which seems to be *dihydrocnidic acid*. By reduction with hydrogen in the presence of platinum black, the lactone gave *cnidic acid*, $\text{OH} \cdot \text{C}_{11}\text{H}_{18} \cdot \text{CO}_2\text{H}$, m. p. 87°, which is unstable and is readily converted into the dihydro-acid. When oxidised with potassium permanganate, the lactone yields phthalic and valeric acids, and therefore would appear to be an isomeride of the lactone, sedanolide, obtained by Ciamician and Silber from oil of celery (A., 1897, i, 484).

K. K.

The Chemical Constituents of Green Plants. XIV. The Acids in the Currant (*Ribes rubrum*) which are Precipitated by Lead Acetate. HARTWIG FRANZEN and EUGEN SCHUMACHER (*Z. physiol. Chem.*, 1921, **115**, 9—37).—The currant contains large quantities of citric acid, and small amounts of malic acid. The former is about forty-seven times the amount of the latter. Tartaric acid is only present as traces. Acids which yield esters with a higher boiling point than triethyl citrate and are precipitated by lead acetate, are also present in very small amounts.

S. S. Z.

The Chemical Constituents of Plants. XVII The Presence of Lactic Acid in the Leaves of the Blackberry (*Rubus fruticosus*). HARTWIG FRANZAN and ERNST KEYSSNER (*Z. physiol. Chem.*, 1921, **116**, 166—168).—The presence of lactic acid was established in the leaves of the blackberry.

S. S. Z.

The Chemical Constituents of Green Plants. XV. The Presence of Lactic Acid in the Leaves of the Raspberry (*Rubus idæus*). HARTWIG FRANZEN and EMMI HERN (*Z. physiol. Chem.*, 1921, **115**, 270—283).—The leaves of the raspberry contain lactic acid. The presence of lactic acid was also established in the opium poppy (*Papaver somniferum*), germinated castor oil seed (*Ricinus communis*), and in the leaves of *Agave Sisalana*.

S. S. Z.

I. Culture Experiments with Soja Beans. II. Occurrence of Urease in Parts of the Plant Other than the Seeds. D. H. WESTER (*Biochem. Z.*, 1921, **122**, 188—192).—Attempts to cultivate soja beans in Holland were unsuccessful. Urease was found in various portions of the plant other than the seeds.

H. K.

Botanical Chemical Observations. EDMUND O. VON LIPPMANN (*Ber.*, 1921, **54**, 3111—3114).—In an isolated case, mannose has been obtained from the fruit of *Symphoricarpus racemosus*; subsequent attempts to repeat the isolation led invariably to the production of dextrose.

A lemon-yellow deposit on the leaves of the ordinary white anemone, collected after a protracted spell of warm weather, was identified as calcium succinate.

The roots of the ordinary reed, collected in early summer, generally contained about 1—3% of sucrose, but occasionally 3—3.5%. This figure is somewhat lower than that recorded recently by Sabalitschka for roots collected in November.

A voluminous black powder found in the hollow of a felled oak became spontaneously heated when spread in a thin layer in bright sunlight, and then contained a considerable proportion of mellitic acid, which, however, was not present in the original specimen.

H. W.

Application of the Biochemical Method for Characterising Dextrose to the Fruits of *Viburnum opulus* and to Extracts of Red *Cinchona* and of Cola. R. ARNOLD (*Bull. Soc. Chim. Biol.*, 1921, **3**, 547—566).—The principle of the method is the synthetic action of emulsin on a solution of dextrose in 50% methyl alcohol, measured by a fall in the reducing power; in all the cases referred to, β -methylglucoside was obtained crystalline. If reducing substances other than sugar are present, it is not enough to extract the material simply with boiling alcohol. The extract must then be purified by basic lead acetate, and impurities must be extracted with wet boiling ethyl acetate. The sugars are then extracted by boiling 95% alcohol. In most fruit, about half the reducing sugar is dextrose, that is, it contains invert-sugar. In extract of Cola nuts only 21.7% of the reducing substances is dextrose, but after hydrolysis by acid it is 48.8%.

G. B.

The Toxic Action of Heavy-metal Salts on Plant Plasma. III. HUGO KAHHO (*Biochem. Z.*, 1921, **122**, 39—42; cf. this vol., i, 94).—The toxicity of various kations of the heavy metals

on plant plasma was investigated. The order followed is approximately that of the electrolytic solution pressure of these kations. Zincion is the most noticeable exception, its toxicity approaching that of copper.

H. K.

The Influence of certain Factors on the Chemical Composition of Sauerkraut. O. R. BRUNKOW, W. H. PETERSON, and E. B. FRED (*J. Amer. Chem. Soc.*, 1921, **43**, 2244—2255).—Inoculation with certain organisms produced a better grade of sauerkraut than is produced by a natural fermentation, but the only organism consistently better than the control was *Bacillus lactis acidi*. The presence of a large number of yeasts may result in a red kraut with undesirable flavour. The concentration of salt in the brine is of importance. The best kraut was obtained when 2% of salt was used, and with concentrations above 3% the kraut was tough and too salt.

The chief products in the fermentation of kraut are lactic acid, acetic acid, and ethyl alcohol. Mannitol may also be produced in varying amounts, depending on the type of organisms present. The relative amounts of these various products can be influenced by inoculation.

W. G.

The Diastatic Action of Malt and its Preparations (Liquid, Syrupy, and Dried Extracts). RAOUL LECOQ (*J. Pharm. Chim.*, 1922, **25**, 18—25).—The diastatic action of malt is practically limited to the temperature range 60—90°. The activity is greatest between 70° and 80°, with an optimum at about 75°. Mixed in sufficient quantity, namely, about 30%, with cooked or uncooked barley flour, saccharification takes place with an approximately corresponding velocity in the temperature range 60—80°, and likewise with an optimum at 75°. The activity of malt itself is three to four times greater than that of any of the extracts prepared commercially from it. The latter consist largely of maltose, the diastase being to a great extent destroyed in the process of manufacture.

G. F. M.

The Sulphur-oxidising Power of Soils. A. DEMOLON (*Compt. rend.*, 1921, **173**, 1408—1410; cf. A., 1912, ii, 382; 1913, i, 579).—By growth on sand cultures containing free sulphur admixed with the sand, oxidation of the sulphur to sulphate by bacterial extracts from soils was obtained. Soils vary considerably in their sulphur-oxidising power, garden soils rich in organic matter giving the best results. The presence of calcium carbonate is only necessary if there is insufficient carbamide present to supply the ammonia necessary to keep the medium neutral. The ammonifying organisms in the soil are apparently responsible for sulphur oxidation, and the property is not bacteriologically specific.

W. G.

Organic Chemistry.

The Composition of Paraffin Wax. I. FRANCIS FRANCIS [with JOHN CLIFFORD POPE and REGINALD HENRY COYSH] (*T.*, 1922, **121**, 496—513).

Synthesis of Trimethylethylmethane [$\beta\beta$ -Dimethylbutane]. (Mlle.) H. VAN RISSEGHEN (*Bull. Soc. chim. Belg.*, 1922, **31**, 62—66; cf. van Risseghem, A., 1921, i, 489, and Markownikow, A., 1899, i, 554).—The preparation of $\beta\beta$ -dimethylbutane from pinacone is carried out by transforming it into pinacolin, which is then treated with phosphorus pentachloride. The resulting product is a mixture of $\beta\beta$ -dichloro- $\gamma\gamma$ -dimethylbutane, a solid, and the unsaturated derivative, $\text{CMe}_3\cdot\text{CCl}\cdot\text{CH}_2$, a liquid. The latter is heated with potassium hydroxide in sealed tubes and the product, dimethylbutinene, distilled off. This is treated with hydrogen in presence of platinum black, the resulting hexane is washed, dried over calcium chloride, and distilled.

The following physical constants have been determined: $\beta\beta$ -dimethylbutane, m. p. -98.2° , d_4^{20} 0.6678, d_4^{15} 0.6538, $n_{\text{H}_a}^{15}$ 1.36972, n_{D}^{15} 1.37158, $n_{\text{H}_\beta}^{15}$ 1.37615, $n_{\text{H}_\gamma}^{15}$ 1.37964; isohexane, $n_{\text{H}_a}^{15}$ 1.37257, n_{D}^{15} 1.37445, $n_{\text{H}_\beta}^{15}$ 1.37914, $n_{\text{H}_\gamma}^{15}$ 1.38251; γ -methylpentane, $n_{\text{H}_a}^{15}$ 1.37753, n_{D}^{15} 1.37929, $n_{\text{H}_\beta}^{15}$ 1.38404, $n_{\text{H}_\gamma}^{15}$ 1.38740; $\beta\gamma$ -dimethylbutane, $n_{\text{H}_a}^{15}$ 1.37905, n_{D}^{15} 1.38092, $n_{\text{H}_\beta}^{15}$ 1.38540, $n_{\text{H}_\gamma}^{15}$ 1.38893; dimethylbutinene, m. p. -81.2° , d_4^{20} 0.6899, d_4^{15} 0.6737, $n_{\text{H}_a}^{15}$ 1.37518, n_{D}^{15} 1.37725, $n_{\text{H}_\beta}^{15}$ 1.38313.

H. J. E.

Tetrapropylethane [$\delta\epsilon$ -Dipropyloctane]. JEAN PICCARD and RAY Q. BREWSTER (*J. Amer. Chem. Soc.*, 1921, **43**, 2626—2629).—When butyrene is reduced with metallic sodium in the presence of a little ether, the products are δ -hydroxyheptane and some $\delta\epsilon$ -dipropyloctane- $\delta\epsilon$ -diol. The hydroxyheptane gives, with phosphorus and iodine, δ -iodoheptane, and this, when treated with sodium in absolute ether, gives *s*-tetrapropylethane [$\delta\epsilon$ -dipropyloctane], $\text{CHPr}_2\cdot\text{CHPr}_2$, b. p. $105\text{--}106^\circ/12\text{ mm.}$, or $220^\circ/760\text{ mm.}$; d^{25} 0.7735; n^{25} 1.4322; surface tension 25.64 dynes/cm. An identical dipropyloctane was obtained by heating the dipropyloctanediol with concentrated hydriodic acid in a sealed tube at 180° for ten hours.

W. G.

Action of Polyhalogenated Compounds of Methane and Ethane on Magnesyl [Magnesium Alkyl] Compounds. B. ODDO and R. BINAGHI (*Gazzetta*, 1921, **51**, ii, 330—337).—The action of iodoform on magnesium phenyl bromide yields principally tetraphenylethane, together with iodobenzene, formed from the intermediate α -iododiphenylmethane, and diphenyl.

The products of the interaction of iodoform and magnesium ethyl bromide are acetylene, ethane, methane, ethyl bromide and

iodide, traces of methyl iodide and di-iodomethane, and an unknown compound with an acute odour recalling that of marine algæ.
T. H. P.

Symmetrical Di-iodoethylenes. G. LATIERS (*Bull. Soc. chim. Belg.*, 1922, **31**, 73—84; cf. Chavanne and Vos, A., 1914, i, 796).—A study from the kinetic point of view of the spontaneous transformation of the two stereoisomeric di-iodoethylenes into each other until equilibrium is reached.
H. J. E.

New Synthesis of Primary Alcohols, and Constitution of Hydrogen Peroxide. B. ODDO and R. BINAGHI (*Gazzetta*, 1921, **51**, ii, 343—348).—When cooled in a mixture of ice and salt, hydrogen peroxide solution and magnesium alkyl haloids interact with formation of primary alcohols: $\text{CH}_2\text{R}\cdot\text{MgX} + \text{H}_2\text{O}_2 = \text{CH}_2\text{R}\cdot\text{OH} + \text{MgX}\cdot\text{OH}$; the decomposition of the magnesium complex by the water present in the peroxide in accordance with the equation $\text{CH}_2\text{R}\cdot\text{MgX} + \text{H}_2\text{O} = \text{MgX}\cdot\text{OH} + \text{R}\cdot\text{CH}_3$, takes place only slowly. The formation of alcohol is not direct, but results from the decomposition of an intermediate additive compound which forms characteristic, yellowish-white globules and floats on the ethereal solution.

These results are discussed in relation to the possible constitutions for hydrogen peroxide, and it is considered probable that the reaction is represented by the equations: $\text{O}:\text{OH}\cdot\text{H} + \text{MgRX} \rightarrow \text{H}\cdot\text{OHR}\cdot\text{OMgX} + \text{H}_2\text{O} \rightarrow \text{MgX}\cdot\text{OH} + \text{H}_2\text{O} + \text{R}\cdot\text{OH}$, these being analogous to the action of a magnesium alkyl haloid on formaldehyde: $\text{O}:\text{CH}\cdot\text{H} + \text{MgRX} \rightarrow \text{H}\cdot\text{CHR}\cdot\text{OMgX} + \text{H}_2\text{O} \rightarrow \text{MgX}\cdot\text{OH} + \text{R}\cdot\text{CH}_2\cdot\text{OH}$.

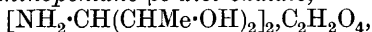
This reaction has been applied to the synthesis of ethyl, isobutyl, and isoamyl alcohols, good yields being obtained.
T. H. P.

Nitro- and Amino-glycols. II. ERICH SCHMIDT and RUDOLF WILKENDORF (*Ber.*, 1922, **55**, [B], 316—322; cf. A., 1919, i, 249).—The preparation of γ -nitro- and γ -amino-pentane- $\beta\delta$ -diols and a new preparation of β -nitrotrimethylene glycol are described.

β -Chloro- β -nitropropane- $\alpha\gamma$ -diol, m. p. 115—116° after previous softening, is obtained by passing a current of dry chlorine through a suspension of sodium β -nitrotrimethylene glycol in anhydrous ether; the corresponding dibenzoate has m. p. 114—115°. The chloronitro-glycol is converted by hydrogen in aqueous solution in the presence of pyridine and palladised barium sulphate into β -nitrotrimethylene glycol (Schmidt and Wilkendorf, *loc. cit.*).

An alcoholic solution of α -nitropropane- β -ol is converted by sodium dissolved in ethyl alcohol into α -nitro- α -sodiumpropane- β -ol, $\text{CH}_3\cdot\text{CH}(\text{OH})\cdot\text{CHNa}\cdot\text{NO}_2$, which is transformed by chlorine in the presence of anhydrous ether into α -chloro- α -nitropropane- β -ol, a colourless liquid, b. p. 91—92°/11 mm. The latter condenses with acetaldehyde in alkaline solution, giving γ -chloro- γ -nitropentane- $\beta\delta$ -diol, $\text{OH}\cdot\text{CHMe}\cdot\text{CCl}(\text{NO}_2)\cdot\text{CHMe}\cdot\text{OH}$, needles, m. p. 118—119°, b. p. 109—112°/0.2 mm. (corresponding dibenzoate, m. p. 115—116°), which is converted by hydrogen and palladised

barium sulphate in aqueous pyridine solution into γ -nitropentane- $\beta\delta$ -diol, m. p. 68—69° after previous softening, b. p. 109—110°/0.8 mm. The nitropentanediol is reduced by hydrogen in aqueous solution and in the presence of oxalic acid and palladised barium sulphate into γ -aminopentane- $\beta\delta$ -diol oxalate,



decomp. 178—179°.

H. W.

Chemical Composition and Physiological Characters of Brain Cephalin. FREDERIC FENGER (*J. Pharm. Expt. Ther.*, 1921, **18**, 51—62).—Cephalin is used as a hæmostatic because it accelerates blood-clotting; this activity is retained practically unchanged for several years in ethereal solution; in the solid condition, moderately pure cephalin is more stable than the highly purified substance. Both the solubility of cephalin in water and its thromboplastic properties depend on the presence of sodium and potassium soaps of the fatty acids constituting the phosphatide.

G. B.

Chloropicrin as a Reagent for the Diagnosis of Mercaptans and Potential Mercaptans. SIR PRAFULLA CHANDRA RÂY and RADHAKISHEN DAS (*T.*, 1921, **121**, 323—328).

The Practice of Precipitation with Lead. HEDWIG LANG-ECKER (*Biochem. Z.*, 1921, **122**, 34—38).—Preparations of basic lead acetate were made by mixing lead acetate and litharge in various molecular proportions and treating the mixture with hot water. The maximum amount of litharge which can be taken up is three molecules. Schmidt's pentabasic lead acetate could not be realised. The solubility of the basic lead acetate falls off with increasing content of lead oxide.

H. K.

Preparation of Chlorinated Acetyl Chlorides. CONSORTIUM FÜR ELEKTROCHEMISCHE INDUSTRIE (D.R.-P. 340872; from *Chem. Zentr.*, 1921, iv, 1101).—Chlorine substitution products of ethylene are treated with oxygen or gases containing oxygen in the presence of non-metals or their compounds as catalysts. Bromine or bromine compounds may be used. The oxidation of trichloroethylene, dichloroethylene, and perchloroethylene, which are themselves nonreactive with oxygen, is facilitated by the presence of small amounts of bromine, nitrogen, or sulphur compounds. Trichloroethylene is oxidised to dichloroacetyl chloride by oxygen in the presence of bromine, iodine, concentrated sulphuric acid, or concentrated nitric acid. Dichloroethylene may be similarly oxidised to chloroacetyl chloride. Perchloroethylene chloride is oxidised in the presence of bromine to trichloroacetyl chloride.

G. W. R.

Esters of Ethylene Halohydrins. J. ALTWEGG and J. LANDRIVON (U.S. Pat. 1393191).—Chloroethyl acetate is prepared by passing gaseous ethylene oxide into boiling acetyl chloride in equimolecular proportion, with immediate and quantitative yield of a product, b. p. 143—144°. Chloroethyl chloroacetate (b. p.

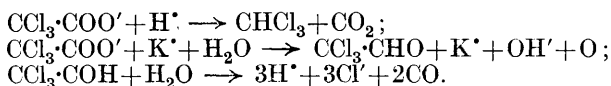
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94—95°) is similarly prepared by the action of ethylene oxide on chloroacetyl chloride at 100°. Bromoethyl acetate is prepared by interaction for several hours of ethylene oxide with acetyl bromide at normal temperature and distillation. Chloroethyl benzoate is prepared by passing an equimolecular proportion of ethylene oxide slowly into benzoyl chloride at 190°, with further rise of temperature, followed by fractional distillation in a vacuum. Chloroethyl *p*-nitrobenzoate is obtained by treating *p*-nitrobenzoyl chloride with ethylene oxide and recrystallising from dilute alcohol.

CHEMICAL ABSTRACTS.

The Action of Ultra-violet Light on Aqueous Solutions of some Organic Acids and their Salts. F. M. JAEGER and G. BERGER (*Rec. trav. chim.*, 1922, **41**, 71—81).—It has been shown (Jaeger, A., 1912, i, 3) that the action of ultra-violet light on trichloroacetic acid to which ferric hydroxide has been added results in the formation of carbon dioxide and hexachloroethane. The authors have now established the fact that, in presence of excess of ferric hydroxide, a different reaction takes place, the products being carbon dioxide and chloroform. Further, if the acid is electrolysed in concentrated aqueous solution, its trichloromethyl ester is formed, together with carbonyl chloride and hydrochloric acid; this ester can be decomposed in presence of catalysts into carbon dioxide and hexachloroethane. A similar investigation of ferric tribromoacetate and pentachloropropionate has been carried out, the products obtained being carbon dioxide with bromoform and tetrachloroethylene respectively. In the case of potassium tribromoacetate, the solution gradually becomes acid under the influence of light, the reaction in dilute solution being represented by: $\text{CBr}_3\cdot\text{COO}' + \text{H}_2\text{O} + \text{K}^* \rightarrow 2\text{H}^* + \text{K}^* + 3\text{Br}' + \text{CO} + \text{CO}_2$. In concentrated solution, a secondary reaction $\text{CBr}_3\cdot\text{COO}' + \text{H}^* \rightarrow \text{CHBr}_3 + \text{CO}_2$ takes place simultaneously but a corresponding solution of the ferric salt yields hexabromoethane, the equation being $2\text{CBr}_3\cdot\text{COO}' + 2\text{Fe}''' \rightarrow \text{C}_2\text{Br}_6 + 2\text{Fe}'' + 2\text{CO}_2$, whilst the free acid is decomposed into bromoform and carbon dioxide.

Potassium trichloroacetate gives more complex results, probably due to the simultaneous occurrence of several different reactions. In fairly dilute solution, a small quantity of free carbon dioxide is formed, but in concentrated solution, carbon monoxide is obtained. For each molecule of the latter, two chlorine atoms are liberated and can be shown to exist in the ionic condition, but the ratio does not remain constant with prolonged exposure to light. Further, chloral is formed under certain conditions and possibly a little free oxygen also. The equations suggested are:



The corresponding decompositions of monochloroacetic and dichloroacetic acids have been studied by Benrath (A., 1911, ii, 681) and by Euler and Cassel (A., 1913, ii, 939); their results are compared

with the decomposition of potassium trichloroacetate, from which the authors obtained dichloroacetaldehyde: $\text{CCl}_3\cdot\text{CH}(\text{OH})\cdot\text{COO}' + \text{K}' \rightarrow \text{CHCl}_2\cdot\text{COH} + \text{CO}_2 + \text{K}' + \text{Cl}'$. Three other substances have also been investigated: sodium chloromalonate, after two days, yields monochloroacetic acid which is partly transformed into glycollic and glyoxylic acids. The latter is probably formed directly from the monochloroacetic acid and not by oxidation of glycollic acid. Potassium α -bromophenylacetate yields bromine ions and benzaldehyde, the latter being obtained, according to the authors, together with formic acid, from the decomposition of mandelic acid, which is the primary product. Triphenylacetic acid, dissolved in a mixture of alcohol and water, yields carbon dioxide and a considerable quantity of triphenylmethane; with more concentrated solutions, the latter is partly replaced by triphenylcarbinol. The conclusion is drawn that the products of the photochemical decomposition of these ions in aqueous solution depend on the character of the other ions that may be present. The effect is seldom the same as that produced by heating the solution, and is scarcely comparable to the effects of electrolysis. The suggestion is made that the specific absorption of the solutions varies with the other ions that may be present and that this accounts for the different results obtained from the various salts of the same acid.

H. J. E.

The Acids of Montan Wax. HANS TROPSCH and A. KREUTZER (*Brennstoff Chem.*, 1922, **3**, 49).—The crude montanic acid, which has hitherto been regarded as the only acid present in montan wax and to which the formulæ $\text{C}_{28}\text{H}_{56}\text{O}_2$ and $\text{C}_{29}\text{H}_{58}\text{O}_2$ have variously been ascribed, was esterified with methyl alcohol, and the resulting ester was separated into two fractions, boiling at $265\text{--}267.5^\circ/5$ mm. and $277.5\text{--}280^\circ/5$ mm., respectively. From each fraction the acid was again isolated and purified by fractional precipitation with magnesium acetate and recrystallisation from acetic acid. The acids obtained had equivalent weights 410.7 and 439.0, and m. p. 82° and $86\text{--}86.5^\circ$, respectively, and it is therefore concluded that the former is an acid of the formula $\text{C}_{27}\text{H}_{54}\text{O}_2$ for which the name *carbocerinic acid* is suggested, and the latter is pure montanic acid of the formula $\text{C}_{29}\text{H}_{58}\text{O}_2$.

G. F. M.

Erucic Acid and its Anhydride. D. HOLDE and C. WILKE (*Z. angew. Chem.*, 1922, **35**, 105).—Erucic acid, which has hitherto never been obtained free from arachic and other saturated fatty acids, was isolated in a pure condition by fractional precipitation of the partly purified acid with lithium acetate. The product obtained had an iodine value of 74.3 compared with 75.1 required by theory, and this figure affords the best criterion for the purity of the substance, as other constants, such as the melting point, are but little affected by the presence of moderate amounts of impurities. The anhydride was obtained by heating the acid under pressure with acetic anhydride and purifying the product by recrystallisation from absolute alcohol. It has m. p. $46\text{--}46.5^\circ$,

is very resistant to *N*/10-aqueous alkali hydroxide and 25% hydrochloric acid, but is completely reconverted into erucic acid by boiling water. G. F. M.

The Action of Halogens on Ethyl Acetoacetate. L. I. SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 216—217).—When bromine is passed into ethyl acetoacetate by a rapid current of air which both introduces the bromine and sweeps out the hydrogen bromide as it is formed, the sole product is the α -bromo-ester. Thus under similar conditions the action of bromine on ethyl acetoacetate is similar to that of chlorine. W. G.

The C₄-Saccharinic Acids. II. The Preparation and Resolution of *dl*- $\alpha\gamma$ -Dihydroxybutyric Acid. Some Derivatives of the Optically Active Acids. J. W. E. GLATTFELD and FRANK V. SANDER (*J. Amer. Chem. Soc.*, 1921, **43**, 2675—2682; cf. A., 1921, i, 7).—*dl*- $\alpha\gamma$ -Dihydroxybutyric acid was prepared from β -hydroxypropionaldehyde by the addition of hydrogen cyanide and subsequent hydrolysis of the nitrile. It was resolved into its active components by means of brucine, and certain of the salts of the active acids were prepared. The configuration of the *l*- and *d*-acids are shown by oxidation to the corresponding malic acids to be respectively $\text{H}\cdot\text{C}\begin{smallmatrix} \text{OH} & \text{H} & \text{OH} \\ | & | & | \end{smallmatrix}\text{—C—C}\cdot\text{CO}_2\text{H}$ and $\text{HC}\begin{smallmatrix} \text{OH} & \text{H} & \text{H} \\ | & | & | \end{smallmatrix}\text{—C—C}\cdot\text{CO}_2\text{H}$.
 $\text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{OH}$

The *d*-acid has $[\alpha]_D^{20} + 14.97^\circ$, b. p. $96^\circ/3$ mm.; brucine salt, m. p. 169° ; $[\alpha]_D^{20} - 20.79^\circ$; quinine salt, m. p. 149° ; $[\alpha]_D^{20} - 106.4^\circ$; calcium salt, $[\alpha]_D^{20} + 17.08^\circ$. The *l*-acid has $[\alpha]_D^{20} - 14.86^\circ$; b. p. $96^\circ/3$ mm.; brucine salt, m. p. 169° ; $[\alpha]_D^{20} - 32.67^\circ$; quinine salt, m. p. 149° ; $[\alpha]_D^{20} - 122.9^\circ$; calcium salt, $[\alpha]_D^{20} - 17.33^\circ$. W. G.

The Aldehyde Acids of the Succinic Series. E. CARRIÈRE (*Ann. Chim.*, 1922, **17**, 38—132).—In part, a more detailed account of work already published (cf. A., 1912, i, 410, 827; 1914, i, 806), with descriptions of new derivatives. Ethyl formylsuccinate gives a semicarbazone, m. p. 126° , a *p*-nitrophenylhydrazone, m. p. 100° , and a benzoyl derivative, m. p. $58\text{—}59^\circ$, b. p. $208\text{—}212^\circ/14$ mm. (cf. Wislicenus, Böklen, and Reuthe, A., 1909, i, 9). With aniline, it yields *ethyl anilinoitaconate*, m. p. 102° , which undergoes cyclisation in the presence of alcoholic potassium hydroxide, giving *ethyl 1-phenylpyrroline-5-one-3-carboxylate*, $\text{NPh} \begin{smallmatrix} < \text{CH} \cdot \text{C} \cdot \text{CO}_2\text{Et} \\ | \\ \text{CO} \cdot \text{CH}_2 \end{smallmatrix}$.

Similarly, with *p*-toluidine, *ethyl toluidinoitaconate*, m. p. 113° , is obtained, and this on cyclisation yields *ethyl 1-p-tolylpyrroline-5-one-3-carboxylate*, m. p. $123\text{—}124^\circ$, which on saponification yields *p*-toluidine, sodium formate, and sodium succinate. With benzylamine, the products are *ethyl benzylaminoitaconate*, m. p. 54° , and *ethyl 1-benzylaminopyrroline-5-one-3-carboxylate*, m. p. 95° .

Ethyl formylsuccinate gives an *oxime*, which on distillation yields a mixture of *ethyl- β -cyanopropionate*, b. p. $114\text{—}115^\circ/18$ mm., and an *oxime*, m. p. 155° , of β -aldehydopropionic acid, isomeric with the one previously described (*loc. cit.*).

Ethylsuccinic acid when warmed with acetyl chloride gives an anhydride, b. p. $140^{\circ}/20$ mm., which gives a monoanilide, m. p. 118° , a dianilide, m. p. 205° , and an acid chloride, b. p. $94-95^{\circ}/14$ mm., of ethylsuccinic acid. The monoanilide when heated at 180° for one and a half hours yields the anil, $\begin{array}{c} \text{CHEt}\cdot\text{CO} \\ | \\ \text{CH}_2-\text{CO} \end{array} > \text{NPh}$, m. p. 74° .

Derivatives prepared from ethyl formylethylsuccinate are its semicarbazone, m. p. 113° ; its p-nitrophenylhydrazone, m. p. 113° ; its phenylurethane, b. p. $220^{\circ}/14$ mm. With phenylhydrazine, it yields ethyl 1-phenyl-5-ethylpyridazine-6-one-5-carboxylate, $\text{N} \begin{array}{c} \text{CH}\cdot\text{CH}(\text{CO}_2\text{Et}) \\ | \\ \text{NPh} \end{array} \text{CO} > \text{CHEt}$, b. p. $225-240^{\circ}/15$ mm., which on saponification gives the free acid, m. p. 179° . With aniline, ethyl formylethylsuccinate yields ethyl anilinoethylitaconate, which on saponification gives 1-phenyl-4-ethylpyrrolidine-5-one-3-carboxylic acid, $\text{NPh} \begin{array}{c} \text{CH}\cdot\text{C}\cdot\text{CO}_2\text{H} \\ | \\ \text{CO}\cdot\text{CHEt} \end{array}$, m. p. 190° , giving an ethyl ester, m. p. 99° . Similarly, ethyl p-toluidinoethylitaconate gives 1-p-tolyl-4-ethylpyrrolidine-5-one-3-carboxylic acid, m. p. 202° , giving an ethyl ester, m. p. 104° .

Thionyl chloride or phosphorus pentachloride reacts with β -aldehydopropionic acid to give chlorobutyrolactone, $\text{CH}_2 \begin{array}{c} \text{CH}_2 \\ | \\ \text{CO}\cdot\text{O} \end{array} > \text{CHCl}$, b. p. $101^{\circ}/15$ mm., which with absolute alcohol gives the acetal, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OEt})_2$.

With pyruvic acid and β -naphthylamine, the ester of β -aldehydopropionic acid gives ethyl naphthacinchoninylpropionate, m. p. 268° . With magnesium ethyl bromide, the aldehyde acid yields γ -ethyl- γ -octandiol, $\text{HO}\cdot\text{CEt}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHEt}\cdot\text{OH}$, m. p. 41° , b. p. $148^{\circ}/20$ mm., giving a monoacetate, b. p. $146-147^{\circ}/18$ mm. In the distillation of the diol, a small amount of material passes over at $80-90^{\circ}/20$ mm., and if this is boiled with 10% sulphuric acid the oxide, $\begin{array}{c} \text{CH}_2\cdot\text{CHEt} \\ | \\ \text{CH}_2-\text{CEt}_2 \end{array} > \text{O}$, b. p. $68-69^{\circ}/18$ mm., is obtained. The diol gives a diphenylurethane, m. p. 121° .

Ethyl β -aldehydopropionate condenses with ethyl malonate in the presence of diethylamine to give triethyl β -carboxymethylbutan- α -dicarboxylate, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}(\text{CH}_2\cdot\text{CO}_2\text{Et})_2$, b. p. $200^{\circ}/15$ mm., which on saponification yields the free acid, m. p. 122° . The acid, when heated on a water-bath with acetyl chloride, gives the anhydride, $\text{CO}_2\text{H}\cdot[\text{CH}_2]_2\cdot\text{CH} \begin{array}{c} \text{CH}_2\cdot\text{CO} \\ | \\ \text{CH}_2\cdot\text{CO} \end{array} > \text{O}$, m. p. 133° , from which a monoanilide, m. p. 151° , and a mono-p-toluidide, m. p. 207° , can be prepared. When β -aldehydopropionic acid, freshly prepared, is condensed with malonic acid in the presence of pyridine, adipenic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}_2\text{H}$, m. p. $208-210^{\circ}$, is obtained.

The acetal of β -aldehydopropionic acid (see above) reacts with magnesium ethyl bromide, giving 5-ethoxy-2:2-diethyltetrahydrofurfuran, $\begin{array}{c} \text{CH}_2-\text{CEt}_2 \\ | \\ \text{CH}_2\cdot\text{CH}(\text{OEt}) \end{array} > \text{O}$, b. p. $69^{\circ}/12$ mm., and γ -diethyloctan-

γ -diol, b. p. $154^{\circ}/12$ mm. (cf. Valeur, A., 1901, i, 317), from which the oxide, $\begin{matrix} \text{CH}_2 \cdot \text{CET}_2 \\ \text{CH}_2 \cdot \text{CET}_2 \end{matrix} > \text{O}$, b. p. $95-96^{\circ}/14$ mm., is obtained by the action of sulphuric acid. For the purpose of proving the identity of the previous diol, γ -ethylhexane- γ -diol, $\text{HO} \cdot \text{CET}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, b. p. $144-145^{\circ}/20$ mm., was prepared by the action of magnesium ethyl bromide on butyrolactone. It gives a *monoacetate*, and a *diphenylurethane*, m. p. 106° .

α -Ethyl- β -aldehydopropionic acid is prepared by hydrolysing ethyl formylethylsuccinate with oxalic acid in aqueous solution. The following derivatives are described: *semicarbazone*, m. p. 156° ; *p-nitrophenylhydrazone*, m. p. 164° ; *oxime*, m. p. 70° ; α -ethyl- β -naphthacinchoninylpropionic acid, m. p. 260° ; a *phenylhydrazide-phenylhydrazone*, $\text{NHPh} \cdot \text{N} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CHEt} \cdot \text{CO} \cdot \text{NH} \cdot \text{NHPh}$, m. p. 175° ; and an *ethyl ester*, b. p. $103-104^{\circ}/20$ mm., which gives a *semicarbazone* and a *p-nitrophenylhydrazone*. During the preparation of the ester, *ethoxybutyrolactone*, b. p. $114-115^{\circ}/20$ mm., is also obtained.

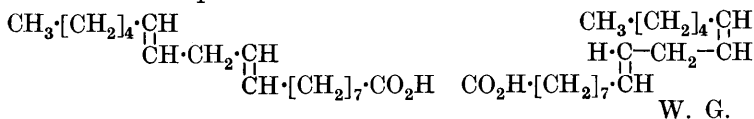
W. G.

The Rotatory Dispersive Power of Organic Compounds. X. The Preparation and Properties of Pure Ethyl Tartrate. THOMAS MARTIN LOWRY and JOHN OUTRAM CUTTER (T., 1922, **121**, 532-544).

Optical Activation of Racemic Acid by *l*-Malic Acid. ALEX. MCKENZIE and NELLIE WALKER (T., 1922, **121**, 349-357).

C_{18} -Acids. III. Four Tetrahydroxystearic Acids derived from Linoleic Acid, and their Significance with Regard to the Linoleic Acid of Common Oils. BEN H. NICOLET and HENRY L. COX (*J. Amer. Chem. Soc.*, 1922, **44**, 144-152; cf. A., 1921, i, 390; this vol., i, 106).—The linoleic acid used in this work was regenerated from the tetrabromide, m. p. 114° , itself prepared from the dried fatty acids of cotton-seed oil. The oxidation of the acid with cold alkaline permanganate yielded two sativic (tetrahydroxystearic) acids, namely, α -sativic acid, m. p. 153° , and β -sativic acid, m. p. 170° (cf. Rollet, A., 1909, i, 759, 760). When linoleic acid was treated with hypochlorous or hypobromous acid and the products were subsequently converted into sativic acids, two other isomerides were obtained. With hypochlorous acid, linoleic acid yielded *dichlorodihydroxystearic acid* as a viscous oil. Similarly, with hypobromous acid the product was *dibromodihydroxystearic acid*, an oil. Either of these compounds when heated with anhydrous potassium acetate and acetic anhydride gave *tetra-acetoxystearic acid*, which on hydrolysis with hot aqueous sodium hydroxide gave a mixture of γ -sativic acid, m. p. 144.5° , and δ -sativic acid, m. p. 135° . In the light of the above facts and the difference in behaviour between linoleic acid and oleic or elaidic acid on bromination and subsequent removal of the bromine by zinc, the authors are of the opinion that only two of the four possible stereoisomeric linoleic acids occur, at least in important

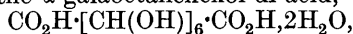
amounts, in linoleic acid as usually prepared. The most probable structures for this pair of isomerides are shown below.



W. G.

Chemistry of the Sugars. III. H. KILIANI (*Ber.*, 1922, 55, [B], 493—505; cf. A., 1921, i, 304; this vol., i, 223).—The lengthening of the carbon chain of aldoses by the hydrocyanic method has hitherto been possible at only one end of the chain. The comparatively ready accessibility of *l*-mannohepturonic acid has now rendered it possible to lengthen the other end.

[With AUG. WINGLER.]—The lactone of *l*-mannohepturonic acid is converted by hydrocyanic acid and ammonia in aqueous solution into the salt, $\text{NH}_2 \cdot \text{CO} \cdot [\text{CH}(\text{OH})]_6 \cdot \text{CO}_2 \cdot \text{NH}_4$, microscopic leaflets, m. p. about 192° (decomp.) after darkening at about 180° , the yield being about 60% of that theoretically possible. The product is hydrolysed by boiling *N*/2-potassium hydroxide solution, thus giving the *potassium* salt, $\text{CO}_2\text{K} \cdot [\text{CH}(\text{OH})]_6 \cdot \text{CO}_2\text{K} \cdot \text{H}_2\text{O}$, microscopic, lustrous leaflets, from which the following salts are obtained by double decomposition: *calcium* salt (+3.5H₂O), which is almost insoluble in water; *zinc* salt (+2H₂O), microscopic granules; *cadmium* salt (+5H₂O); *lead* salt, anhydrous granules; normal *quinine* salt (+3H₂O), small, lustrous needles, m. p. 201° ; normal *brucine* salt (+9H₂O), m. p. (anhydrous) 170 — 171° (decomp.). The calcium salt is transformed by the calculated quantity of oxalic acid into the α -galaoctanehexol-di-acid,



well-defined, prismatic plates, decomp. 200° after darkening at about 190° . The corresponding *monolactone* is most readily prepared by decomposing the lead salt with hydrogen sulphide in the presence of water and evaporation of the filtrate at 60 — 70° ; it crystallises in microscopic prisms without definite melting point. The *dilactone*, short prisms, decomp. 200° , which dissolve sparingly

in water, is obtained by dissolving the calcium salt in warm dilute hydrochloric acid and concentrating the solution at 55° ; it does not reduce Fehling's solution. From its mode of production, two configurations are possible for the dibasic acid for which, by reason of its optical inactivity, the annexed symmetrical formula is adopted. Drastic reduction of the dicarboxylic acid by means of hydriodic acid should lead to the formation of sebacic acid, which, up to the present, has not been thus isolated, an amorphous, apparently unsaturated, acid being obtained in its place.

The dilactone gives a *diphenylhydrazide*, $\text{C}_{20}\text{H}_{26}\text{O}_8\text{N}_4$, colourless, microscopic leaflets, m. p. 285 — 286° , after becoming discoloured at 250° .

[With AUG. WINGLER.]—The following derivatives of *l*-manno-*m*⁴:

hepturonic acid have been prepared: *phenylhydrazone-phenylhydrazide*, $C_{19}H_{24}O_6N_4$, colourless, microscopic leaflets, m. p. 199° (from the lactone of *l*-mannohepturonic acid and four molecular proportions of phenylhydrazine in aqueous acetic acid solution at the atmospheric temperature); *phenylosazone-phenylhydrazide*, $C_{25}H_{28}O_5N_6$, yellow needles, m. p. $203\text{--}204^\circ$ (from the same mixture as used for the preceding compound, but in boiling solution); *p*-nitrophenylhydrazone, long, intensely yellow, coarse needles, m. p. 167° (decomp.) when rapidly heated; *semicarbazone*, microscopic crystals, m. p. $174\text{--}175^\circ$ (decomp.).

l-Mannohepturonic acid behaves as an aldose towards iodine and sodium hydroxide solution; it is interesting to note that ketonic sugars which contain a terminal methyl group adjacent to $CH(OH)$ or CO appear to react similarly (cf. the production of iodoform from lactic or *l*ævulinic acid).

Polyhydroxy-acids are converted into their lactones with very varying degrees of readiness; many examples are quoted and discussed, but it does not seem possible at present to give a satisfactory explanation of the observed facts.

β -Galaheptonic acid is oxidised by nitric acid to the monolactone of β -*galaheptanepentoldi-acid*, well-defined crystals which darken between 145° and 180° without actually melting. It could not be converted into a di-lactone. The salts of the corresponding dibasic acid appear to have little tendency towards crystallisation.

It is considered that Bergmann's recently proposed definition of a sugar (this vol., i, 227) lays too great emphasis on osazone formation, and it is pointed out that, according to it, ordinary sucrose would no longer be regarded as a sugar. H. W.

Mutarotation of Dextrose under the Influence of Sodium Chloride. HANS MURSCHHAUSER (*Biochem. Z.*, 1921, **125**, 158—178).—Addition of pure sodium chloride to dextrose solution undergoing mutarotation causes an increase of the velocity of mutarotation inversely proportional to the increase of concentration of the salt. Impurities in sodium chloride influence the velocity constant considerably. Ordinary cooking salt almost doubles the constant, whilst a fused, analytically pure sodium chloride showed an eight-fold increase due to development of alkali. H. K.

The Influence of Sodium Chloride on the Mutarotation of Dextrose in Hydrochloric Acid Solution. I. HANS MURSCHHAUSER (*Biochem. Z.*, 1921, **126**, 40—54).—In decinormal hydrochloric acid solution, the velocity constants for the mutarotation of dextrose show an increase proportional to the concentration of sodium chloride in the solution. H. K.

The Influence of Dextrose on the Dialysis of Sucrose through a Parchment Membrane. The Possibility of the Separation of Dextrose from Sucrose by Dialysis. LEON A. CONGDON and HARRY R. INGERSOLL (*J. Amer. Chem. Soc.*, 1921, **43**, 2588—2597).—In mixtures of dextrose and sucrose, the

influence of dextrose on the dialysis of sucrose is of such a character as to keep the ratio of the percentage of original dextrose to percentage of original sucrose dialysed approximately constant at about 2.5 : 1, irrespective of the concentration of the sucrose, provided that the concentration of the dextrose is not less than 2% and the time of dialysis has exceeded three hours. In solutions containing less than 2% of dextrose, the dextrose dialyses at a much greater rate and at a dextrose concentration of 0.125% the above ratio becomes 5 : 1. With such a dilute solution of dextrose containing 6.25% of sucrose it was found that the whole of the dextrose was removed after fifty-one hours' dialysis. W. G.

An Improved Method for Preparing Raffinose. E. P. CLARK (*J. Amer. Chem. Soc.*, 1922, **44**, 210—213; cf. Hudson and Harding, A., 1914, i, 1166).—In this improved method the cotton-seed meal is extracted by percolation, which must be done quickly. The extract is purified by treatment with basic lead acetate and the excess of lead is removed by the addition of oxalic acid. The sugar is then thrown out of solution as the insoluble calcium raffinosate. To regenerate the raffinose, this compound is decomposed with carbon dioxide as in the manufacture of sucrose. The resulting solution is evaporated under diminished pressure until it contains 70—75% of total solids and then the raffinose is caused to crystallise out by the addition of alcohol. A simple stirring device for the rapid and convenient carbonation of the raffinosate is described. W. G.

Xylan. E. SALKOWSKI (*Z. physiol. Chem.*, 1921, **117**, 48—60).—Improvements in the author's method of preparation of xylan (A., 1902, i, 293) are described. The formula, $C_{10}H_{18}O_9$, previously given to xylan, is replaced by $C_5H_8O_4$. On hydrolysis, xylan takes up one molecule of water and is converted into xylose. A factor is introduced for calculating xylose from the cuprous oxide obtained on heating with Fehling's solution. S. S. Z.

Sulphur in Agar. CARL NEUBERG and HEINZ OHLE (*Biochem. Z.*, 1921, **125**, 311—313).—Preliminary observations pointing to the existence of sulphur in organic combination in agar. Hydrogen sulphide is evolved by bacterial action and hydrolysis sets free sulphuric acid. H. K.

The Change of Glycogen under the Influence of Light. GUSTAV BAYER (*Biochem. Z.*, 1921, **124**, 97—99).—Glycogen exposed to sunlight becomes insoluble in water. From its reactions the author considers this to be due either to a polymerisation or to a physical alteration of the surface of the glycogen whereby the hydrophilic sol-forming surface layers are transformed into a dehydrated form which can no longer show imbibition. H. K.

Cellulose Acetate from Wood Cellulose. ERIK HAGGLUND, NILS LÖFMANN, and EDUARD FÄRBER (*Cellulosechemie*, 1922, **3**, 13—19).—Cellulose extracted from sawdust by the action of 40% hydrochloric acid is not a suitable material for the preparation of

cellulose acetate. With sulphite wood pulp, satisfactory products can be obtained after a suitable preliminary treatment. Dehydration of the cellulose by heating with acetic acid and acetic anhydride is unfavourable to the acetylation process; traces of water are favourable. The best products were obtained by the following procedure: 5 grams of sulphite cellulose are subjected to a preliminary treatment with 20 grams of acetic acid (100%), 0.5 gram of water, and 0.5 gram of sodium hydrogen sulphate at 50—70° for seventeen hours; 25 grams of acetic anhydride are added to the cooled mixture, the temperature not being allowed to rise above 60°. When the cellulose has dissolved, the reaction is completed by warming at 70° for about half an hour; 5.5—6 c.c. of water are then added and the viscous solution is digested at 50° for sixty-five to seventy hours in order to obtain a cellulose acetate which is soluble in acetone and insoluble in chloroform. J. F. B.

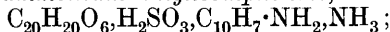
The Solubility of Cellulose Acetate in the Salts of the Alkali- and Alkaline-earth Metals. K. SCHWEIGER (*Z. physiol. Chem.*, 1921, 117, 61—66).—The solubility of various preparations of cellulose acetate in concentrated solutions of a number of the above salts is given. With concentrated salt solutions, there is no scission of the acetyl groups, but the cellulose molecule is degraded.

S. S. Z.

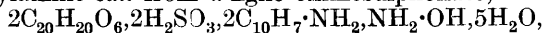
Constitution of Pine Lignin. II. PETER KLASON (*Ber.*, 1922, 55, [B], 448—455).—It has been shown previously that α -lignin, $C_{22}H_{22}O_7$, is the main constituent of pine wood. Since it contains an acetyl group which is eliminated as acetic acid during the sulphite treatment, the residue, $C_{20}H_{20}O_6$, must be present in α -lignosulphonic acid. The homogeneity of calcium α -lignosulphonate is established by the uniformity of the specimens of the β -naphthylamine salt obtained from it by fractional precipitation with β -naphthylamine hydrochloride. In course of time the sulphite liquors deposit gypsum and darken in colour and then give a β -naphthylamine salt containing a less sulphur content than is normal, thus confirming the author's view that the presence of calcium inhibits the formation of free lignosulphonic acid during the boiling process and that the occurrence of the latter is the cause of the so-called "black boiling." The following salts have been prepared: α -naphthylamine α -lignosulphonate,



a yellowish-white precipitate which, in contrast to the β -naphthylamine derivative, is not a cyclic compound; β -naphthylamine α -methylignosulphonate, $C_{31}H_{31}O_8NS$, an internal salt; β -naphthylamine salt from ammonium α -lignosulphonate,



β -naphthylamine salt from α -ligno-oximesulphonate,

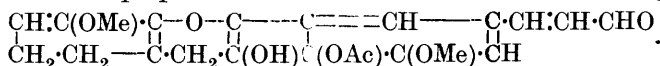


and the corresponding semicarbazide compound,



the composition of which indicates that the acid, at any rate in its salt, has double the molecular weight ascribed to it previously.

α -Lignosulphonic acid is oxidised by hydrogen peroxide at the atmospheric temperature, and the product is precipitated as the α -naphthylamine salt, $C_{40}H_{38}O_{11}N_3S$, the composition of which indicates that the aldehydic has become oxidised to the carboxyl group and a methylene to the ketonic group. β -Naphthylamine α -lignosulphonate can be acetylated by means of acetic anhydride, two acetyl groups being introduced thereby into the molecule, thus proving the presence of two hydroxyl groups one of which can be methylated, and is therefore united to the benzenoid nucleus, whereas the other is more positive in character and is hence attached to a more aliphatic group. These observations, coupled with the behaviour of α -lignosulphonic acid towards hydrogen peroxide, lead the author to propose the annexed modified formula for α -lignin :



H. W.

Lignin. I and II. KARL H. A. MELANDER (*Cellulosechemie*, 1921, 2, 41—43, 69—73; cf. A., 1921, i, 849).—Among the products obtained by the addition of sodium chloride to waste sulphite liquors is the sodium salt of an α -ligninsulphonic acid. One hundred grams of the crude product, containing about 27% of sodium chloride, yield about 25 grams of the free acid; the sodium salt contains 2.96—3.78% Na and 4.41—5.10% S. The acid is precipitated by aromatic bases, the *o*-toluidine salt being particularly examined. Analysis gave results which indicated formulæ varying from $C_{31}H_{34}O_{10}$ to $C_{34}H_{44}O_{11}$ for lignin; the latter substance was shown to contain an acetyl group. The products analysed were, however, admittedly mixtures.

CHEMICAL ABSTRACTS.

Methylation of Lignin. E. HEUSER, R. SCHMITT, and L. GUNKEL (*Cellulosechemie*, 1921, 2, 81—86).—Lignin obtained by the action of hydrochloric acid (*d* 1.2) on sawdust, when treated with methyl sulphate and sodium hydroxide, gave 96% of *methyl-lignin* (methoxyl content, 20.65%, increasing by repeated methylation to 26.29%). The methoxyl content is completely removed only by repeated treatment with hydrochloric acid in a sealed tube, when a product is obtained containing 67.45—69.30% C and 4.16—4.50% H. Methyl-lignin prepared from this substance contained only 5.79% of methoxyl. A sodium hydroxide solution of lignin, prepared at 170° in an autoclave, when methylated with methyl sulphate had a methoxyl content of 24.7%.

CHEMICAL ABSTRACTS.

Derivatives of Straw Lignin. F. PASCHKE (*Cellulosechemie*, 1922, 3, 19—21; cf. A., 1921, i, 772).—Derivatives have been prepared from lignin obtained by the digestion of straw with sodium carbonate and having a composition corresponding with $C_{40}H_{45}O_{13}$. With phenylhydrazine, on heating, a violent reaction takes place and formation of aniline, water, and ammonia. The yield of ligninphenylhydrazone, $C_{58}H_{57}N_6O_{10}$, is 80%; it is soluble in alcohol, acetone, and tetrachloroethane, the solutions drying in

the form of a brown varnish film. With nitrosodimethylaniline (1 part), lignin (1.5 parts), concentrated hydrochloric acid (1 part), and acetic acid (50 parts), on boiling for two hours, a condensation product is obtained having the properties of a dyestuff, *lignocyanin*, $C_{104}H_{101}N_{16}O_{26}$, analogous to gallocyanin and dyeing silk directly from dilute acetic acid solutions, cotton only when mordanted; the colour is brownish-violet. By the prolonged action of sulphuryl chloride at the ordinary temperature, a product containing 12.22% of chlorine and 11.04% of sulphur is obtained; with sulphuryl chloride at 100° under pressure, the resulting product contains 38.22% of chlorine and no sulphur; both products are free from methoxyl groups; the solutions of the latter dry as a varnish. With phosphorus pentachloride dissolved in excess of tetrachloroethane, lignin reacts violently with formation of a compound containing 19.18% of chlorine, corresponding with the formula $C_{38}H_{46}O_{15}Cl_5$. This compound also gives solutions which dry to a varnish.

J. F. B.

Synthesis of the Humic Acids. WILHELM ELLER (*Brennstoff Chem.*, 1922, **3**, 49—52 and 55—56; cf. A., 1920, i, 733).—Polemical. The author maintains that the humic acids contain a benzene nucleus, are closely related to the substances prepared by him by the oxidation of phenols in alkaline solution, and are not derivatives of furan as suggested by Marcussen (A., 1921, i, 313; ii, 590) and by Jonas.

G. F. M.

Natural and Artificial Humic Acids. K. G. JONAS (*Brennstoff Chem.*, 1922, **3**, 52—55).—Polemical. The author contends that Eller's synthetic products do not resemble the naturally occurring humic acids.

G. F. M.

Complex Metallic Ammines. VII. Conductivities of Diethylenediaminecobaltic Bromides. JAMES COOPER DUFF (T., 1922, **121**, 450—454).

Constitution of Glutamine. H. THIERFELDER (*Z. physiol. Chem.*, 1921, **114**, 192—198; cf. Johnson and Guest, A., 1912, i, 316).—1-Acetyl-2-thiohydantoin-5-propionamide prepared from *d*-glutamine and potassium thiocyanate has m. p. 209° and on hydrolysis yields 2-thiohydantoin-5-propionic acid. The latter compound on treatment with chloroacetic acid was converted into hydantoin-5-propionic acid. Owing to this reaction, which is characteristic of the α -amino-acids, the author ascribes the following formula to glutamine: $NH_2 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH(NH_2) \cdot CO_2H$.

S. S. Z.

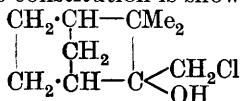
Cystine. ALICE R. THOMPSON MERRILL (*J. Amer. Chem. Soc.*, 1921, **43**, 2688—2696).—In the preparation of cystine from wool by hydrolysis with hydrochloric acid, the yield is materially increased by boiling for twelve hours instead of three. The zone of hydrogen-ion concentration most favourable for the precipitation of the cystine from the resulting solution is 10^{-3} to 10^{-6} , and in order to obtain the cystine free from tyrosine it is advisable to precipitate it from a solution having a concentration of about 10^{-3} .

Using sodium acetate as a buffer in the hydrolysed wool solution, it was found that when the maximum yield of cystine was obtained the hydrogen-ion concentration was 10^{-4} . The highest yield of cystine thus obtained was 5.2% of the weight of the wool taken. For the purification of crude cystine, its solution may be decolorised by norit which has been previously boiled with dilute hydrochloric acid, and in that case very little of the cystine is absorbed. W. G.

Synthesis of 2-Hexosamic Acids and 2-Hexosamines. P. A. LEVENE (*Biochem. Z.*, 1921, **124**, 37—83).—A detailed summary of work previously published by the author and his co-workers on this subject (A., 1915, i, 601, 782, 944; 1916, i, 203, 712, 713; ii, 3; 1917, i, 633; 1918, i, 530, 532; 1919, i, 475, 476; 1921, i, 318). H. K.

Monochlorocarbamide. Preparation of Chlorohydrins by its Action on Ethylenic Hydrocarbons. ANDRÉ DETEUF (*Bull. Soc. chim.*, 1922, [iv], **31**, 169—176; 176—181; cf. this vol., i, 236).—The results obtained by using the method previously described (*loc. cit.*) with different ethylenic hydrocarbons are detailed. With amylene, the product is the chlorohydrin of amylene glycol, $\text{OH}\cdot\text{CMe}_2\cdot\text{CHMeCl}$, which, when heated at 130° with anhydrous oxalic acid, gives chloroamylene and with alcoholic potassium hydroxide yields amylene oxide. When warmed with aniline, the chlorohydrin gives methyl isopropyl ketone. $\beta\gamma$ -Dimethylbutylene gives with chlorocarbamide β -chloro- γ -hydroxy- $\beta\gamma$ -dimethylbutane. Δ^8 -Hexene yields β -chloro- γ -hydroxyhexane. ϵ -Methyl- Δ^a -hexene yields α -chloro- β -hydroxy- ϵ -methylhexane, b. p. $97\text{--}98^\circ/23$ mm., $d^{20} 1.044$; $n^{14} 1.45662$. On oxidation with chromic acid, it gives α -chloro- ϵ -methylhexan- β -one, b. p. $118^\circ/40$ mm. Δ^8 -Octene yields β -chloro- γ -hydroxyoctane, b. p. $99\text{--}110^\circ/14$ mm.; $d^{20} 1.001$; $n^{19} 1.45232$. On oxidation, it yields α -chloroethyl pentyl ketone, b. p. $92^\circ/16$ mm., giving a semicarbazone, m. p. 145° . With alcoholic sodium hydroxide, this chlorohydrin gives $\beta\gamma$ -octene oxide, $\text{CH}_3\cdot[\text{CH}_2]_4\cdot\text{CH}\begin{smallmatrix} \text{CHMe} \\ \text{O} \end{smallmatrix}$, b. p. $70\text{--}75^\circ/18$ mm.; $d^{18} 0.858$; $n^{18} 1.42085$.

With cyclic hydrocarbons, the following results were obtained. Styrene yielded α -chloro- β -hydroxy- β -phenylethane, b. p. $128^\circ/17$ mm.; $d^{20} 1.225$; $n^{17} 1.55405$, which with sodium ethoxide gave ethyl β -hydroxy- β -phenylethyl ether, b. p. $240\text{--}245^\circ/760$ mm.; $d^{20} 1.054$. cycloHexene yielded 1-chloro-2-hydroxycyclohexane, b. p. $84\text{--}85^\circ/16$ mm.; m. p. 8° ; $d^{20} 1.138$; $n^{20} 1.49097$, which with potassium hydroxide in anhydrous ether gave cyclohexyl oxide. Under similar conditions, menthene gave the chlorohydrin of menthene glycol, b. p. $120\text{--}125^\circ/14$ mm.; $d^{20} 1.063$; $n^{20} 1.48422$. Camphene gave the chlorohydrin of camphene glycol, m. p. 96° ; b. p. $125\text{--}130^\circ/14$ mm. Its constitution is shown by its behaviour to be



W. G.

Guanidonium Salts. W. MARCKWALD and F. STRUWE (*Ber.*, 1922, **55**, [B], 457—463).—Guanidonium chlorate and perchlorate have been described by Marckwald (D.R.-P. 309297, 309298) as powerful explosives (cf. Mannelli and Bernardini, *Brit. Pat.* 155627). The latter is obtained readily by heating a mixture of equivalent amounts of dicyanodiamide and ammonium perchlorate at 160°, and thus forms a convenient initial material for the preparation of guanidine, the following salts of which are now described. *Guanidonium thiosulphate* (from an alcoholic solution of guanidonium perchlorate and saturated aqueous potassium thiosulphate), $(\text{CN}_3\text{H}_6)_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$; *guanidonium sulphite*, $(\text{CN}_3\text{H}_6)_2\text{SO}_3$, a colourless, crystalline compound; *guanidonium hydrogen sulphide*, $(\text{CN}_3\text{H}_6)\text{HS} \cdot \text{H}_2\text{O}$, yellow leaflets; *guanidonium xanthate*, $\text{CN}_3\text{H}_6 \cdot \text{S} \cdot \text{CS} \cdot \text{OEt}$, pale yellow crystals, m. p. 113°; *guanidonium borate*, $(\text{CN}_3\text{H}_6)_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$, colourless crystals; *guanidonium stannate*, $(\text{CN}_3\text{H}_6)_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$, long, lustrous crystals; *guanidonium metasilicate*, $(\text{CN}_3\text{H}_6)_2\text{SiO}_3 \cdot x\text{H}_2\text{O}$; guanidonium formate, m. p. 70—75°; *guanidine nitromethane*, $\text{CN}_3\text{H}_5 \cdot \text{CH}_3 \cdot \text{NO}_2$, small, colourless needles; *guanidonium phenoxide*, $\text{CN}_3\text{H}_6 \cdot \text{OPh}$, colourless crystals, m. p. 67°; *guanidonium p-tolylxide*, m. p. 147—150°; *guanidine benzenesulphonamide*, $\text{CN}_3\text{H}_5 \cdot \text{NH}_2 \cdot \text{SO}_3\text{Ph}$, m. p. 183° (decomp.); *guanidine phthalimide*, $\text{CN}_3\text{H}_5 \cdot \text{NH} \cdot (\text{CO})_2 \cdot \text{C}_6\text{H}_4$, m. p. 176—179° (decomp.).

Guanidine has been obtained in the solid state by mixing alcoholic solutions of guanidonium perchlorate and potassium hydroxide, removal of precipitated potassium perchlorate and concentration of the solution in a vacuum at 30—35°; the product contains 92.73—99.55% of guanidine and melts somewhat indefinitely at about 50°. It has been described by Veley (*T.*, 1908, **93**, 652) as a weak base, but his observations are not in harmony with those of Ostwald or of Morrell and Bellars (*T.*, 1907, **91**, 1012). It is now found that solutions of guanidonium hydroxide behave like those of the alkali hydroxides towards solutions of metallic salts; the strength of the base is established in addition by its ability to form stable salts with very weak acids. H. W.

Pyrofulmin, a Decomposition Product of Mercury Fulminate. LANGHANS (*Z. ges. Schiess. u. Sprengstoffw.*, 1922, **17**, 9—11, 18—21, 26—28).—Mercury fulminate is completely changed into a non-explosive substance by heating at 90° for about one hundred hours. The product is yellowish-brown and shows the unchanged crystalline form of mercury fulminate. The change can be followed by determining the mercury in the substance electrolytically. A gradual rise takes place from 70.42% (the value for the pure fulminate) to between 74 and 76.6% in the non-explosive substance, which is named *pyrofulmin*. Pyrofulmin is insoluble in water and in the usual organic solvents, and is neutral to litmus. It swells up on heating, giving off white, choking vapours. Its content of mercury is not constant, but never exceeds 76.6%, nitrogen 9.88%, carbon 6.21%, oxygen 7.51%. The loss of weight of the fulminate on heating therefore consists mainly of

carbon and oxygen. Pyrofulmin is probably not a definite compound. Its reactions point to its being a mixture of mercuric oxycyanide, $\text{Hg}(\text{OCN})\cdot\text{CN}$, with a little mercuric oxide.

H. C. R.

Solubility of Potassium Ferrocyanide in Water. Ice Curve and Cryohydric Point. E. FABRIS (*Gazzetta*, 1921, **51**, ii, 374—380).—The solubility of potassium ferrocyanide in grams of the salt per 100 grams of water between 0° and 100° is represented by two almost rectilinear curves meeting at 80° . This temperature is given in Landolt's tables as the transformation point of the hydrate, $\text{K}_4\text{Fe}(\text{CN})_6\cdot 3\text{H}_2\text{O}$ into $\text{K}_4\text{Fe}(\text{CN})_6\cdot x\text{H}_2\text{O}$, but evidence of this transformation is obtainable neither by the dilatometric method nor by analysis of the solid phase. The author has traced the freezing-point curve, the cryohydric point being -1.58° , which corresponds with the concentration 13.1 grams of the anhydrous salt per 100 grams of water.

T. H. P.

Symmetrical Diisopropylhydrazine and its Derivatives. HARRY L. LOCHTE, JAMES R. BAILEY, and WILLIAM A. NOYES (*J. Amer. Chem. Soc.*, 1921, **43**, 2597—2603).—Dimethylketazine may readily be reduced by means of colloidal platinum, using Skita's method (cf. A., 1913, i, 53, 54), and a yield of more than 90% of *s*-diisopropylhydrazine is obtained provided there is enough hydrochloric acid present to neutralise the base formed. *s*-Diisopropylhydrazine, $\text{CHMe}_2\cdot\text{NH}\cdot\text{NH}\cdot\text{CHMe}_2$, is a pale straw-coloured liquid, b. p. $124-124.5^\circ/740$ mm.; n_D^{25} 1.4087; d_4^{25} 0.7712, giving a *hydrochloride*, m. p. 198° (corr.), an *oxalate*, and crystalline condensation products with potassium cyanate and phenylcarbimide. With phenylthiocarbimide, it yields *diisopropylphenylthiosemicarbazide*, $\text{CHMe}_2\cdot\text{NH}\cdot\text{N}(\text{CS}\cdot\text{NHPh})\cdot\text{CHMe}_2$, m. p. 129.5° (corr.).

W. G.

The Preparation of Mercury Dialkyl Compounds from the Grignard Reagent. C. S. MARVEL and V. L. GOULD (*J. Amer. Chem. Soc.*, 1922, **44**, 153—157).—The reaction between an excess of the Grignard reagent and a mercuric haloid furnishes a very satisfactory method for the preparation of mercury dialkyl compounds, provided the proper precautions are observed. Any unchanged magnesium must be removed from the Grignard reagent before adding the mercuric haloid, and after the whole of the mercuric haloid has been added, the mixture must be boiled for ten to twelve hours to complete the reaction. The following compounds have been prepared by this method: mercury dimethyl, b. p. $92^\circ/740$ mm. (corr.); mercury diethyl, b. p. $97-99^\circ/125$ mm.; mercury dipropyl, b. p. $81-84^\circ/19$ mm.; mercury diisopropyl, b. p. $119-121^\circ/125$ mm.; mercury dibutyl, b. p. $120-123^\circ/23$ mm. When a magnesium alkyl bromide reacts with an excess of mercuric chloride, a mixture of mercury alkyl chloride and bromide is obtained. To obtain each of these compounds pure, the halogen of the alkyl haloid must be the same as that of the mercuric salt.

W. G.

Mixed Organometallic Compound of Aluminium. V. THOMAS (*Compt. rend.*, 1922, **174**, 464—465).—Aluminium when left in contact for a long time with methylene iodide in the absence of a solvent reacts with it without any appreciable evolution of gas, the mixture ultimately setting solid. A white, crystalline compound was obtained which it was not possible to purify, as it was highly reactive. If the aluminium and methylene iodide are allowed to react in the presence of anhydrous ether, a gas is evolved which is absorbed by bromine and attacked by permanganate. The gas has the formula $(CH_2)_n$, but apparently is not ethylene. The solid product of the reaction in ether is also highly reactive.

There is some indication that other metals, and in particular lead, are also capable of attacking methylene iodide in the absence of a solvent without any gas being evolved. W. G.

Kinetics of Open Saturated Chains of Carbon Atoms in Relationship to the Baeyer Strain Theory. Z. WOJNICZ-SIANOZENCKI (*Roczniki Chemji*, 1921, **1**, 244—275).—It is shown that the kinetics of an open saturated chain of carbon atoms may be treated by the theory of probabilities. If it be admitted that the limiting distance over which the carbon atom can exert a chemical force is not more than 2.101 times that which is normal for the two atoms connected by a single linking, then it is shown that the probability of the formation of polymethylene rings containing various numbers of carbon atoms follows the order $\zeta_2 > \zeta_5 > \zeta_6 > \zeta_7 > \zeta_3 > \zeta_4 > \zeta_8$, where ζ_n is the probability of formation of an n -membered carbon ring. This indicates that the double linking is more easily formed than the five-membered ring, and this more easily than the six-membered ring, and so on. This appears to be in keeping with experimental work, which is often contradictory to the usually adopted hypothesis. J. F. S.

[**Lignite Producer Tar.**] FRANZ FISCHER (*Ber.*, 1922, **55**, [B], 505—506).—A criticism of Ruhemann's recent communication (this vol., i, 22). H. W.

The Ethylation of Benzene and Naphthalene. C. H. MILLIGAN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1922, **44**, 206—210).—Balsohn's method (cf. A., 1879, 785) for the ethylation of benzene may be modified by the introduction of high speed stirring so that ethylene can be made to react with benzene in the presence of aluminium chloride at 70—90° so rapidly and completely that this becomes a practical method for the ethylation of benzene. A mixture of ethyl-, diethyl-, etc., up to hexaethyl-benzenes is obtained, but may fairly readily be separated into its components. If the polyethylbenzenes are stirred with benzene in the presence of the aluminium chloride from the previous reaction, they will give up some of their ethyl groups to the benzene. In a similar way, naphthalene may readily be ethylated by stirring it vigorously in benzene with polyethylbenzenes and aluminium chloride at 80°.

W. G.

The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. V. Heteronuclear Dinitro-derivatives. HAROLD BURTON and JAMES KENNER (T., 1922, 121, 489—496).

The Nitration of *m*-Nitrotoluene. OSCAR LISLE BRADY (T., 1922, 121, 328—331).

Some New Derivatives of Sulphobenzide [Diphenylsulphone]. EUG. GRANDMOUGIN (*Compt. rend.*, 1922, 174, 393—395).—In part a recapitulation of previous work (this vol., i, 251). 3:3'-Diaminosulphobenzide can be converted into the corresponding halogenated derivatives by the Sandmeyer reaction. 3:3'-Dichlorosulphobenzide has m. p. 108°; 3:3'-di-iodosulphobenzide has m. p. 158°. 2:2'-Dinitrosulphobenzide, m. p. 189°, was obtained by the oxidation of *o*-dinitrophenyl sulphide with potassium dichromate and sulphuric acid. To obtain unsymmetrical derivatives of sulphobenzide, sulphinic acids may be condensed with chloronitro-derivatives of aromatic hydrocarbons. Thus 1-chloro-2:4-dinitrobenzene and β -naphthalenesulphinic acid yield 2:4-dinitrophenyl- β -naphthylsulphone, m. p. 228°. W. G.

Theory of Carbonium Compounds. F. KEHRMANN (*Ber.*, 1922, 55, [B], 507—511).—A reply to Hantzsch (this vol., i, 24, 25).—The author is not convinced of the superiority of Hantzsch's complex formulæ over his own quinolide formulæ, or of the incorrectness of his theory of the sexavalency of carbon in carbonium salts (A., 1918, i, 311). H. W.

Elimination of Hydrogen from Aromatic Nuclei and Union of the Latter by means of Aluminium Chloride. V. Experiments with Benzil, Stilbene, and Phenanthrene. R. SCHOLL and G. SCHWARZER (*Ber.*, 1922, 55, [B], 324—330; cf. Scholl and Seer, this vol., i, 258).—Phenanthraquinone is formed in 25% yield when an intimate mixture of benzil and anhydrous aluminium chloride is heated at 120° during one hour; in addition, two substances are produced which are soluble in sodium hydroxide solution; these have not been examined fully.

Stilbene is readily converted by aluminium chloride into a polymeride which softens at about 165° after previous darkening and becomes carbonised at a higher temperature; according to determinations of molecular weight in boiling benzene, polymerisation has not proceeded beyond the trimeric stage (cf. Liebermann and Mitter, A., 1912, i, 464). The substance is oxidised by potassium permanganate or chromic acid in the presence of glacial acetic acid without giving well-characterised products; it is converted by nitric acid (*d* 1.15) at 150° into a nitrogen-free mixture of acids ($C_8H_5O_3$)_x.

Phenanthrene is converted by aluminium chloride in the presence of nitrobenzene at the atmospheric temperature into a black mass. In the presence of carbon disulphide, on the other hand, a yellow, amorphous product, decomp. about 225°, is obtained which is not identical with the substance derived from stilbene. Its nature

has not been elucidated fully, but it is possibly a polymeride of phenanthrene, although analyses of it agree better with the composition ($C_{14}H_{11}$)_x; it is readily converted by nitric acid into an amorphous nitro-compound.

H. W.

New Preparation of *cyclo*Alkylamines. ALPHONSE MAILHE (*Compt. rend.*, 1922, **174**, 465—467).—*cyclo*Hexanone gives with hydrazine hydrate a mixture of its hydrazone, b. p. 195°, and its ketazine, b. p. 270°. When the mixed vapours of these two substances are passed along with hydrogen over nickel at 180° an excellent yield of *cyclo*hexylamine together with some *dicyclo*hexylamine is obtained. Under similar conditions, *o*-methyl*cyclo*hexanone gives its hydrazone and its ketazine, and these when hydrogenated together give principally *o*-methyl*cyclo*hexylamine, b. p. 150°; d_4^{20} 0.8836; giving a *hydrochloride*, m. p. 280°. A small amount of *di*-*o*-methyl*cyclo*hexylamine, b. p. 268—270°, giving a *hydrochloride*, m. p. 226°, is also obtained. *m*-Methyl*cyclo*hexanone only gives its hydrazone, b. p. 215—220°, which when hydrogenated gives almost exclusively the primary amine, *m*-methyl*cyclo*hexylamine, b. p. 152°/750 mm.; d_4^{20} 0.8956, giving a *phenylcarbamide*, m. p. 145°. *p*-Methyl*cyclo*hexanone gives its hydrazone, b. p. 215°, and its ketazine, b. p. 280—285°. The mixture of these two substances on hydrogenation yields *p*-methyl*cyclo*hexylamine, b. p. 153°/750 mm.; d_4^{20} 0.9057 (giving a *hydrochloride*, m. p. 245°), together with some *di*-*p*-methyl*cyclo*hexylamine, b. p. 275—278°, giving a *hydrochloride*, m. p. 198°. In all cases, a very good yield of the primary amine is obtained and only a small amount of the secondary amine.

W. G.

The Dinitrotoluidines. OSCAR LISLE BRADY, JAMES NELSON EDMUND DAY, and WILLIAM JOSEPH WOODGATE ROLT (T., 1922, **121**, 526—532).

***p*-Cymene.** III. **The Bromination of 2-Amino-*p*-cymene.** ALVIN S. WHEELER and IRA W. SMITHEY (*J. Amer. Chem. Soc.*, 1921, **43**, 2611—2618).—2-Acetyl-amino-*p*-cymene on bromination in carbon tetrachloride solution yields 3(?)*-bromo*-2-acetyl-amino-*p*-cymene, $C_8H_7MePrBr \cdot NHAc$, m. p. 122.5°. When hydrolysed with concentrated hydrochloric acid, it yields 3(?)*-bromo*-2-amino-*p*-cymene, b. p. 169—170°/20 mm.; d_4^{20} 1.30125; n_D^{20} 1.5781, giving a *hydrochloride*, m. p. 205—210° (decomp.), and a *hydrobromide*, m. p. 200—205° (decomp.). In an endeavour to establish the position of the bromine atom in the ring, the acetyl derivative was oxidised with neutral permanganate, 3(?)*-bromo*-2-acetylaminotoluic acid, m. p. 215°, being obtained, which on hydrolysis gave 3(?)*-bromo*-2-aminotoluic acid, m. p. 151°, in the form of its *hydrochloride*, m. p. 190° (decomp.). This bromoaminotoluic acid is not identical with the only one known, namely, 5-bromo-2-amino-*p*-toluic acid, m. p. 186—187°, and hence the bromine must be in position 3 or 6, and the authors prefer the position 3 as representing an ortho-compound.

3-Bromo-2-amino-*p*-cymene can be diazotised and the product

coupled with the original base or other amines, and the following compounds are described: 2-Diazoamino-3-bromo-*p*-cymene, m. p. 143—146° (decomp.); 2-benzenediazoamino-3-bromo-*p*-cymene, m. p. 152—154° (decomp.), giving a *hydrochloride*, m. p. 161—162° (decomp.); 2-*p*-nitrobenzenediazoamino-3-bromo-*p*-cymene, has m. p. 158° (decomp.). On reversing the process in the last case by diazotising the *p*-nitroaniline and adding the bromoaminocymene, a product, m. p. 163° (decomp.), is obtained. These compounds of *p*-nitroaniline are yellow and dissolve in alkaline solutions, with the formation of a rich magenta colour which disappears when the solution is acidified. There is thus probably formed a pseudo or nitronic acid (cf. Hewitt and Mitchell, T., 1907, **91**, 1254).

In the purification of *p*-cymene, isolated from spruce turpentine, itself a by-product in the manufacture of paper by the sulphite process, it is necessary in addition to the steps previously given (cf. A., 1920, i, 751) to extract the cymene with a limited amount of concentrated sulphuric acid or it acquires a yellow colour on keeping and does not behave satisfactorily when nitrated or brominated.

W. G.

Derivatives of Aminodiphenyl. A. GARCÍA BANÚS and JUAN FERRER TOMÁS (*Anal. Fís. Quím.*, 1921, **19**, 293—312).—4-Dimethylaminodiphenyl (García Banús, *ibid.*, 1914, **12**, 173), m. p. 119—120°, is prepared by alternate addition of methyl sulphate and 30% sodium hydroxide solution to aminodiphenyl in aqueous solution. By the action of sodium nitrite on the preceding compound in dilute hydrochloric acid solution at -5°, 3-nitro-4-dimethylaminodiphenyl is obtained, m. p. 119—120°. It forms large, garnet-red, monoclinic crystals [$a : b : c = 1.111 : 1 : 1.0961$, $\beta = 90^\circ 16' 30''$]. A secondary derivative is also obtained in small quantity, colourless crystals, m. p. 112—115°. By passing hydrogen chloride into an ethereal solution of the nitroamine, the *hydrochloride* is obtained in white, silky crystals, unstable apart from their mother-liquors. Nitration of dimethylaminodiphenyl gives the 3-nitro-derivative at first, but by further nitration a compound crystallising in large, colourless needles, is obtained, m. p. 122°. It is probably 3 : 5 : 2' : 4'-tetranitro-4-dimethylaminodiphenyl. Reduction of the 3-nitro-derivative gives 3-amino-4-dimethylaminodiphenyl; it forms silky crystals, m. p. 59—60°; b. p. 200°/15 mm. By reduction of 4-nitro-3-aminodiphenyl, 3 : 4-diaminodiphenyl is obtained in grey plates, m. p. 102—103°. The action of nitrous acid on dimethyl anilines containing a negative group in the para position is discussed.

G. W. R.

Hydrogenation by Formic Acid of some Quaternary Salts of Hexamethylenetetramine. MARCEL SOMMELET and JEAN GUIOTH (*Compt. rend.*, 1922, **174**, 687—689).—When hexamethylenetetramine benzylchloride is warmed with formic acid, it undergoes hydrogenation, carbon dioxide is liberated, and one of the principal products is benzyldimethylamine. With other quaternary salts of the tetramine, the yields depended on the nature of the salt.

Thus acyclic derivatives of the type of the ethiodide or the *n*-butiodide, or salts like the phenylpropiodide gave very poor yields. On the other hand, substituted benzyl salts such as the *p*-ethylbenzylchloride gave satisfactory yields, but in such cases there was a secondary reaction producing benzaldehyde. W. G.

Behaviour of Allyl- and Benzyl-amino-oxides towards Sodium Hydroxide Solution. JAKOB MEISENHEIMER, HELLMUTH GREESKE, and AMALIE WILLMERSDORF (*Ber.*, 1922, **55**, [B], 513—522).—The rearrangement of methylallylaniline *N*-oxide to *N*-phenyl-*N*-methyl-*O*-allylhydroxylamine (A., 1920, i, 35) is reproduced by ethylallylaniline *N*-oxide, and by benzylmethyl-aniline oxide, but not by dialkylallylamino-oxides.

[H. GREESKE.]—Ethylallylaniline *N*-oxide, characterised by its *picrate*, $C_{11}H_{15}ON, C_6H_3O_7N_3$, granular crystals, m. p. 120—122°, is converted by aqueous sodium hydroxide into *N*-phenyl-*N*-ethyl-*O*-allylhydroxylamine, $NMePh \cdot O \cdot C_3H_5$, a yellow oil, b. p. 104°/15—16 mm.

[A. WILLMERSDORF.]—Diethylallylamine, b. p. 105—113°, is obtained from diethylamine and allyl bromide; its *picrate*, $C_7H_{15}N, C_6H_3O_7N_3$, forms irregular prisms, m. p. 94—95·5°. Diethylallylamine oxide *picrate*, $C_7H_{15}ON, C_6H_3O_7N_3$, crystallises in needles or prisms, m. p. 138°. Dimethylallylamine, best prepared by the process of Partheil and von Broich (A., 1897, i, 263), furnishes an oxide, of which the *picrate*, $C_5H_{11}N, C_6H_3O_7N_3$, forms dark yellow needles, m. p. 136°. Benzylmethylalaniline (Wedekind, A., 1899, i, 351), yields a *picrate*, $C_{14}H_{15}N, C_6H_3O_7N_3$, prisms, m. p. 127°, and an oxide (*picrate*, $C_{14}H_{15}ON, C_6H_3O_7N_3$, yellow prisms, m. p. 130°); it suffers rearrangement by alkali hydroxide to *N*-phenyl-*O*-benzyl-*N*-methylhydroxylamine, $NMePh \cdot O \cdot C_7H_7$,

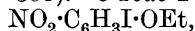
a yellow oil, soluble in cold concentrated hydrochloric acid, and reprecipitated on dilution. J. K.

cycloHexene Oxide and o-Methylcyclohexanol. MARCEL GODCHOT and PIERRE BÉDOS (*Compt. rend.*, 1922, **174**, 461—464).—*cyclo*Hexene is quantitatively oxidised in chloroform solution by perbenzoic acid to *cyclo*hexene oxide. The oxide behaves towards magnesium methyl iodide in exactly the same manner as does ethylene oxide itself, the product being *o*-methyl-*cyclo*hexanol. This alcohol, although having the same b. p., 163—164°, as has the methyl-*cyclo*hexanol obtained by Sabatier and Mailhe (cf. A., 1905, i, 275) by the hydrogenation of cresol, is apparently not the same alcohol, but a position isomeride. It gives a *phenylurethane*, m. p. 81—82°, and a *hydrogen phthalate*, m. p. 99—100°. The alcohol obtained from cresol gives a *phenylurethane*, m. p. 104°, and a *hydrogen phthalate*, m. p. 117—118°. The two alcohols are apparently *cis-trans* isomerides. W. G.

Solubilities and Cooling Curves of the Mononitrophenols. L. L. CARRICK (*J. Physical Chem.*, 1921, **25**, 628—659).—The various equations for calculating the solubility have been applied

to the solubility of the three nitrophenols and found to be unsuitable for calculating the solubility of these substances in acetone, benzene, ethyl alcohol, or ethyl ether. The solubility of the three isomerides has been determined in the solvents named at a series of temperatures over the range 0—104.2°. Many of the determinations at the higher temperatures were carried out in sealed tubes. The experimental values have been compared with those calculated by Findlay's equation, $R=R'+C(t'-t)$ (A., 1902, ii, 386), and by Hildebrand's equation, $\log N = -L(T_m - T)/4.58T \cdot T_m$ (A., 1916, ii, 518; 1918, ii, 36, 65); the agreement is not good in either case, but is considerably better in the case of the former equation than in the latter. Cooling curves have been determined for the three binary systems made up of pairs of the mono-nitrophenols, and also for the systems made up of the eutectics from each binary system and the third nitrophenol. In the system *o*-nitrophenol-*p*-nitrophenol, the eutectic lies at 34.5° and has a composition 27% of the para constituent; the system *o*-nitrophenol-*m*-nitrophenol has a eutectic at 31.5° with 70% of *o*-nitrophenol; the system *m*-nitrophenol-*p*-nitrophenol gives a eutectic at 61° having a composition 45.5% of *p*-nitrophenol. The melting points of the various mixtures have been calculated by means of the Le Chatelier and van Laar equation, $\log_e x = -L(T_0 - T)/RT_0T$, and found to be in good agreement with the observed values. It is shown that this law may be used equally well for calculating the cooling curves of ternary mixtures. The mononitrophenols in the presence of one another behave as ideal solutions. Benzene is shown to be a good solvent for the extraction of *o*-nitrophenol from aqueous solutions of the mixed mononitrophenols. J. F. S.

Nitration of 5-Iodo-2-nitrophenetole. C. APOSTOLO (*Gazzetta*, 1921, **51**, ii, 396—398).—5-Iodo-2-nitrophenetole,



obtained by the action of concentrated potassium hydroxide solution on alcoholic 5-iodo-1 : 2-dinitrophenetole solution, forms crystals, m. p. 86—87°. When treated with fuming nitric acid at the ordinary temperature, it yields 5-iodo-2 : 4-dinitrophenetole (or 5-iodo-2 : 6-dinitrophenetole), $\text{OEt}\cdot\text{C}_6\text{H}_2\text{I}(\text{NO}_2)_2$, which crystallises in lustrous, pale yellow needles, m. p. 111—112°. T. H. P.

The Nitration of Halogenated Phenols. L. CHAS. RAIKORD (*J. Amer. Chem. Soc.*, 1922, **44**, 158—165; cf. Upson, A., 1904, i, 734; Zincke and Hedenström, A., 1907, i, 124).—When 3 : 5-dibromo-*o*-cresol is nitrated by the action of sodium nitrite on its solution in glacial acetic acid, 5-bromo-3-nitro-*o*-cresol, m. p. 90—91° (cf. Upson, *loc. cit.*), and 3-bromo-5-nitro-*o*-cresol, m. p. 120° (decomp.) (cf. Robertson, T., 1908, **93**, 788), are obtained. When 3-bromo-5-nitro-*o*-cresol is reduced by stannous chloride and hydrochloric acid, it yields 3-bromo-5-amino-*o*-cresol, m. p. 142° (decomp.), isolated as its *hydrochloride*. The hydrochloride when warmed with acetic anhydride and anhydrous sodium acetate yields 3-bromo-5-acetylamino-2-acetoxytoluene, m. p. 169°.

which with cold aqueous sodium hydroxide gives 3-bromo-5-acetyl-amino-o-cresol, m. p. 154—155°. The amino-hydrochloride described above, when oxidised with ferric chloride, gives 3-bromo-2 : 5-toluquinone (cf. Claus and Jackson, A., 1889, 128). 5-Bromo-3-nitro-o-cresol, like its isomeride, when reduced yields 5-bromo-3-amino-o-cresol, m. p. 113°, giving a *hydrochloride*, which on acetylation yields 5-bromo-3-acetyl-amino-2-acetoxymtoluene, m. p. 199—200°. W. G.

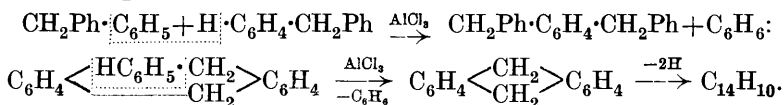
[**Tautomerism of Resorcinol.**] W. FUCHS (*Ber.*, 1922, 55, [B], 491—492).—Polemical (cf. Fuchs and Elsner, A., 1920, i, 545; 1921, i, 241; Herzog and Zeisel, A., 1920, i, 732). H. W.

Elimination of Hydrogen from Aromatic Nuclei and Union of the Latter by means of Aluminium Chloride. VI. Experiments with Phenol-ethers and with Diphenylmethane. ROLAND SCHOLL and CHRISTIAN SEER (*Ber.*, 1922, 55, [B], 330—341; cf. this vol., i, 258).—Elimination of hydrogen and union of the aryl residues occur with particular ease in the cases of α -naphthyl alkyl ethers, less readily with the corresponding β -naphthyl ethers, and, according to preliminary experiments, to a very restricted extent with phenolic ethers. Reaction is effected in the presence of nitrobenzene and there can be no doubt but that the latter exercises a specific influence probably by saturating the subsidiary valencies of the carbon of the aromatic nucleus, and thus rendering the hydrogen atom mobile and also by utilisation of the eliminated hydrogen. The aluminium chloride appears to have the dual function of activating the aromatically combined hydrogen atom and also the nitro-group of nitrobenzene, probably by the formation of readily dissociable molecular compounds.

4 : 4'-*Diethoxy*-1 : 1'-*dinaphthyl*, colourless, lustrous leaflets, m. p. 212—213°, is prepared in 70% yield by the gradual addition of anhydrous aluminium chloride to a solution of α -naphthyl ethyl ether in anhydrous benzene at the atmospheric temperature; hydrogen chloride is not thereby evolved. The same substance is obtained when ethyl chloroformate is added to the mixture, thus showing that the union of the naphthyl residues occurs with much greater rapidity than the fission of the ester. 4 : 4'-*Dimethoxy*-1 : 1'-*dinaphthyl* crystallises in colourless, lustrous needles, m. p. 252—253°. 2 : 2'-*Dimethoxy*-1 : 1'-*dinaphthyl*, m. p. 190—191°, and diresorcinyll tetramethyl ether, long, brown needles, m. p. 124°, are also described.

[With HEINRICH NEUMANN.]—The behaviour of aromatic hydrocarbons having mobile hydrogen atoms towards aluminium chloride has also been investigated. Anthracene and phenanthrene are very readily attacked in the presence of nitrobenzene, but the isolation of homogeneous products of the reaction has not been found possible. On the other hand, diphenylmethane reacts readily with aluminium chloride at the atmospheric temperature and in the absence of solvent without formation of resinous products; in this case, however, union of the benzene nuclei does not occur,

benzene and anthracene being the only substances isolable. The change appears to proceed in accordance with the scheme :



The isolation of *o*- or *p*-dibenzylbenzene which are presumed to be formed intermediately has not been effected. On the other hand, it is shown that *mesodihydroanthracene* is dehydrogenated by aluminium chloride at the atmospheric temperature to anthracene, probably with simultaneous formation of a corresponding quantity of more fully hydrogenated products, and that anthracene readily yields a molecular compound with aluminium chloride (cf. Lavaux and Lombard, A., 1910, i, 548). H. W.

Catalytic Preparation of *cyclo*Hexanetriols. J. B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1922, **174**, 616—618).—*cyclo*Hexanetriols may readily be prepared by catalytic reduction in the presence of nickel in alcohol or water at about 140° under pressure of the corresponding trihydroxybenzenes (cf. this vol., i, 136). Under these conditions, pyrogallol gives a mixture of two isomeric *cyclo*hexane-1 : 2 : 3-triols, of which one has m. p. 145°, b. p. 290°, and gives a triacetate, m. p. 47°, b. p. 288°, and the other has m. p. 95°, b. p. 225°, and gives a triacetate, b. p. 238°. Under similar conditions, phloroglucinol gives a mixture of isomeric *cyclo*hexane-1 : 3 : 5-triols, b. p. 245—260°; and 1 : 2 : 4-trihydroxybenzene gives a mixture of isomeric *cyclo*hexane-1 : 2 : 4-triols, b. p. 260—280°. W. G.

The Transfer of Hydrogen from an Alcohol to an Aldehyde. C. H. MILLIGAN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1922, **44**, 202—205).—By passing the vapours of an aldehyde mixed with ethyl alcohol over cerium oxide at 300—380°, the aldehyde is hydrogenated to the corresponding alcohol and the ethyl alcohol oxidised to acetaldehyde. In this way, benzyl, phenylethyl, and heptyl alcohols and citronellol have been prepared from the corresponding aldehydes. The yields are low and the life of the catalyst is short as it becomes foul owing to the production of gummy products, probably arising from the condensation of the aldehydes. If the cerium oxide is replaced by copper on an inert support benzaldehyde is reduced to toluene. W. G.

Phenyldi- α -naphthylcarbinol and Phenyldi- α -naphthylmethyl. C. S. SCHOEPFLE (*J. Amer. Chem. Soc.*, 1922, **44**, 188—194; cf. Gomberg and Schoepfle, A., 1917, i, 551; 1920, i, 26).—Phenyldi- α -naphthylcarbinol (cf. Elbs, A., 1887, 943) is best prepared by the interaction of ethyl benzoate and magnesium α -naphthyl bromide in toluene at 110—115°. The carbinol has m. p. 166—167° and gives additive compounds with ether, ethyl acetate, acetone, and ethyl alcohol of the type $\text{C}_{27}\text{H}_{20}\text{O} \cdot \text{EtOH}$, and with benzene, $2\text{C}_{27}\text{H}_{20}\text{O} \cdot 3\text{C}_6\text{H}_6$. With acetyl chloride, it

yields *phenyldi- α -naphthylchloromethane*, m. p. 165—167° (decomp.), and with acetyl bromide *phenyldi- α -naphthylbromomethane*, m. p. 125—127° (decomp.). Both these compounds give additive compounds with *mercuric, stannic, ferric, aluminium, and zinc chlorides*, all of which are unstable, decomposing in a short time to give *phenyldi- α -naphthylfluorene*, which was also obtained by boiling an acetic acid solution of *phenyldi- α -naphthylcarbinol*. *Phenyldi- α -naphthylmethane*, m. p. 204° (cf. Elbs, *loc. cit.*) was prepared by reducing the carbinol with zinc dust and acetic acid at 75—80°. *Phenyldi- α -naphthylmethyl* was obtained by shaking a benzene solution of the above chloromethane with molecular silver in the absence of air. It was very unstable and could only be obtained in solution. It readily undergoes auto-reduction, giving *phenyldi- α -naphthylmethane* and *phenyldi- α -naphthylfluorene*. It also absorbs oxygen, but attempts to prepare a peroxide were not successful. With hydrochloric acid in the absence of air, it gives *phenyldi- α -naphthylmethane* and *phenyldi- α -naphthylchloromethane*. W. G.

Influence of Substitution in the Ortho-, Meta-, and Para-positions on the Absolute Affinity of Benzoic Acid. I. H. N. K. RORDAM (*Z. physikal. Chem.*, 1921, **99**, 474—498).—The absolute affinities (free energy changes) between silver oxide and benzoic, *o*-, *m*-, and *p*-toluic acids, and cinnamic acid, were measured by an electromotive method. Silver oxide exists in two modifications: (a) the electrolytically precipitated oxide, unstable at the ordinary temperature but stable at higher temperatures; (b) the ordinary precipitated oxide, stable at the ordinary temperature but unstable at higher temperatures. The transition temperature was calculated as 132°. The affinity of benzoic acid is reduced by the introduction of methyl into the benzene nucleus, the effect being greatest in the *o*-position. The effects in the *m*- and *p*-positions were weaker and approximately equal. The absolute affinity of cinnamic acid towards silver oxide is 37% greater than that of benzoic acid, whereas the conductivity measurements would, on the assumption that the strength is proportional to the ionisation, make benzoic acid almost twice as strong as cinnamic acid. The *E.M.F.* of the oxy-hydrogen cell was calculated as 1.227 volts at 25°, in agreement with the results of Nernst and Wartenberg and of Brönsted. The lower value calculated by Lewis arises from the fact that the dissociation pressures of silver oxide, measured at higher temperatures, referred to one form, whilst the *E.M.F.* measurements, carried out at lower temperatures, referred to the second form, of silver oxide. If account is taken of this, all the results are in agreement. A method for the determination of hydrogen ions is indicated. J. R. P.

The Reduction of Ethyl Benzoate and some other Benzene Derivatives by Sodium and Absolute Alcohol. HERVÉ DE POMMERAU (*Compt. rend.*, 1922, **174**, 685—687).—When ethyl benzoate is reduced by sodium in absolute alcohol, the main product is *cyclohexanecarboxylic acid* together with a little cyclo-

hexylcarbinyl alcohol, b. p. 188°/760 mm., giving a *urethane*, m. p. 63°. Under similar conditions, benzaldehyde gives toluene and *cyclohexanecarboxylic acid*, but phenol, phenetole, and aniline do not undergo reduction. Nitrobenzene gives aniline with a little hydrazobenzene. W. G.

Solubility of the Isomeric Toluic Acids in the Three Xylenes. CHAPAS (*Compt. rend.*, 1922, 174, 610—611).—The solubilities of the three toluic acids in the three xylenes expressed as grams of the acid dissolved in 100 grams of the xylene at 14° are :—

	<i>o</i> -Xylene.	<i>m</i> -Xylene.	<i>p</i> -Xylene.
<i>o</i> -Toluic acid	7.11	5.78	7.39
<i>m</i> -Toluic acid	8.63	8.57	10.32
<i>p</i> -Toluic acid.....	1.05	0.91	1.47

W. G.

The Action of Light on the Cinnamic Acids and the Constitution of the Truxillic Acids. A. W. K. DE JONG (*Ber.*, 1922, 55, [B], 463—474).—During recent years, a number of papers on these subjects have been published by Stobbe and Störmer, in which the author's work has not been taken into account; the latter is now published in a more extended form.

The conversion of *allocinnamic* into β -truxillic acid is preferably effected by the action of direct sunlight on the cooled acid; the presence of benzoic, α - or β -truxillic acids in the *allo*-acid is inhibitive, whereas that of *trans*-cinnamic acid is highly favourable. Further experiment shows that *trans*-cinnamic acid can form α - and β -truxillic acids, that the production of β -truxillic acid from *allocinnamic* acid does not take place directly but indirectly through the *trans*-acid and that β -truxillic acid is not formed by the union of molar quantities of the *allo*- and *trans*-acid. Illumination of non-recrystallised *trans*-cinnamic acid yields solely α -truxillic acid, but, if illumination is interrupted and the acid is recrystallised, β -truxillic acid is produced to a greater or less extent. The latter acid appears to be produced from β -cinnamic acid, which is readily formed by pouring a solution of the α -acid in alcohol, nearly saturated at the atmospheric temperature, into a large volume of water or by dissolving the α -acid in ammonia and adding an excess of hydrochloric acid to the solution. It may be noted that *allo*-, α -, and β -cinnamic acids are not converted into truxillic acids by exposure to red, yellow, or green light.

Stobbe and Störmer have observed the production of β -truxillic acid, but seldom of α -truxillic acid, when *allocinnamic* acid is illuminated, whereas the author has found that the α -acid is formed in considerable quantity; the discrepancy is to be ascribed to the differing temperatures used during the experiment, rise in temperature favouring the formation of the α -acid.

The presence of δ -truxillic and β -cocaic acids in the natural truxillic acid (Störmer, A., 1921, i, 179) has been established previously by the author (A., 1911, ii, 552).

The constitutions assigned to α -, γ -, δ -, and ϵ -truxillic acids by

Störmer and Förster (A., 1919, i, 444) are in agreement with those proposed previously by de Jong (A., 1918, i, 172), but this is not the case with β -truxillic and β -cocaic acids.

Störmer's proposal (A., 1921, i, 179) to divide the acids into the truxillic and truxinic series is criticised adversely; it appears preferable to retain the original names until the structure of the compounds is definitely elucidated.

H. W.

Preparation of *ar*-Tetrahydronaphthylthiolacetic Acids.

TETRALIN G. M. B. H. (Brit. Pat. 148419).—Tetrahydronaphthalene is sulphonated with chlorosulphonic acid at a temperature not exceeding 5°; the resulting sulphonyl chlorides are reduced with zinc dust and hydrochloric acid to a mixture of 1- and 2-*tetrahydronaphthylthiols*, and after purification by distillation under reduced pressure (b. p. 143–147°/15 mm.) they are condensed in alkaline solution with monochloroacetic acid with the formation of 1- and 2-*tetrahydronaphthylthiolacetic acids*, $C_{10}H_{11} \cdot S \cdot CH_2 \cdot CO_2H$. The two acids are separated by adding a concentrated ammonium chloride solution to the reaction mixture when the ammonium salt of the 2-acid separates in crystalline flakes. From the mother-liquors, the 1-acid is precipitated with hydrochloric acid as a voluminous, white precipitate, which after crystallisation from benzene melts at 133–135°. The 2-acid, precipitated from the solution of its ammonium salt, melts at 69–70°. Both acids are easily converted into "tetrahydronaphthylthioindigo."

G. F. M.

Friedel and Crafts' Reaction. Some Substituted Phthalic Anhydrides with Toluene and Aluminium Chloride.

WALTER A. LAWRENCE (*J. Amer. Chem. Soc.*, 1921, **43**, 2577–2581; cf. A., 1920, i, 741).—When toluene is condensed with unsymmetrical phthalic anhydrides in the presence of aluminium chloride, it gives, in some cases, two acid products and in others only one. The physical properties of the toluoylnitrobenzoic acids are very similar to those of the benzoylnitrobenzoic acids (*loc. cit.*).

With 3-nitrophthalic anhydride, toluene gives 2-nitro-6-*p*-toluoylbenzoic acid, m. p. 262–265° (decomp.), and 3-nitro-2-*p*-toluoylbenzoic acid, m. p. 123–126° (decomp.). With 4-nitrophthalic anhydride, the products are 4-nitro-2-*p*-toluoylbenzoic acid, m. p. 101–105° (decomp.), and a small amount of a compound, m. p. 211–218° (decomp.). With 3-acetylaminophthalic anhydride, the products are two *p*-toluoylaminobenzoic acids, m. p. 256–257° and 206°, respectively, in which the toluoyl group is, in each case, in position 2 or 6 and the amino-group in position 3 or 2. With 4-acetylaminophthalic anhydride, practically the whole of the yield consisted of one *p*-toluoylaminobenzoic acid, m. p. 135–136°, the toluoyl group being in position 2 or 6 and the amino-group in position 4 or 3. A small amount of an unidentified compound, m. p. 180–183°, was also obtained. Tetrachlorophthalic anhydride gave with toluene 2 : 3 : 4 : 5-tetrachloro-6-*p*-toluoylbenzoic acid, m. p. 174–175° (corr.) (cf. 1914, Brit. Pat. 8917), giving a methyl ester, m. p. 96–97° (corr.).

Tetrabromophthalic anhydride gave 2 : 3 : 4 : 5-tetrabromo-6-*p*-toluoylbenzoic acid, m. p. 212° (corr.), giving a methyl ester, m. p. 162.5° (corr.); and tetraiodophthalic anhydride gave 2 : 3 : 4 : 5-tetraiodo-6-*p*-toluoylbenzoic acid, m. p. 266° (corr.), giving a methyl ester, m. p. 199° (corr.). W. G.

Homogentisic Acid. II. The Behaviour of Homogentisic Acid when Boiled with Ferric Chloride. CARL TH. MÖRNER (*Z. physiol. Chem.*, 1921, **117**, 67—84; cf. A., 1912, i, 459).—When homogentisic acid is distilled with a concentrated solution of ferric chloride, the distillate contains a substance which crystallises in leaflets, m. p. 89 — 90° , and when heated on the water-bath sublimes, yielding thin, broad, iridescent needles. S. S. Z.

Homogentisic Acid. III. CARL TH. MÖRNER (*Z. physiol. Chem.*, 1921, **117**, 85—90).—Homogentisic acid crystallises with one molecule of water in monoclinic prisms. It forms a lactone at 130° , at which temperature it partly sublimes. At about 17.5° , its solubility in water is 1 : 1.8. S. S. Z.

Quinhydrones of the Maleic Anhydride Series. PAUL PFEIFFER [with E. FLATER] (*Ber.*, 1922, **55**, [B], 413—429).—In a previous communication (Pfeiffer and Böttler, A., 1919, i, 62), it has been shown that maleic anhydride and analogous substances give more or less deeply coloured solutions in hydrocarbons, phenols, amines, etc., although, in general, the isolation of the additive compounds in the solid state was not found possible. The close analogy of maleic anhydride to the quinones was thus demonstrated, and it was pointed out that the relationship between maleic anhydride and furan is the same as that between *p*-benzoquinone and benzene. The work has now been extended in a variety of directions which show that the presence of the group, $\text{CO} \cdot \dot{\text{C}} : \dot{\text{C}} \cdot \text{CO}$ —, is necessary for the formation of quinhydrones and that it is largely a matter of indifference whether it is present in a closed ring, as in *p*-benzoquinone or maleic anhydride, or in an open chain, as in phthalaldehyde or *s*-phthalyl chloride. In particular, tetrahalogenated phthalic anhydrides exhibit a great power of forming solid additive products with many classes of compounds and are to be classed in this respect with *s*-trinitrobenzene and picric acid. The precise rôle of the halogen atoms has not been elucidated (cf. Pratt and Perkins, A., 1918, i, 167; Pratt and Young, A., 1918, i, 540). Since the anhydrides unite with aromatic hydrocarbons as well as with the corresponding phenols, amines, etc., it is evident that the compounds are formed by saturation of affinity between one or both oxygen atoms of the anhydride component and the unsaturated carbon atoms of the benzenoid component, thus $\text{C}_6\text{Cl}_4\text{C}_2\text{O}_3 \dots \text{C}_n\text{H}_m$.

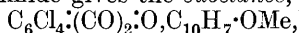
The following compounds are derived from tetrachlorophthalic anhydride, and contain the components in equimolecular ratio. In general, they are formed by allowing a solution of the requisite constituents in hot glacial acetic acid to cool slowly. With mesitylene, the substance $\text{C}_6\text{Cl}_4 \cdot (\text{CO})_2 \cdot \text{O} \cdot \text{C}_6\text{H}_3\text{Me}_3$, pale yellow needles which

evolve the hydrocarbon slowly at the atmospheric temperature; with naphthalene, greenish-yellow, silky needles; with 1-methylnaphthalene, greenish-yellow needles; with acenaphthene, golden-yellow, slender needles, m. p. 237—240°; with anthracene, golden-yellow, lustrous needles, m. p. 195°; with phenanthrene, long, yellow needles, m. p. 190°; with α -bromonaphthalene, pale yellow needles which dissociate when heated gently; with α -naphthol, orange-coloured, lustrous needles, m. p. 250°; with β -naphthol, small, yellow needles, m. p. 210°; with α -naphthyl ethyl ether, deep yellow needles which dissociate when heated gently; with β -naphthyl methyl ether, greenish-yellow needles which dissociate when heated; with diphenylene oxide, long, greenish-yellow, lustrous needles; with carbazole, yellow, lustrous needles, m. p. 210°.

Tetrachlorophthalic anhydride does not appear to unite with stilbene; its additive product with 2 : 4 : 5 : 2' : 4' : 5'-hexamethylstilbene has been described previously (Pfeiffer and Böttler, *loc. cit.*). Maleic anhydride does not give crystalline additive compounds with α -naphthyl ethyl ether or β -naphthyl methyl ether, and bromomaleic anhydride does not give solid products with β -naphthol or β -naphthyl methyl ether. Solid compounds were not prepared from phthalic anhydride and α -naphthyl ethyl ether, from tetrachlorophthalic anhydride and diphenylamine, or from phthalic anhydride and acenaphthene.

3 : 6-Dichlorophthalic anhydride gives a crystalline compound, with acenaphthene, $C_6H_2Cl_2(CO)_2 \cdot O \cdot C_{12}H_{10}$, lemon-yellow needles, m. p. 119—120°, but not with carbazole.

Tetrachlorophthalimide gives the substance,



lemon-yellow crystals with α -naphthyl methyl ether and a similar compound, small, lemon-yellow needles, with α -naphthyl ethyl ether; both substances lose the ethereal component when heated gently.

Tetrabromophthalic anhydride yields crystalline additive compounds with naphthalene, pale greenish-yellow needles, acenaphthene, long, dark yellow needles, and α -naphthyl ethyl ether, small, dark yellow needles; the compounds dissociate into their components when heated.

Chloranil and acenaphthene yield the substance, $C_6Cl_4O_2 \cdot C_{12}H_{10}$, black, lustrous needles.

Solid, additive compounds were not obtained from chloranil and fluorene, diphenylene oxide and carbazole, or 2 : 2'-dihydroxydiphenyl, from bromanil and acenaphthene, from 2 : 5-dichloroquinone and diphenylene oxide, β -naphthol, α -bromonaphthalene, or β -naphthyl methyl ether.

Phthalaldehyde gives an orange-yellow solution in dimethylaniline in which phthalide dissolves with development of colour; on the other hand, the solutions of the aldehyde and phthalide in concentrated sulphuric acid are colourless and pale greenish-yellow respectively.

Terephthalyl chloride gives a coloured solution in guaiacol or acenaphthene, whereas the similar solutions of isophthalyl chloride

are colourless. Both chlorides yield yellow solutions in dimethyl-aniline. H. W.

The Formation and Stability of *spiro*-Compounds. VII. The Application of the Dieckmann Reaction to Esters of the Glutaric Series. GEORGE ARMAND ROBERT KON (T., 1922, 121, 513—526).

The Preparation and Properties of Several Phenylalkylsuccinic Acids. FRED W. UPSON and T. J. THOMPSON (J. Amer. Chem. Soc., 1922, 44, 181—188).—Two methods are suggested for the preparation of phenylalkylsuccinic acids. In the first, alkyl cyanohydrins are condensed with benzyl cyanide by means of sodium methoxide or ethoxide (cf. Avery and Upson, A., 1908, i, 343) and in the second, the esters of α -bromo-fatty acids are condensed with benzyl cyanide by means of sodamide. The resulting nitriles are, in each method, saponified. The following new succinic acids are described: *Phenylmethylsuccinic acid*, $\text{CO}_2\text{H}\cdot\text{CHMe}\cdot\text{CHPh}\cdot\text{CO}_2\text{H}$, m. p. 182° ; *phenylethylsuccinic acid*, m. p. 196° ; *phenyl-n-propylsuccinic acid*, m. p. 213° ; and *phenyl-isobutylsuccinic acid*, m. p. 183.4° . In the second method of preparation, the intermediate product is in each case a half nitrile, half ester of the required succinic acid, the nitrile group being adjacent to the phenyl group. The complete hydrolysis of the nitriles or nitrile esters of phenylisopropyl- and phenylisobutylsuccinic acids cannot be brought about by the usual acid or alkali methods, but these substances must be heated in a sealed tube at 130 — 140° for from twenty-four to thirty hours.

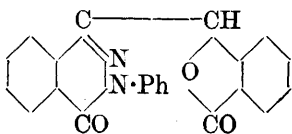
It was found that when the sodium phenylacetone nitrile obtained by the action of sodamide on phenylacetone nitrile was left exposed to the air after the evaporation of the solvent ether, the material underwent vigorous auto-oxidation. From an examination of the products of this oxidation, the authors suggest that the constitution of this sodium derivative is best represented by $\text{CHPh}\cdot\text{C}\cdot\text{NNa}$.

W. G.

Stilbene-2 : 2'-dicarboxylic Acid. PAUL RUGGLI and R. ERNEST MEYER (Helv. Chim. Acta, 1922, 5, 28—59).—A number of derivatives of stilbene-2 : 2'-dicarboxylic acid have been examined with the object of preparing tolane-2 : 2'-dicarboxylic acid; the great readiness with which these substances pass into compounds containing the lactone ring has prevented the fulfilment of the original purpose.

Diphthalyl-lactonic acid, $\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{CH}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ (cf. Reissert, A., 1913, i, 622), is prepared by the reduction of phthalic anhydride by zinc dust in neutral, aqueous-alcoholic solution and

is characterised by its conversion by phenylhydrazine in alcoholic solution into 3-phenyl-1-phthalidophthalazone (annexed formula), colourless, silky needles, m. p. 207° . It is reduced by zinc dust in alkaline solution to hydrodiphthal-



lactonic acid, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{CH} \cdot \text{CH}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. 198.5° (*methyl* ester, colourless needles, m. p. 115° , *ethyl* ester, m. p. 76° , *amide*, minute needles, m. p. $227-228^\circ$). Hydrodiphthalyl-lactonic acid is converted by potassium cyanide at $215-230^\circ$ into stilbene-2 : 2'-dicarboxylic acid, $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. $263-265^\circ$, when heated rapidly.

[With P. HUBERT.]—The chlorination of stilbene-2 : 2'-dicarboxylic acid suspended in chloroform does not proceed uniformly; in addition to considerable quantities of resinous matter, a *substance*, possibly, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{CCl} \cdot \text{CHCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{H}$, m. p. 177° , is formed. Sodium stilbene-2 : 2'-carboxylate is very readily brominated in aqueous solution, but the primary dibromide loses sodium bromide immediately and passes into hydrodiphthalyl, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{CH} \cdot \text{CH} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{CO}$, m. p. $255-257^\circ$ after softening at 240° . In the hope of avoiding ring closure, the behaviour of the esters of stilbene-2 : 2'-dicarboxylic acid towards halogens has been examined (the diethyl ester has m. p. $79-80^\circ$, the *ethyl hydrogen* ester, m. p. $138-139^\circ$, and the *dimethyl* ester, long, colourless needles, m. p. $101-102^\circ$). The methyl ester combines very readily with chlorine, but, even at 0° , the primary product loses methyl chloride and passes into the *methyl* ester of *chlorohydrophthalyl-lactonic acid*, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{CH} \cdot \text{CHCl} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, coarse, glassy crystals, m. p. $136.5-137.5^\circ$. In a similar manner, the ethyl ester gives *ethyl chlorohydrophthalyl-lactonate*, colourless rods, m. p. 143° . The methyl ester is converted by a molecular proportion of potassium hydroxide in alcoholic solution into *methyl benzylidenephthalide-o-carboxylate*, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{C} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, colourless needles, m. p. $123.5-125^\circ$ (*dibromide*, m. p. $221-222^\circ$), which is converted by an excess of potassium carbonate into deoxybenzoin-2 : 2'-dicarboxylic acid (the latter may be similarly prepared directly from the chloro-ester). Ethyl stilbene-2 : 2'-dicarboxylate is converted by bromine in carbon tetrachloride solution into the *dibromide*, m. p. 162° , but the corresponding *compound*, m. p. 198° (decomp.), from the methyl ester is obtained in better yield; in the latter case, elimination of methyl bromide occurs to some extent with the formation of the *methyl* ester of bromohydrodiphthalyl-lactonic acid, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{CH} \cdot \text{CHBr} \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me}$, m. p. 133° . The latter loses hydrogen bromide when heated somewhat above its melting point and yields a *compound*, $\text{C}_{17}\text{H}_{12}\text{O}_4$ (probably methylhydrodiphthalyl, $\text{CO} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{CH} \cdot \text{CMe} \langle \text{C}_6\text{H}_4 \rangle_{\text{O}} \text{CO}$), which appears to pass under the influence of alkali into *methyldeoxybenzoin-2 : 2'-dicarboxylic acid*, m. p. $275-277^\circ$.

The behaviour of the normal dibromides of the stilbene-2 : 2'-dicarboxylic esters towards alkalis and amines has been examined. With one, two, or four molecular proportions of alcoholic potash,

the ester groups are hydrolysed and potassium salts of brominated acids are produced which are protected against further action by their insolubility. Reaction proceeds most smoothly when an excess of potassium carbonate is used in boiling aqueous-alcoholic solution and then leads to the formation of deoxybenzoin-2:2'-dicarboxylic acid which has m. p. 193° (decomp.) after softening at 180°, and, after resolidification, m. p. 222—245° (indefinite) after softening at 216°. (The acid is characterised further by its transformation into 3-phenyl-1-o-carboxybenzylphthalazone, colourless needles, m. p. 206°, and 3-carbamido-1-o-carboxybenzylphthalazone, pale yellow needles, m. p. [indefinite] 232°, to a red liquid.) With four molecular proportions of sodium ethoxide, the ester dibromides give the sodium salts of a mixture of acids which can only be separated from one another with considerable difficulty, in part owing to the ease with which some of them pass into lactones; it was found possible, however, to isolate deoxybenzoin-2:2'-dicarboxylic acid and an acid, m. p. 250°, which gave analytical results in agreement with those required by tolane-2:2'-dicarboxylic acid (the amount obtained was too small to permit further investigation). Pyridine causes the removal of bromine from stilbene-2:2'-dicarboxylic ester bromides with re-formation of the parent stilbene-2:2'-dicarboxylic esters; triethylamine has a similar effect at 170°. Since, according to Pfeiffer (A., 1912, i, 618), this behaviour is characteristic of the α -stilbenedibromides, and in the present instance it was not found possible to isolate the second isomerides, it appeared useless to study the bromides further, and the work was therefore continued with the dichlorides, attempts to avoid the undesired ring closure observed with the methyl and ethyl esters (see above) being made by suitable substitution in the carboxyl groups.

Amyl stilbene-2:2'-dicarboxylate, colourless, matted needles, m. p. 60—62°, yields resinous substances when treated with chlorine; amyl chloride is thereby eliminated. *Phenyl stilbene-2:2'-dicarboxylate*, transparent prisms, m. p. 206°, does not give crystalline chloro-derivatives; the corresponding *dibromide*, colourless granules, m. p. 222° (decomp.), is decomposed with difficulty by pyridine with regeneration of the parent ester. *Stilbene-2:2'-dicarboxyl chloride*, pale yellow needles, m. p. 159°, is prepared from the acid and thionyl chloride; in spite of its relative stability towards water, it appears to have the symmetrical structure. When chlorinated in the presence of warm chloroform, it gives 7:7'-*dichlorostilbene-2:2'-dicarboxyl chloride*, which is isolated in the form of the corresponding *methyl ester*, $C_{18}H_{14}O_4Cl_2$, colourless crystals, m. p. 183°; in cold solution, the methyl ester of chlorohydrodiphthalyl-lactonic acid is the main product of the change. Stilbene-2:2'-dicarboxyl chloride is transformed by ammonia into the *di-amide*, small, colourless crystals, m. p. 319°, by aniline into the *di-anilide*, m. p. 299°, and a *substance*, $C_{16}H_9O_2Cl$, long, slender needles, m. p. 203°, by methylaniline into the *di-methylanilide*, m. p. 175°, and a *product*, probably $C_6H_4 \begin{smallmatrix} \text{CH} \\ \diagup \quad \diagdown \\ \text{CO} \end{smallmatrix} C \cdot C_6H_4 \cdot NMePh$, m. p. 196°, and by *p*-bromomethylaniline into the *di-p-bromo-*

methylanilide, $C_{30}H_{24}O_2N_2Br_2$, a colourless, crystalline powder, m. p. 200° ; the latter substance gives additive *products* with a molecular proportion of benzene or ethyl alcohol, m. p. 167° and 104° , respectively. Treatment of the nitrogenous compounds with chlorine gives resinous products.

The action of phosphorus pentachloride on deoxybenzoin-2 : 2'-dicarboxylic acid and subsequent treatment of the initial product with methyl alcohol, leads to the isolation of methyl benzyldiene-phthalide-*o*-carboxylate instead of the desired 7-chlorostilbene-2 : 2'-dicarboxyl chloride.

4-Nitro-2-cyanotoluene, m. p. 105° , is condensed with benzaldehyde to 4-nitro-2-cyanostilbene, which is converted by bromine in carbon tetrachloride solution into 4-nitro-2-cyanostilbene *di-bromide*, colourless needles, m. p. $195-197^\circ$. The latter is transformed by pyridine or potassium carbonate into 4-nitro-2-cyanostilbene, by sodium ethoxide into resinous products. H. W.

Bile Salts. X. The Further Degradation of Deoxycholic Acid. HEINRICH WIELAND and WILHELM SCHULENBURG (*Z. physiol. Chem.*, 1921, **114**, 167—191; cf. A., 1921, i, 112, 113, 178).—To prepare the ketotricarboxylic acids, $C_{23}H_{34}O_7$, pyrocholoidanic acid is dissolved in alkali hydroxide in the cold and after thirty minutes the solution is made acid to Congo red with hydrochloric acid. The precipitate contains a mixture of the two isomerides. The β -acid is obtained by extracting the precipitate with ether and by further extracting the ethereal solution with alkali and acidifying. The β -acid crystallises as the hydrate, m. p. $110-115^\circ$. The anhydrous acid after crystallisation has m. p. $180-185^\circ$, and $[\alpha]_D^{19} -56.3^\circ$ in alcohol. The same pyrocholoidanic acid is obtained from it as from the α -acid. *Prosolannellic acid*, $C_{23}H_{34}O_9$, is obtained by dissolving the α -ketotricarboxylic acid in alkali hydroxide, oxidising with potassium permanganate, and precipitating with acid. The hydrated acid crystallises in spherical aggregates of lustrous needles, m. p. 220° , but on exposure in a vacuum it loses 3.45% of water and then has m. p. 180° , $[\alpha]_D^{16} +75.5^\circ$ in alcohol. *Pyroprosolannellic acid*, $C_{22}H_{30}O_6$, prepared from prosolannellic acid by distillation in a vacuum at 300° , crystallises in colourless prisms, m. p. 172° . The *diketo-dicarboxylic acid*, $C_{22}H_{32}O_6$, was obtained from this pyro-acid by boiling in alcoholic solution with sodium ethoxide. The *sodium salt* crystallises in needles. The free acid crystallises in large, colourless plates, m. p. 173° . *Solannellic acid* was prepared both by the oxidation of prosolannellic acid and of the α -ketotricarboxylic acid, $C_{23}H_{34}O_7$, with fuming nitric acid; it crystallises in white rosettes of needles, m. p. $202-203^\circ$ (decomp.), $[\alpha]_D^{14} +35.1^\circ$ in alcohol. *Pyrosolannellic acid*, $C_{22}H_{32}O_9$, prepared by heating solannellic acid at 270° in a vacuum, crystallises as whetstone-shaped crystals, m. p. 272° . *Norsolannellic acid*, $C_{22}H_{32}O_{12}$, obtained by oxidising the pyro-acid with fuming nitric acid, crystallises in lustrous needles, m. p. $228-229^\circ$ (decomp.), $[\alpha]_D^{18} +9.9^\circ$ in 1% alcohol. This acid is also obtained together with

another acid by oxidising pyrodeoxybilianic acid with fuming nitric acid. S. S. Z.

Sulphite Liquor Lactone. S. V. HINTIKKA (*Pappers-Travärrö- och Industritidskrift for Finland*, 1921, No. 10, 150; *Cellulose-chemie*, 1921, 2, 87—88).—The author has repeated Holmberg's experiment (A., 1921, i, 25) using birch and aspen woods, but failed to obtain the crystalline lactone reported by Holmberg. It may be that this compound is characteristic of the sulphite waste liquor from pine wood. CHEMICAL ABSTRACTS.

Cubebin. IV. Derivatives of Cubebinolide. EFISIO MAMELI (*Gazzetta*, 1921, 51, ii, 353—374; cf. A., 1908, i, 20; 1909, i, 503; 1913, i, 421).—When subjected to oxidation under various conditions, cubebin always yields a greater or less proportion of cubebinolide, together with other products. Thus, the action of light, mercuric acetate, hydrogen peroxide, silver oxide, dichromate and sulphuric acid, permanganate, etc., on cubebin yields cubebinolide; nitric acid and bromine yield respectively dinitro- and dibromo-cubebinolide, the central grouping undergoing no oxidation. Just as was observed with cubebin, cubebinic esters, and cubebinol, the action of the more energetic oxidising agents, such as potassium permanganate, on cubebinolide or its derivatives results in complete combustion of the alicyclic grouping, with formation of piperonylic acid.

These results show that the non-primary alcoholic group is the point most readily attacked in the cubebin molecule. The formation of a γ -lactone, like the property of yielding internal ethers with a pentagonal nucleus when treated with a dehydrating agent, represents one of the fundamental chemical characters of cubebin.

The compound, m. p. 183—184°, obtained by the action of nitric acid on cubebinolide, is found to be a dinitrocubebinolide, $C_{20}H_{16}O_6(NO_2)_2$, and to be identical with the compound erroneously described by Peinemann (A., 1896, i, 494) as dinitrocubebin, $C_{20}H_{18}O_6(NO_2)_2$. The two nitro-groups pass one into each of the two piperonylic nuclei existing in cubebin; oxidation of dinitrocubebinolide by means of potassium permanganate yields nitro-

piperonylic acid, $CH_2<\begin{array}{c} O \\ \diagup \quad \diagdown \\ O \end{array}\begin{array}{c} NO_2 \\ \diagdown \quad \diagup \\ CO_2H \end{array}$, m. p. 172°.

In the formation of the two bromo-derivatives of cubebin described by Weidel (A., 1878, 80) and by Angeli and Mola (A., 1895, i, 24), respectively, two of the six oxygen atoms present in the cubebin molecule are displaced, so that the molecule undergoes transformation more profound than mere bromination, this being due to the dehydrating action of the hydrobromic acid evolved during the reaction. Treatment of cubebin with bromine in acetic acid solution containing finely divided calcium carbonate yields: (1) A compound, m. p. 177—178°, which contains two bromine atoms in the molecule, exhibits no lactonic properties, and is to be investigated later, and (2) the compound, $C_{20}H_{16}O_6Br_2$, m. p.

137°, which was obtained previously by the action of bromine on cubebinolide in alcoholic solution and may be regarded as the dibromo-derivative of cubebinolide or as the lactone of dibromohydroxycubebinic acid.

Cubebinolide forms monoclinic crystals, m. p. 63—64° [VIOLA and FERRARI: $a : b : c = 0.20367 : 1 : 0.19998$; $\beta = 109^\circ 4'$]. Concentrated sulphuric acid colours cubebinolide reddish-violet or black and becomes green or greenish-red; if water is added, the acid is completely decolorised, whilst the solid remains dark violet.

Dinitrocubebinolide, $C_{20}H_{16}O_6(NO_2)_2$, crystallises in microscopic, canary-yellow, acicular prisms, m. p. 183—184°, and with concentrated sulphuric acid gives a deep orange-yellow solution which slowly turns yellow and, on dilution with water, gradually becomes decolorised and deposits a straw-yellow precipitate. In chloroform solution it is unaffected by bromine.

With concentrated sulphuric acid, dibromocubebinolide gives a reddish-yellow coloration, which changes immediately to violet-brown and then to dirty green, addition of water causing gradual decolorisation of the solution and deposition of a dirty green precipitate.

The *amide* of *hydroxycubebinic acid*, $C_{20}H_{21}O_6N$, forms stellate aggregates of white, acicular crystals, m. p. 129—130°, decomposing at 165°, and exhibits chemical behaviour analogous to that of the *amide* of *dibromohydroxycubebinic acid*, $C_{20}H_{19}O_6NBr_2$, which crystallises in tufts or fan-shaped aggregates of silky, white needles, m. p. 164—167°, and decomposes at 170°; with benzene, it forms an additive compound, $6C_{20}H_{19}O_6NBr_2 + 5C_6H_6$. T. H. P.

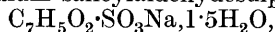
Reactivity of the Nitrobenzaldehydes. GUSTAV HELLER, HILDE LAUTH, and ARNOLD BUCHWALDT (*Ber.*, 1922, **55**, [B], 483—489).—*o*-Nitrobenzaldehyde condenses readily with pyruvic acid in the presence of hydrogen chloride to give *o*-nitrocinnamoylformic acid, but similar compounds cannot be obtained from *m*- and *p*-nitrobenzaldehyde. A review of the literature does not indicate any great difference between the reactivities of the three compounds, and this view is confirmed by a series of experiments now recorded. The peculiar action of the *o*-nitroaldehyde towards pyruvic acid is attributed to the intimate relationship of the nitro-group to the ortho-side chain which cannot be easily expressed by a formula.

The action of sodium hydroxide on a solution of *p*-nitrobenzaldehyde and propaldehyde in alcohol gives *p*-nitro- α -methylcinnamaldehyde, pale yellow needles, m. p. 112—113°; the corresponding *m*-nitro-compound has m. p. 83°. *o*-Nitrostyryl dichloromethyl ketone (from *o*-nitrobenzaldehyde and $\alpha\alpha$ -dichloroacetone) crystallises in colourless prisms, m. p. 106—107°; the corresponding *p*- and *m*-nitro-compounds have m. p. 125° and 116—117°, respectively. *Ethyl* α -*p*-nitrobenzylideneacetate (from an alcoholic solution of the components in the presence of piperidine) forms colourless needles, m. p. 164°, whereas the corresponding ortho-derivative could not be caused to crystallise. *o*-Nitro- α -methyl-

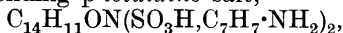
styryl methyl ketone, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH} : \text{CMe} \cdot \text{COMe}$, clusters of pale yellow needles, m. p. $62-63^\circ$, is obtained from *o*-nitrobenzaldehyde and methyl ethyl ketone. It is reduced by zinc dust and concentrated hydrochloric acid in ice-cold alcoholic solution to *o*-amino- α -methylstyryl methyl ketone, m. p., anhydrous, 124° (decomp.), hydrated, m. p. 82° (*benzoyl* derivative, long needles, m. p. 86°); if reduction is effected without cooling, 2:3-dimethylquinoline, m. p. 68° , is produced. It is remarkable that ring closure of the isolated amino-compound cannot be effected by warming with water or acids. *o*-Nitro- α -methylstyryl methyl ketone, slender, pale yellow needles, m. p. $95-96^\circ$ (corresponding amino-compound, pale yellow prisms, m. p. 120°), and *m*-nitro- α -methylstyryl methyl ketone, m. p. 78° , are also described. H. W.

Preparation of Phenylacetaldehyde. SHINTARÔ KODAMA (Jap. Pat. 37212).—One part of phenylalanine is dissolved in excess of 10–25% sulphuric acid and about 0.5 part of 25–30% sodium nitrite is gradually added at the ordinary temperature; part of the α -hydroxy- β -phenylpropionic acid formed crystallises, the remainder being separated in 90% yield as the calcium salt by boiling with calcium carbonate and adding calcium chloride solution. When heated at $120-140^\circ$ for two to three hours, α -hydroxy- β -phenylpropionic acid is converted into its anhydride, and in a vacuum at $250-300^\circ$ it produces phenylacetaldehyde in 60% yield. The latter substance is isolated as the compound with sodium hydrogen sulphite. Cinnamic acid is produced as a by-product in the second treatment. CHEMICAL ABSTRACTS.

Reduction of Substituted Salicylic Acids. HUGO WEIL and KARL BRIMMER (*Ber.*, 1922, 55, [B], 301–305).—Sulphosalicylic acid is reduced by sodium amalgam in the presence of boric acid to sulphosalicylaldehyde in good yield if the latter is protected by a suitable mixture of sulphite and hydrogen sulphite. The aldehyde is precipitated by the addition of aniline, and the compound thus produced is decomposed by steam in alkaline solution, whereby sodium salicylaldehydesulphonate,



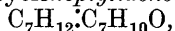
is obtained. Sulphosalicylaldehyde condenses with dimethylaniline in the presence of concentrated sulphuric acid, and the product is converted by sodium hydroxide into the sodium salt, $\text{C}_{23}\text{H}_{25}\text{ON}_2 \cdot \text{SO}_3\text{Na} \cdot 2\text{H}_2\text{O}$, silvery leaflets, which is oxidised to a bluish-green dye. Disulphosalicylic acid is reduced similarly to disulphosalicylaldehyde, the potassium (+ $2\text{H}_2\text{O}$) and barium (+ $2.5\text{H}_2\text{O}$) salts of which are described. Potassium salicylaldehydesulphonate is converted by a small amount of *p*-toluidine into the salt, $\text{C}_{14}\text{H}_{11}\text{ON}(\text{SO}_3\text{K})_2 \cdot \text{H}_2\text{O}$, whereas the disulphoaldehyde yields the corresponding *p*-toluidine salt,



with a relatively larger amount of the base. The aldehyde gives a phenylhydrazone which was isolated in the form of its barium salt, $\text{C}_{13}\text{H}_{10}\text{ON}_2(\text{SO}_3)_2\text{Ba}$.

2-Hydroxybenzene-1 : 3-dialdehyde, long, colourless, hair-like crystals, is obtained by the reduction of *o*-aldehydosalicylic acid; the corresponding *phenylhydrazone*, $C_{20}H_{18}ON_4$, forms yellow crystals. **4-Hydroxybenzene-1 : 2-dialdehyde**, slender, yellow needles, is prepared similarly from *p*-aldehydosalicylic acid; the corresponding *phenylhydrazone* is a yellow, crystalline precipitate. The aldehyde condenses with dimethylaniline in the presence of concentrated sulphuric acid at 110° to form the *substance*, $C_{40}H_{46}ON_4$, which is oxidised by lead peroxide to a blue dye. H. W.

Some Derivatives of Suberone. MARCEL GODCHOT and PIERRE BRUN (*Compt. rend.*, 1922, **174**, 618—620).—Suberone condenses with itself under the influence of calcium hydride (cf. A., 1919, i, 447) to give *cycloheptylidenecycloheptanone*,



b. p. $143\text{--}145^\circ/8$ mm.; d^{14}_4 0.9936; n^{14}_D 1.5144. When reduced by sodium in absolute alcohol, this ketone gives *cycloheptylcycloheptanol*, $C_7H_{13} \cdot C_7H_{12} \cdot OH$, b. p. $158\text{--}161^\circ/20$ mm.; d^{13}_4 0.9908; n^{13}_D 1.5133, which gives an *allophanic* ester, $C_{14}H_{25}O \cdot CO \cdot NH \cdot CO \cdot NH_2$, m. p. 183° .

When brominated in solution in carbon tetrachloride, suberone yields (?) **2 : 7-dibromosuberone**, m. p. 68° , which possesses intense sternutatory and blistering properties. With dilute sodium hydroxide in the cold, it gives a *compound*, obtained as a syrup, which is probably a dihydroxycycloheptanone. W. G.

Syntheses by means of Sodamide. XI. Substitution Derivatives of Benzoylcyclopropane. ALBIN HALLER and EUGÈNE BENOIST (*Ann. Chim.*, 1922, [ix], **17**, 25—37).—Ethyl benzoylacetate condenses with ethylene bromide in the presence of sodium ethoxide to give ethyl 1-benzoylcyclopropane-1-carboxylate (cf. Perkin, T., 1883, **47**, 840), giving an *oxime*, m. p. 152° . The ester on saponification gives the free acid, which on heating at 150° is decomposed, giving benzoylcyclopropane. A better yield of this compound is obtained by the action of cyclopropanecarboxyl chloride on benzene in the presence of aluminium chloride. Benzoylcyclopropane is decomposed by sodamide in moist benzene, giving cyclopropane and benzamide, but in dry benzene, in the presence of this condensing agent, it reacts with alkyl haloids, giving alkylbenzoylcyclopropanes. In this way, the authors have prepared 1-benzoyl-1-methylcyclopropane, b. p. $127\text{--}128^\circ/18$ mm.; d^{25}_4 1.038; n^{25}_D 1.53650; n^{25}_D 1.54171; giving an *oxime*, m. p. 115° (decomp.), and a *p*-nitrophenylhydrazone, m. p. 112° ; 1-benzoyl-1-allylcyclopropane, b. p. $136\text{--}137^\circ/16$ mm.; and 1-benzoylbenzylcyclopropane, m. p. $33\cdot5^\circ$; d^{25}_4 1.0795; n^{25}_D 1.57229; n^{25}_D 1.57782; n^{25}_B 1.59231; n^{25}_γ 1.90469. With sodamide in moist benzene, these three compounds behave differently. The methyl derivative gives benzamide and methylcyclopropane, the allyl derivative is undecomposed, and the benzyl derivative gives 1-benzylcyclopropane-1-carboxylamide, m. p. 84° , from which the free acid, m. p. 103° , is obtained on hydrolysis. On oxidation, benzoylbenzylcyclopropane gives a *compound*,

$C_{17}H_{14}O_2$, m. p. 86—87°, on which molecular weight determinations do not give results corresponding with dibenzoylcyclopropane.

The following physical constants are recorded: Benzoylcyclopropane, d^{25}_4 1.0453; n^{25}_a 1.53798; n^{25}_D 1.54335; n^{25}_β 1.55701; n^{25}_γ 1.56992; ethyl 1-benzoylcyclopropanecarboxylate, d^{25}_4 1.1355; n^{25}_a 1.52899; n^{25}_D 1.53525; n^{25}_β 1.54862; n^{25}_γ 1.55674. W. G.

The Synthesis of β -Keto-bases from Acetophenone, Formaldehyde, and Amine Salts. C. MANNICH and G. HEILNER (*Ber.*, 1922, 55, [B], 356—365).—The synthesis, previously applied to aliphatic ketones (A., 1917, i, 634) and to cyclohexanone (A., 1920, i, 850), has now been extended to acetophenone as a typical fatty-aromatic ketone.

ω -Dimethylaminopropiophenone hydrochloride, leaflets or needles, m. p. 156°, is readily obtained when equivalent quantities of acetophenone, paraformaldehyde, and dimethylamine hydrochloride are heated to boiling in concentrated alcoholic solution: $COMePh + CH_2O + NHMe_2 \cdot HCl \rightarrow CPh \cdot CH_2 \cdot CH_2 \cdot NMe_2 \cdot HCl + H_2O$. The corresponding base is a colourless liquid, b. p. 110—112°/14 mm. (oxime, plates, m. p. 108°). It is oxidised by potassium permanganate to benzoic acid, carbon dioxide, and dimethylamine. It is very readily hydrolysed (by treating the hydrochloride with steam) to dimethylamine and phenyl vinyl ketone. Reduction leads to the formation of different substances according to the experimental conditions. Hydrogenation of the hydrochloride with palladium and hydrogen generally gives α -phenyl- γ -dimethylaminopropane- α -ol hydrochloride, $OH \cdot CHPh \cdot CH_2 \cdot CH_2 \cdot NMe_2 \cdot HCl$, leaflets, m. p. 135—136° (the corresponding free base is a liquid; the hydrochloride of the benzoate has m. p. 170°), but, on one occasion, proceeded to the production of γ -dimethylamino-*n*-propylbenzene. Treatment of ω -dimethylaminopropiophenone with activated aluminium in ethereal solution only gives the corresponding secondary alcohol in minor amount, the main product being a mixture of $\alpha\zeta$ -bis-dimethylamino- $\gamma\delta$ -diphenylhexane- $\gamma\delta$ -diols,

$NMe_2 \cdot CH_2 \cdot CH \cdot CPh(OH) \cdot CPh(OH) \cdot CH_2 \cdot CH_2 \cdot NMe_2$,
[α -form, m. p. 146°, β -variety, m. p. (indefinite) 107°, after softening at about 100°].

The action of methylamine hydrochloride on formaldehyde and acetophenone leads to the production of $\alpha\alpha'$ -bisphenacylmethylmethyllamine, $(CPh \cdot CH_2 \cdot CH_2)_2NMe$, and ω -methylaminopropiophenone, $COPh \cdot CH_2 \cdot CH_2 \cdot NHMe$. The former, which is formed in larger quantity, crystallises in small rods or needles, m. p. 142°, and yields a hydrochloride, needles grouped in rosettes, m. p. 162°. The latter is a very unstable liquid which is most conveniently obtained by the action of a current of steam on the hydrochloride of the tertiary base; its hydrochloride crystallises in leaflets, m. p. 139—141°. The reduction of $\alpha\alpha'$ -bisphenacylomethylmethyllamine by activated aluminium in the presence of moist ether does not proceed uniformly; it was found possible with some difficulty to isolate two crystalline substances [leaflets, m. p. 205°, and slender needles, m. p. (indefinite) 180°, after softening at about 170°] to

which, on the results of analysis, the formula $C_{19}H_{23}O_2N$ is assigned. Probably they represent the racemic and meso-forms of the cyclic pinacone, $NMe \begin{matrix} < CH_2 \cdot CH_2 \cdot CPh \cdot OH \\ CH_2 \cdot CH_2 \cdot CPh \cdot OH \end{matrix}$ H. W.

Glyoximes and Peroxides. D. BIGIAVI (*Gazzetta*, 1921, 51, ii, 324—329).—Angeli, Alessandri, and Aiazzi-Mancini (A., 1911, i, 544) found that the action of magnesium phenyl bromide on the peroxide of piperylmethylglyoxime yields piperonylonitrile and acetophenone, the latter probably resulting from decomposition of a nitronic acid. The author has now extended this reaction to other peroxides and investigated the conditions in which nitriles yield ketones when treated with magnesium alkyl derivatives.

The action of magnesium phenyl bromide on benzonitrile in ethereal solution yields an appreciable proportion of benzophenone, and piperonylonitrile, under similar conditions, gives a compound which melts indistinctly at about 50° , but could not be identified with phenyl piperonyl ketone.

The interaction of magnesium methyl iodide and piperylmethylglyoxime peroxide in benzene solution gives piperonylonitrile and acetopiperone, $CH_2 \cdot O_2 \cdot C_6H_3Ac$, the latter being undoubtedly formed by further action of the magnesium derivative on the nitrile. The action of magnesium phenyl bromide on anisylmethylglyoxime peroxide in benzene solution yields anisonitrile and, by treatment of the aqueous liquid with dilute sulphuric acid, a green oil which is probably the nitroso-alcohol derived from the isomeric nitronic acid, $CPhMe \cdot NO \cdot OH \rightarrow NO \cdot CPhMe \cdot OH$; this nitroso-alcohol decomposes rapidly, giving a brown oil, consisting principally of acetophenone.

Closely related to the structure of the peroxides is that of the dioximes obtained when the former are reduced by means of zinc and the calculated proportion of acetic acid. Beckmann and Köster's conclusion that such dioximes are *amphi*-dioximes (A., 1893, i, 474), $\begin{matrix} R \cdot C & \text{---} & C \cdot R' \\ || & & || \\ NOH & & NOH \end{matrix}$, is of doubtful accuracy, since in the

reaction on which it is based phosphorus pentachloride is used, and preference may be given to the *syn*-dioxime structure corresponding with Koreff's formula for the peroxides, $\begin{matrix} C & \text{---} & C \\ || & & || \\ NO \cdot & & NO \end{matrix}$ (A., 1886, 363). These dioximes exhibit, indeed, properties distinguishing them from their isomerides: they have lower melting points and are unstable, undergoing isomerisation when heated; when their diacetyl derivatives are hydrolysed and, in some cases, when the dioximes themselves are heated, furazans are formed more readily than from the isomeric dioximes.

Extension of Tschugaev's experiments (A., 1908, i, 554) shows that *syn*-glyoximes with both radicles aliphatic form complex nickel compounds, whereas those with one or two aromatic radicles do not form such compounds. Dimethylglyoxime, obtained by reduction of the peroxide, forms the red nickel complex salt. Of the two piperylmethylglyoximes, the γ -compound, m. p. 159° ,

formed on reduction of the peroxide, forms no complex, but the β -dioxime, m. p. 209° , prepared by heating the γ -isomeride at 160° , forms a dark red *nickel complex*, $C_{30}H_{18}O_8N_4Ni$. Of the four dioximes of camphor (Forster, T., 1903, **83**, 519), only the α -isomeride, m. p. 199° , obtained by reduction of the peroxide, forms a *nickel complex*, $C_{30}H_{44}O_6N_6Ni_2$; this result is in agreement with the conclusions given above, since in the camphordioximes the two aliphatic radicles united to the group $\cdot C(NO\dot{H})\cdot C(NO\dot{H})\cdot$ are joined to form a ring.

Benzoylglyoxime peroxide gives the same dioxime when reduced by means of zinc and the calculated amount of acetic acid as by reduction with platinum black and hydrogen, and the same is the case with camphordioxime peroxide. T. H. P.

Crystallography of Derivatives of Benzophenone. F. M. JAEGER (*Z. Kryst. Min.*, 1921, **56**, 46—61; from *Chem. Zentr.*, 1921, iii, 1159—1160).—Crystallographic descriptions are given of a number of derivatives of benzophenone. Benzophenone, m. p. 36° and 48.5° ; rhombic bipyramidal ($a:b:c=0.8511:1:0.6644$). 2-Nitrobenzophenone, m. p. 105° ; monoclinic prismatic ($a:b:c=0.8961:1:0.4706$, $\beta=87^\circ 42.5'$). 2-Chlorobenzophenone, lustrous, colourless needles, m. p. 45.5° ; monoclinic prismatic ($a:b:c=0.4985:1:0.4706$, $\beta=83^\circ 8'$). 2-Iodobenzophenone, colourless crystals, m. p. 32° ; triclinic pinacoidal ($a:b:c=1.0966:1:1.4193$, $\alpha=98^\circ 57'$, $\beta=83^\circ 22.5'$, $\gamma=93^\circ 9'$). 2:4-Dibromobenzophenone, colourless plates, m. p. 55° ; rhombic bipyramidal ($a:b:c=0.7168:1:0.2945$). 2:4'-Dibromobenzophenone, prisms and tablets, m. p. 62° ; monoclinic prismatic ($a:b:c=1.0962:1:0.5951$, $\beta=68^\circ 25.5'$). 2-Bromobenzophenone, m. p. 42° ; monoclinic prismatic ($a:b:c=0.5045:1:0.9322$, $\beta=83^\circ 24.5'$). 2:4'-Dichlorobenzophenone, m. p. 66° ; monoclinic prismatic ($a:b:c=0.5139:1:0.4654$, $\beta=81^\circ 21'$). 2:4:6-Trichlorobenzophenone, m. p. 102° ; triclinic pinacoidal ($a:b:c=1.3908:1:1.1537$, $\alpha=120^\circ 41'$, $\beta=110^\circ 27.5'$, $\gamma=77^\circ 20'$). 2:4:6-Tribromobenzophenone, m. p. 147° ; triclinic pinacoidal ($a:b:c=1.3939:1:1.1065$, $\alpha=120^\circ 59.5'$, $\beta=108^\circ 44'$, $\gamma=75^\circ 20'$). 2-Chloro-4'-nitrobenzophenone, yellow tablets from benzene, thick plates or prisms from ethyl acetate, m. p. 107.5° ; rhombic bipyramidal ($a:b:c=2.6857:1:1.7153$). 2-Chloro-4'-aminobenzophenone, yellow crystals, m. p. 112° ; monoclinic prismatic ($a:b:c=0.5141:1:0.4824$, $\beta=81^\circ 5'$). 4-Chloro-3-nitrobenzophenone, short, light yellow prisms, m. p. 105° ; rhombic bipyramidal ($a:b:c=0.9363:1:0.5740$). 4-Chloro-4'-nitrobenzophenone, light yellow, flat needles, m. p. 100.8° ; triclinic pinacoidal ($a:b:c=1.166:1:0.995$, $\alpha=119^\circ 27'$, $\beta=122^\circ 36'$, $\gamma=89^\circ 40'$). 4-Bromo-3-nitrobenzophenone, light yellow, flat needles or prisms, m. p. 113° ; rhombic bipyramidal ($a:b:c=1.5453:1:0.3847$). 4-Bromo-3-aminobenzophenone, light yellow tablets, m. p. 85° ; monoclinic prismatic ($a:b:c=1.9883:1:1.1745$, $\beta=86^\circ 58'$). 4:4'-Dibromo-3-nitrobenzophenone, yellow needles, m. p. 119.5° ; monoclinic sphenoidic (?) ($a:b:c=2.6352:1:4.4498$, $\beta=89^\circ 10.75'$). 4-Bromo-3:4'-dinitrobenzophenone, long, light yellow needles, m. p. 139.5° ; rhombic

bipyramidal ($a : b : c = 1.6350 : 1 : 1.288$). 4-Methylbenzophenone, monoclinic prismatic ($a : b : c = 1.0117 : 1 : 0.4118$, $\beta = 84^\circ 46'$); a second form is rhombohedral and hemimorphic ($a : c = 1 : 1.2254$). 3:4'-Dimethylbenzophenone, m. p. 82° ; monoclinic prismatic ($a : b : c = 1.0409 : 1 : 0.4154$, $\beta = 88^\circ 15'$). 2:5-Dimethylbenzophenone, m. p. 36° ; rhombic bipyramidal ($a : b : c = 0.8371 : 1 : 0.4048$). 2:4:6-Trimethylbenzophenone, m. p. 35° ; rhombic bisphenoidic ($a : b : c = 0.7682 : 1 : 0.2243$). 2-Bromo-4-ethoxybenzophenone, prisms, m. p. 79.5° ; rhombic bipyramidal ($a : b : c = 0.6907 : 1 : 0.6915$).

G. W. R.

Hydroxynaphthaquinone. IV. New Derivatives of 2:3:8-Tribromo-5-hydroxy-1:4-naphthaquinone. ALVIN S. WHEELER and T. M. ANDREWS (*J. Amer. Chem. Soc.*, 1921, **43**, 2582—2587; cf. A., 1919, i, 490).—Further evidence is given of the marked reactivity of the bromine atom in position 8 in 2:3:8-tribromo-5-hydroxy-1:4-naphthaquinone. It can be replaced by chlorine or by hydroxyl, phenylamino-, *o*-tolylamino-, *p*-tolylamino-, or *p*-bromophenylamino-groups. If the bromine atom in position 8 is first replaced by a hydroxyl group and the product then reduced by zinc dust in acid solution, a dibromotetrahydroxynaphthalene is obtained, but if zinc dust in alkaline solution is used, a tetrahydroxynaphthalene is obtained. Reduction of the original tribromonaphthaquinone with zinc dust in acid solution gives a tribromotrihydroxynaphthalene. The sodium salt of 2:3:8-tribromo-5-hydroxy-1:4-naphthaquinone gives ethers when boiled with alkyl haloids.

The following new compounds are described:

1:4:5:8-Tetrahydroxynaphthalene, m. p. 224° . 2:3-Dibromo-1:4:5:8-tetrahydroxynaphthalene, $C_{10}H_2Br_2(OH)_4$, m. p. 164 — 166° , giving a tetra-acetyl derivative, m. p. 149 — 150° . 2:3-Dibromo-8-hydroxy-5-acetoxy-1:4-naphthaquinone, m. p. 197° . 2:3:8-Tribromo-1:4:5-trihydroxynaphthalene, m. p. 106 — 107° , giving a triacetyl derivative, m. p. 219 — 220° ; and with water a compound, m. p. 168° . 2:3-Dibromo-8-hydroxy-5-methoxy-1:4-naphthaquinone, m. p. 209 — 210° , and 2:3-dibromo-8-hydroxy-5-ethoxy-1:4-naphthaquinone, m. p. 134 — 136° , giving a sodium salt, which dyes silk a champagne colour. 8-Chloro-2:3-dibromo-5-acetoxy-1:4-naphthaquinone, m. p. 159.5 — 160° .

By boiling tribromojuglone in alcoholic solution with certain aromatic bases, the following arylamino-derivatives were obtained: 2:3-Dibromo-5-hydroxy-8-anilino-1:4-naphthaquinone, m. p. 234.5 — 235.5° ; 2:3-dibromo-5-hydroxy-8-*o*-toluidino-1:4-naphthaquinone, m. p. 187.5 — 189° ; 2:3-dibromo-5-hydroxy-8-*p*-toluidino-1:4-naphthaquinone, m. p. 216 — 217° ; 2:3-dibromo-5-hydroxy-8-*p*-bromoanilino-1:4-naphthaquinone, m. p. 254 — 256° . With *p*-nitroaniline a compound, m. p. 159.5 — 160° , containing a high percentage of bromine was obtained.

W. G.

Production of Hydroxy-derivatives of Anthraquinone. ARTHUR HUGH DAVIES and SCOTTISH DYES, LTD. (Brit. Pat. 174101).—Dihydroxyanthraquinones are obtained by heating in

an autoclave monochloroanthraquinones and solutions of alkali hydroxides in presence of oxidising agents such as chlorates or nitrates. For example, alizarin is obtained by heating a mixture of 78 parts of 2-chloroanthraquinone, 275 parts of sodium hydroxide, 11.3 parts of sodium chlorate, and 850 parts of water for twenty-four hours at 170°. The reaction mixture is diluted with 2000 parts of water, boiled, filtered, and the residue again extracted with boiling sodium hydroxide solution. From the combined filtrates, the alizarin is precipitated by the addition of hydrochloric acid.

G. F. M.

Alizarin-iron Lakes. ARTHUR W. BULL and J. R. ADAMS (*J. Physical Chem.*, 1921, **25**, 660—664).—The adsorption isotherm of *N*/10-sodium hydroxide by hydrated ferric oxide has been determined at 22°. The adsorption of sodium alizarin by hydrated ferric oxide suspensions was also determined at the same temperature and the amount of sodium hydroxide set free ascertained; this quantity was found to be small in all cases. The influence of alizarin on the adsorption of sodium hydroxide by ferric hydroxide is also found to be very small. The experimental data indicate that the iron-alizarin lake described by Biltz (A., 1906, ii, 78) is not a true chemical compound ferric alizarate, but an adsorption complex of ferric hydroxide and sodium alizarin.

J. F. S.

Arylaminoanthraquinone Derivatives. A. LÜTTRINGHAUS and L. EIFFLAENDER (U.S. Pat. 1394851).—The preparation is effected by treating an aminoanthraquinone compound containing one or more amino-groups (substituted or unsubstituted) with metal arylamides in the presence of primary amino-compounds such as aniline. For example, 1-amino-4-anilino-2-methylantraquinone is obtained when magnesium shavings are boiled with aniline and sodamide, and the magnesium anilide caused to react with 1-amino-2-methylantraquinone, the product being extracted with acetone and recrystallised from glacial acetic acid. Variations of the process are described by means of which the following may be prepared: 1-amino-4-anilino-2-methylantraquinone (violet-black prisms, m. p. 244°), (?) 1-amino-4-anilinoanthraquinone (m. p. 232°), 1-amino-4-*p*-toluidino-2-methylantraquinone, di-anilinoanthraquinone (dark violet crystals, m. p. 152°). The last-named compound, when oxidised with air in aniline solution at 90° containing some sodium or potassium hydroxide, yields anthraquinonedihydro-*N*-phenylphenazine, m. p. 233°.

Similar reactions may be applied to the aminochloroanthraquinones.

CHEMICAL ABSTRACTS.

A New Class of Coloured Reduction Products of 1-Benzoylanthraquinones or of 2 : 3-Phthaloylbenzophenones. ALFRED SCHAAERSCHMIDT (*Ber.*, 1922, **55**, [B], 489; cf. A., 1915, i, 566, 696; 1916, i, 408).—A reply to Scholl (A., 1921, i, 872).

H. W.

Amino- and Anilino-phenanthraquinones. KURT BRASS and ERWIN FERBER (*Ber.*, 1922, **55**, [B], 541—556). Vat dyes cannot be prepared by interaction of phenanthraquinone with *p*-diamines

n* 2

in the same way as from α -naphthaquinone (Pummerer and Brass, A., 1911, i, 654; Brass and Papp, A., 1920, i, 398; Brass, A., 1912, i, 1874) or anthraquinone (D.R.-P. 230409, 243489). Instead, valueless, dark coloured products of high melting point are obtained. After attempts to prepare 2-anilinophenanthraquinone, $C_{20}H_{13}O_2N$, a black powder, by interaction of 2-bromophenanthraquinone with aniline, or acetanilide, or derivatives, had failed, this compound was obtained by heating 2-aminophenanthraquinone (best obtained from the nitro-derivative by means of sodium hyposulphite or sodium hydrogen sulphide) with bromobenzene and pyridine at $160-170^\circ$ in presence of copper. From 2-acetylaminophenanthraquinone, $C_{16}H_{11}O_3N$, reddish-violet needles, m. p. 324° (decomp.), ethyl bromide and pyridine at 180° , 2-ethylaminophenanthraquinone, $C_{16}H_{13}O_2N$, crystallising in violet-black nodules, is obtained. 2-Acetyl-amino-9:10-phenanthraquinyl diacetate, $C_{20}H_{17}O_5N$, needles, m. p. 228° , results from the acetylating reduction of 2-aminophenanthraquinone. 2-op-Dinitroanilinophenanthraquinone, $C_{20}H_{11}O_6N_3$, m. p. 280° , from chloro-2:4-dinitrobenzene, is easily converted into 2-op-dinitroanilinodiphenyleneglycollic acid, a brown, amorphous powder [lead salt ($C_{20}H_{12}O_7N_3$) $_2$ Pb]. Similarly, 2-oo'-p-trinitroanilinophenanthraquinone, $C_{20}H_{10}O_8N_4$, minute reddish-brown plates, m. p. $304-305^\circ$, furnishes 2-oo'-p-trinitroanilinodiphenyleneglycollic acid, $C_{20}H_{12}O_9N_4$ [lead salt ($C_{20}H_{11}O_9N_4$) $_2$ Pb]. 4-Aminophenanthraquinone is best prepared from the nitro-derivative by means of sodium hydrogen sulphide. 2-Bromo-9:10-phenanthraquinyl dibenzoate (D.R.-P. 151981) is best prepared by benzoylation of a solution of the 2-bromophenanthraquinone in sodium hyposulphite solution in presence of hydrogen, and does not react with aniline.

J. K.

Syntheses by means of Sodamide. X. The *p*-Aminobenzylidene- and *p*-Aminobenzyl-camphors and some of their Derivatives. ALBIN HALLER and PAUL BOUDIN (*Ann. Chim.*, 1922, [ix], 17, 5—25).—Depolymerised *p*-aminobenzaldehyde condenses with *d*-camphor in the presence of sodamide, giving *d*-*p*-aminobenzylidenecamphor, m. p. 133° ; $[\alpha]_D + 745^\circ$ (in alcohol), which gives an acetyl derivative, m. p. 208° ; $[\alpha]_D + 427^\circ$; a hydrochloride, m. p. 184° (decomp.), a hydrobromide, m. p. 208° (decomp.), and a sulphate. When the sulphate is treated with potassium nitrite and sulphuric acid in alcoholic solution, it yields benzylidenecamphor, but in aqueous solution the product is *p*-hydroxybenzylidenecamphor, m. p. 207° . When *p*-aminobenzylidenecamphor is diazotised and the product submitted to the Sandmeyer reaction, *p*-chlorobenzylidenecamphor, m. p. 109° ; $[\alpha]_D + 385^\circ$; *p*-bromobenzylidenecamphor, m. p. 134° , or *p*-cyanobenzylidenecamphor, m. p. 162° , b. p. $251^\circ/16$ mm. (decomp.); $[\alpha]_D + 425^\circ$, are obtained. If the diazonium salt is coupled with β -naphthol, β -hydroxynaphthalene-1-azo-*p*-benzylidenecamphor, m. p. 220° , is the product. *p*-Aminobenzylcamphor, m. p. 82° ; $[\alpha]_D + 214^\circ$, is obtained by reducing the benzylidene compound in alcoholic solution with sodium amalgam. The following compounds derived from it are described. *p*-Acetyl-

aminobenzylcamphor, m. p. 172° ; $[\alpha]_D +176^{\circ}$; *benzylcamphor*, m. p. 52° ; *p-hydroxybenzylcamphor*, m. p. 184° ; $[\alpha]_D +406^{\circ}$; *p-chlorobenzylcamphor*, m. p. 73° ; $[\alpha]_D 92.9^{\circ}$; *p-bromobenzylcamphor*, m. p. 90° ; $[\alpha]_D +87.9^{\circ}$; *p-cyanobenzylcamphor*, m. p. 145° ; $[\alpha]_D +334.5^{\circ}$, and β -*hydroxynaphthalene-1-azo-p-benzylcamphor*, m. p. 129° .
W. G.

Biogenesis of Oil of Peppermint. R. E. KREMERS (*J. Biol. Chem.*, 1922, **50**, 31—34).—An investigation of the cohobated oils of American and Japanese peppermints showed that the latter consisted almost wholly of pulegone, whilst the former contained menthone and menthol as main constituents, and, in addition, 1-methylcyclohexan-3-one. Acetone was present in the cohobated aqueous distillate.

Schemes for the possible biogenesis of the main constituents of the oils of peppermint (*Mentha piperita*) and spearmint (*Mentha spicata*) are outlined.
E. S.

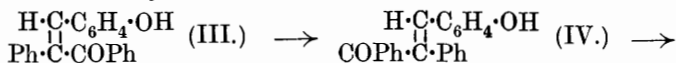
Oil of *Satureja montana* of Italian Origin. P. LEONE and E. ANGELESCU (*Gazzetta*, 1921, **51**, ii, 386—390).—This oil contains 28% of carvacrol, 1.58% of esters, 10% of alcohols which have not been identified, 27% of cymene, and 14% of dipentene (cf. *J. Soc. Chem. Ind.*, 1922, 269A).
T. H. P.

Oil of *Thymus vulgaris* of Italian Origin. P. LEONE and E. ANGELESCU (*Gazzetta*, 1921, **51**, ii, 391—395).—This oil contains 38% of phenols consisting almost solely of thymol, 19% of free alcohols probably composed mostly of borneol and linalool, 18% of cymene, and small proportions of esters and free acids (cf. *J. Soc. Chem. Ind.*, 1922, 269A).
T. H. P.

The Composition of the Essential Oil of Turpentine from Aleppo. GEORGES DUPONT (*Compt. rend.*, 1922, **174**, 395—398).—The essential oil of turpentine from Aleppo contains a small amount of material which does not distil over except at a temperature much higher than the boiling point of pinene. This fraction is found to consist of *i*-bornyl acetate and a sesquiterpene not identified, the composition of the fresh essence being approximately *d*-pinene 95%, *i*-bornyl acetate 1.14%, sesquiterpene 3.8%.
W. G.

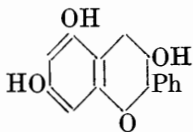
Estimation of the Molecular Magnitude of Caoutchouc by Chemical Methods. C. HARRIES and FRITZ EVERS (*Wiss. Veröffentl. Siemens-Konzern*, 1921, **1**, 87—95).—Reduction of the dihydrochloride of caoutchouc in ethylene dichloride solution by means of zinc dust, yields a large amount of α -hydrocaoutchouc as a light yellow, amorphous, somewhat elastic mass melting between 120° and 130° . From its molecular weight in bromoform, it appears to be a polymeride of $C_{35}H_{62}$ or $C_{40}H_{70}$. α -Hydrocaoutchouc is readily converted into an ozonide and yields a hydrochloride (m. p. 190 — 195°) and a bromide. The conclusion is drawn that the caoutchouc molecule contains 35 or 40 carbon atoms, most probably the latter, and that the structural formula contains eight $CH_2 \cdot C(CH_3) \cdot CH \cdot CH_2$ groups joined together in a 32-atom ring.
A. R. P.

Ring Opening in the Benzopyrylium Series. HERMAN DECKER and PAUL BECKER (*Ber.*, 1922, **55**, [B], 375—394; cf. Decker and Fellenberg, *A.*, 1907, i, 950; 1909, i, 116; Decker and Felser, *A.*, 1908, i, 906, 1003).—The interest in the benzopyrylium dyes has been enhanced greatly by the discovery of the wide distribution in plants. Examination has now been made of the opening of the ring of a pyranol which does not contain a hydroxyl group. A suitable initial material is found in the product of the condensation of deoxybenzoin with salicylaldehyde. The changes which have been realised are expressed by the following scheme: $C_6H_4 \begin{smallmatrix} \text{CH}=\text{CPh} \\ \text{O}=\text{CPh} \end{smallmatrix}$ (I.) $\rightarrow C_6H_4 \begin{smallmatrix} \text{CH}=\text{CPh} \\ \text{O}—\text{CPh}\cdot\text{OH} \end{smallmatrix}$ (II.) \rightarrow



$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CHO} + \text{CH}_2\text{Ph}\cdot\text{COPh}$. The phenomena are very closely similar to those observed when coumarin is treated with solutions of alkali hydroxides.

The relationships of the pyranols to the anthocyanidanoles is also discussed. The parent substance of the latter appears to be 3:5:7-trihydroxy-2-phenylbenzopyran (annexed formula) which may be expected to pass by fission of the ring into the derivative of vinyl alcohol, $C_6H_2(\text{OH})_3\cdot\text{CH}\cdot\text{C}(\text{OH})\cdot\text{COPh}$, and subsequently into the ketone, $C_6H_2(\text{OH})_3\cdot\text{CH}\cdot\text{CO}\cdot\text{COPh}$. The latter would decompose into benzoic and formic acids, which have been observed frequently, and methylphloroglucinol, which has not been isolated up to the present.



Deoxybenzoin condenses with salicylaldehyde in hydrochloric acid solution to give 2:3-diphenylbenzopyrylium chloride in 88.5% yield (cf. Decker and Fellenberg, *loc. cit.*); if the condensation is arrested by the addition of carbon dioxide or acetic acid when the mixture has attained its maximal colour, *o*-coumarophenone is precipitated in quantitative yield. 2:3-Diphenylbenzopyran-2-ol (formula II), almost colourless plates, m. p. 123—124°, is obtained by the gradual addition of a solution of the double salt of ferric chloride and 2:3-diphenylbenzopyrylium chloride in glacial acetic acid to water; it is almost unaffected by cold, dilute hydrochloric acid or sodium hydroxide solution, but dissolves readily in the hot reagents. It reacts readily with hot aliphatic alcohols, yielding the corresponding ethers, $C_6H_4 \begin{smallmatrix} \text{CH}\cdot\text{CPh} \\ \text{O}—\text{CPh}\cdot\text{OAlk} \end{smallmatrix}$ (*ethyl ether*, m. p.

77—78°; *methyl ether*, m. p. 75—76°; *propyl ether*, coarse prisms, m. p. 70—71°; *isobutyl ether*, prisms, m. p. 68—69°. The ethyl is converted into the *isobutyl* compound when warmed with an excess of *isobutyl* alcohol). If the crystalline carbinol is warmed with sodium hydroxide solution (1%) until the maximal intensity of colour is developed and the solution is then cooled, *trans-α-phenyl-o-coumarophenone* [α -salicylylidenedeoxybenzoin] (formula IV) is deposited in the form of the characteristic *sodium* salt, dark

red, lustrous needles ($+3\text{H}_2\text{O}$), from which the free substance, pale red needles, m. p. $154\text{--}155^\circ$, is liberated by carbon dioxide. The latter is re-converted by hydrochloric acid into 2:3-diphenylbenzopyrylium chloride, which is identified as the additive compound with ferric chloride. α -Phenyl-*o*-coumarophenone is isomerised when heated at its melting point or in the presence of boiling toluene to phenylbenzopyranol, m. p. $123\text{--}124^\circ$. It is hydrolysed by boiling alcoholic sodium hydroxide solution to deoxybenzoin and salicylaldehyde. It is converted by methyl sulphate in the presence of sodium hydroxide into the corresponding ether, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CPhBz}$, pale yellow, lustrous needles, m. p. 141° .

The analogy of phenylbenzopyranol with coumarin suggests that, under the action of alkali hydroxide, the *sodium* salt of an unstable *cis*-phenyl-*o*-coumarophenone is initially formed which passes into the more stable *trans*-variety. This appears to be the case, since an emulsion of the carbinol is dissolved immediately by sodium hydroxide with the formation of a yellow solution from which concentrated sodium hydroxide precipitates an amorphous yellow salt. Attempts to isolate the free *cis*-phenyl-*o*-coumarophenone (formula III) were unsuccessful owing to its immediate re-conversion into phenylbenzopyranol. Its intermediate existence is, however, placed beyond doubt by the isolation of its *methyl ether*, irregular hexagonal platelets, m. p. $111\text{--}112^\circ$.

The action of sodium hydroxide on an alcoholic solution of deoxybenzoin and salicylaldehyde leads to the formation of a *polymeride* of the latter, colourless leaflets, m. p. $120\text{--}121^\circ$, in place of the desired diphenylcoumaroketone.

It appeared desirable to follow the sequence of changes with a benzopyrylium salt which leads to the production of a ketone of established constitution. This is effected with 2-phenylbenzopyranol. The colourless emulsion of the latter is slowly dissolved by sodium hydroxide, probably with initial formation of the *cis*-ketone; when, however, the solution has attained its maximal intensity of colour, it yields *trans*-coumarophenone when treated with carbon dioxide or the sodium salt of this compound when treated with concentrated sodium hydroxide. Protracted warming of the alkaline solution of *trans*-coumarophenone leads to the almost quantitative production of acetophenone and salicylaldehyde.

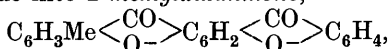
H. W.

The Xanthone Series. ANNA MARIE V. DEM KNESEBECK and FRITZ ULLMANN (*Ber.*, 1922, **55**, [B], 306—316).—A continuation of the work of Ullmann and Schmidt (*A.*, 1920 i, 53).

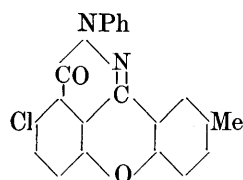
3:6-Dichlorophthalic anhydride condenses with *p*-cresol in the presence of aluminium chloride and acetylene tetrachloride to form 3:6-dichloro-2-*p*-hydroxy-*m*-toluoylbenzoic acid,

$\text{OH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{CO}\cdot\text{C}_6\text{H}_2\text{Cl}_2\cdot\text{CO}_2\text{H}$,
pale brown needles, m. p. 187° . The latter is transformed by boiling potassium carbonate solution (20%) into 7-chloro-2-methylxanthone-8-carboxylic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_2\text{Cl}\cdot\text{C}_6\text{H}_3\text{Me}$,

pale yellow needles, m. p. 286° (corr., decomp.), the *potassium* salt of which is described. When heated above its melting point, the acid loses carbon dioxide and gives 7-chloro-2-methylxanthone, colourless needles, m. p. 169° (corr.). The acid contains a mobile halogen atom, and is therefore converted by potassium phenoxide in the presence of copper powder into 7-phenoxy-2-methylxanthone-8-carboxylic acid, colourless needles, m. p. 270—280° (corr.), according to the rate of heating (the *sodium* salt is described). The phenoxy-acid is transformed by concentrated sulphuric acid or, preferably, by successive treatment with phosphorus pentachloride and aluminium chloride into 2-methyldixanthone,



pale yellow needles, m. p. 349—352° (decomp.), which is converted by hydrazine hydrate into the corresponding *azine*, $\text{C}_{21}\text{H}_{12}\text{O}_2\text{N}_2$, long, vivid yellow, matted needles, m. p. 273° (decomp.), which gives a *hydrochloride*, $\text{C}_{21}\text{H}_{13}\text{O}_2\text{N}_2\text{Cl}$, red needles, m. p. about 274° (decomp.). 7-Chloro-2-methylxanthone-8-carboxylic acid yields only traces of methylanilinoxanthonecarboxylic acid when heated with aniline and copper powder, the chief product being 7-anilino-2-methylxanthone, yellowish-green needles, m. p. 255—259° (corr.). 7-Chloro-N-phenyl-2-methylpyridazonexanthone (annexed formula), yellow needles, m. p. 264—266° (corr.), is readily obtained by heating 7-chloro-2-methylxanthone-8-carboxylic acid with phenylhydrazine; it is converted by boiling aniline in the presence of potassium and copper acetates into 7-anilino-N-phenyl-2-methylpyridazonexanthone, unusually slender, yellowish-green crystals, m. p. 257—258° (corr.).



3 : 4-Dichloro-2-p-hydroxy-m-toluoylbenzoic acid, m. p. 265° (corr.), is prepared from 3 : 4-dichlorophthalic anhydride in the manner described for the 3 : 6-dichloro-isomeride.

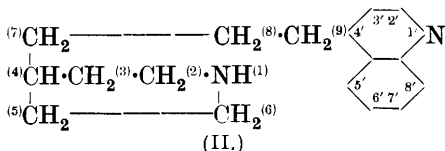
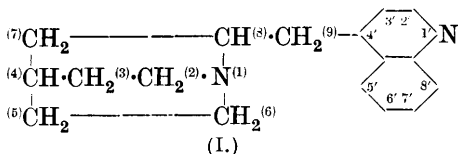
It is converted readily by boiling alkalis into 5-chloro-2-methylxanthone-8-carboxylic acid, pale brown needles, m. p. 289—295° (corr.), in which the halogen atom is not replaced by boiling aniline in the presence of copper powder. The acid is transformed by boiling phenylhydrazine into 5-chloro-N-phenyl-2-methylpyridazonexanthone (annexed formula), long, thin needles, m. p. 266—271° (corr.).

H. W.

Some Reactions of Benzanthrone. ARTHUR GEORGE PERKIN and GEORGE DOUGLAS SPENCER (T., 1922, 121, 474—482).

Cinchona Alkaloids. XXIII. Nomenclature and Isomerism Phenomena. PAUL RABE (Ber., 1922, 55, [B], 522—532; cf. A., 1921, i, 438).—For the parent substance (I) of the cinchona-alkaloids, the name "*ruban*" is suggested, as a basis of

nomenclature, indicative of their occurrence in the *Rubiaceæ*, whilst the compound (II) from which the toxins are derived is termed *rubatoxan*.



Objection is taken to the extension of the term "quinatoxin" to those 4-quinolyl ketones (Ruzicka, A., 1921, i, 585) not derived from 9-rubatoxanone. Of the thirty-two stereoisomeric forms of 3-vinyl-9-rubanol (cinchonine) to be anticipated from the presence of

four asymmetric carbon atoms, with an asymmetric trivalent nitrogen atom, only sixteen are actually capable of existence, owing to the fact that the nitrogen atom and one of the carbon atoms constitute the terminals of the quinuclidine bridge. Similarly, only those 9-rubatoxanones in which the configuration of the atoms and groups attached to the nitrogen atom of the piperidine ring is suitable can give rise to 9-rubanones. Probably for this reason, the yield of 9-rubanone from 9-rubatoxanone (see following abstract) is only 50% (a methoxyrubatoxanone gave a similar result), although those rubatoxanones derived from the alkaloids themselves by the Pasteur rearrangement, and therefore having the necessary configuration, under similar conditions furnish yields of at least 80%.

J. K.

Cinchona Alkaloids. XXIV. Synthesis of Vinyl-free Quinatoxins and Quinaketonones. PAUL RABE, KARL KINDLER, and OTTO WAGNER (*Ber.*, 1922, **55**, [B], 532—541).—An account of the synthesis, previously foreshadowed (A., 1920, i, 78), of 6'-methoxy-9-rubatoxanone and of 6'-methoxy-9-rubanone. Ethyl β -4-piperidylpropionate, for the preparation of which improvements are described, furnishes a 1-benzoyl derivative, $\text{C}_{17}\text{H}_{23}\text{O}_3\text{N}$, a yellow oil, b. p. $240^\circ/8$ mm., from which, by condensation with ethyl cinchonate and subsequent hydrolysis, 9-rubatoxanone is obtained as a viscid, yellow oil, with a bitter taste, and showing the reactions of the cinchotoxins (*platinichloride*, $\text{C}_{17}\text{H}_{20}\text{ON}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$). From its 8-bromo-derivative (*dihydrobromide*, yellow crystals, m. p. 184°), 9-rubanone is obtained in 50% yield by the action of sodium carbonate solution; it forms a viscid, yellow oil, with a bitter taste (*picrate*, $\text{C}_{23}\text{H}_{21}\text{O}_8\text{N}_5$, yellow needles, m. p. 170 — 180°). A similar series of compounds follows from the replacement of ethyl cinchonate by ethyl quinate in the above reactions. 6'-Methoxy-9-rubatoxanone (*platinichloride*, $\text{C}_{18}\text{H}_{22}\text{O}_2\text{N}_2 \cdot \text{H}_2\text{PtCl}_6 \cdot 2\text{H}_2\text{O}$, sinters at 265° and melts at 278 — 285° after drying in a vacuum; *monopicrolonate*, $\text{C}_{28}\text{H}_{30}\text{O}_7\text{N}_6$, m. p. 152° ; *monopicrate*, an oil) is a viscid, reddish-yellow oil, with a bitter taste, and exhibits the reactions of the quinatoxins.

6'-Methoxy-9-rubanone, from 8-bromo-6'-methoxy-9-rubatoxanone in 40% yield, is an oil with a bitter taste and showing the reactions of quinone; it gives a *picrate*, $C_{24}H_{23}O_9N_5$, sintering at 168° , m. p. $173-174^\circ$. The *monopicrotonate*, $C_{28}H_{28}O_7N_6$, m. p. $148-150^\circ$, the *platinichloride*, $C_{18}H_{20}O_2N_2 \cdot H_2PtCl_6 \cdot 2H_2O$, needles, m. p. 300° , preceded by sintering at 260° . J. K.

Strychnos Alkaloids. XXX. Reactions of Cacotheline.

HERMANN LEUCHS, FRITZ OSTERBURG, and HANS KAEHRN (*Ber.*, 1922, **55**, [B], 564—572; cf. A., 1921, i, 883).—The preparation of cacotheline [a name unfortunately given to the nitrate of a base] is described. Like methylcacotheline (A., 1920, i, 178), it contains the quinone grouping, CO . . . CO, a nitro-group, secondary and tertiary nitrogen atoms (the latter as nitrate), a carboxylic, and a secondary alcoholic group. *Cacotheline base methyl ester hydrochloride*, $C_{22}H_{24}O_7N_3Cl \cdot H_2O$, forms reddish-brown needles; the *ethyl ester hydrochloride*, $C_{23}H_{26}O_7N_3Cl \cdot 3H_2O$, crystallises in small needles. The *oxime of cacotheline base*, $C_{21}H_{22}O_7N_4 \cdot 4H_2O$, forms yellow needles [*sulphate*, $(C_{21}H_{22}O_7N_4)_2 \cdot H_2SO_4 \cdot xH_2O$, yellow needles; *acetate*, $C_{21}H_{22}O_7N_4 \cdot C_2H_4O_2 \cdot 4H_2O$, yellow needles; *nitrate*, $C_{21}H_{22}O_7N_4 \cdot HNO_3 \cdot H_2O$, prisms; *hydrobromide*, $C_{21}H_{22}O_7N_4 \cdot HBr \cdot 3H_2O$;

methyl ester, $C_{22}H_{24}O_7N_4$, brown needles; *ethyl ester*, gelatinous]. The *oxime hydrochloride*, $C_{21}H_{23}O_7N_4Cl \cdot 3H_2O$, prepared from cacotheline and hydroxylamine hydrochloride, crystallises in yellow needles and yields a *methyl ester*, $C_{22}H_{25}O_7N_4Cl \cdot 4H_2O$, yellow prisms or needles, and a gelatinous ethyl ester. The oxime is reconverted by nitric acid into cacotheline, and by reduction into a *diaminophenol (trihydrobromide)*, $C_{21}H_{27}O_3N_4Br_3$, brown needles or leaflets). The *methyl ester of a nitrosoamine*, $C_{22}H_{25}O_6N_5$, green prisms, results from the action of methyl alcoholic ammonia on the methyl ester of the oxime hydrochloride. *Cacotheline base monophenylhydrazone*, $C_{27}H_{27}O_6N_5 \cdot 4H_2O$, brownish-yellow prisms, is prepared from its *hydrochloride*, $C_{27}H_{28}O_6N_5Cl \cdot 3H_2O$, yellow leaflets, which is obtained from the corresponding oxime. *Cacotheline monosemicarbazone*, $C_{22}H_{24}O_7N_6 \cdot HNO_3 \cdot 3H_2O$, yellow needles, is converted by alkali into the *monosemicarbazone of the free base*, $C_{22}H_{24}O_7N_6 \cdot 4H_2O$, yellow needles or prisms. *Cacotheline base methylmethosulphate*, $C_{23}H_{27}O_{11}N_3S$, yellowish-brown leaflets.

J. K.

Some Compounds of Piperidine with Haloids. CLIFFORD S. LEONARD (*J. Amer. Chem. Soc.*, 1921, **43**, 2618—2626).—A new series of haloid compounds may be prepared from piperidine by reaction with haloids of trivalent arsenic, antimony, and phosphorus and of quadrivalent silicon, tin, and titanium in normal heptane as solvent. These new compounds are considered to be piperidinium compounds and to correspond with Werner's primary compounds. Confirmation of this belief is afforded by the fact that they themselves further unite with metallic salts as does ammonium chloride. Thus the piperidine-arsenic compound gives a crystalline additive complex with lead iodide and a pale yellowish-

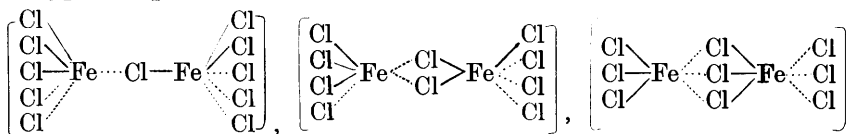
green compound with mercuric iodide. The following compounds are described: *Arsinetri-1-piperidinium chloride*, $\text{As}(\text{C}_5\text{H}_{10}\text{N}, \text{HCl})_3$, crystallising in white needles, m. p. 238° , giving additive compounds with lead iodide, mercuric iodide, and arsenic tri-iodide. *Stibinetri-1-piperidinium chloride*, $\text{Sb}(\text{C}_5\text{H}_{10}\text{N}, \text{HCl})_3$, m. p. 235° . *Silicane-tetra-1-piperidinium chloride*, $\text{Si}(\text{C}_5\text{H}_{10}\text{N}, \text{HCl})_4$, m. p. 238° . *Dichlorostannanedi-1-piperidinium chloride*, $\text{SnCl}_2(\text{C}_5\text{H}_{10}\text{N}, \text{HCl})_2$, m. p. 201° . *Titananetetra-1-piperidinium chloride*, $\text{Ti}(\text{C}_5\text{H}_{10}\text{N}, \text{HCl})_4$, which was very unstable and could not be obtained pure. A phosphorus compound was also prepared, but could not be isolated in a sufficiently pure state for analysis.

These compounds could be hydrolysed with dilute alkali and the free piperidine distilled into standard acid and estimated. This, coupled with the estimation of chlorine in the distillation residues, served as the method of analysis, as carbon could not be estimated by the combustion method.

α -Methylamyl iodide reacts with piperidine in heptane to give α -methylamylpiperidinium iodide, $\text{C}_6\text{H}_{13}\cdot\text{C}_5\text{H}_{10}\text{N}, \text{HI}$, m. p. 133° . This is considered to be analogous in structure to the piperidine-metalloid compounds described above.

W. G.

The Constitution of some Ferri-chloride(-thiocyanate, -nitrate) Compounds with Pyridine or Quinoline. R. F. WEINLAND and A. KISSLING (*Z. anorg. Chem.*, 1921, **120**, 209—231).—A large number of new complex compounds containing ferric chloride and pyridine or quinoline, with or without other constituents, have been prepared and formulæ suggested for them. It is pointed out that the constitution of such compounds is much more difficult to decide than that of similar cobalt and chromium compounds on account of the greater mobility of the constituents and the necessity for working in non-aqueous solutions. To account for the composition of the majority of the compounds under consideration, it is necessary to assume a complex anion containing two atoms of metal, each having the co-ordination number 6. Assuming that one, two, or three chlorine atoms may form a bridge between the two atoms of iron, complex anions of the following types are possible:

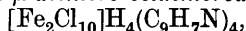


The chlorine atoms can be replaced by other groups in the usual way. The following compounds are described.

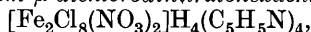
(1) *Pyridinium tetrachloroferrate*, $[\text{FeCl}_4]\text{HC}_5\text{H}_5\text{N}$, crystallises from a concentrated hydrochloric acid solution of its constituents in bright yellow needles, stable in dry air.

(2) *Tripyridinium- μ -trichloro-hexachlorodiferrate*,
 $2\text{FeCl}_3, 3\text{HCl}, 3\text{C}_5\text{H}_5\text{N}$,

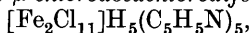
is not new, and is the most readily prepared of these compounds. The formula suggested is $[\text{Cl}_3:\text{Fe}:\text{Cl}_3:\text{Fe}:\text{Cl}_3]\text{H}_3(\text{C}_5\text{H}_5\text{N})_3$.

(3) *Tetraquinolinium-μ-dichloro-octachlorodiferrate*,

forms olive-green crystals of rhombohedral habit from alcoholic or aqueous hydrochloric acid solution.

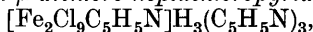
(4) *Tetrapyridinium-μ-dichlorodinitratohexachlorodiferrate*,

crystallises from an aqueous solution of ferric nitrate and pyridine hydrochloride in yellow needles. The corresponding quinoline salt is similar, and both are stable in dry air.

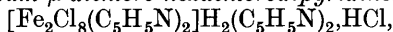
(5) *Pentapyridinium-μ-chlorodecachlorodiferrate*,

was obtained in the form of green leaflets from an alcoholic solution of (2) and pyridine hydrochloride in the mol. ratio 1 : 10 to 1 : 20. It is very hygroscopic and unstable.

(6) *Tripyridinium-hexachloroferrate*, $[\text{FeCl}_6]\text{H}_3(\text{C}_5\text{H}_5\text{N})_3$, is obtained instead of (5) when a greater proportion of pyridine hydrochloride is used, and forms unstable pale green leaflets.

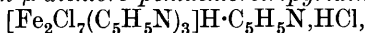
(7) *Tripyridinium-μ-dichloro-heptachloropyridinediferrate*,

is obtained by triturating (2) with 1 mol. proportion of pyridine in ether; it forms an orange, crystalline powder. The orange colour is characteristic of compounds containing pyridine in the complex anion.

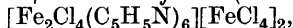
(8) *Dipyridinium-μ-dichloro-hexachlorodipyridinediferrate*,

can be obtained from (7) by crystallisation from alcohol, together with (10), and is closely related constitutionally to (11); it forms square, orange leaflets.

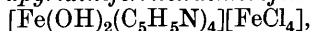
(9) *Dipyridinium-μ-dichloro-tetrachlorodinitratodipyridinediferrate*, $[\text{Fe}_2\text{Cl}_6(\text{NO}_3)_2(\text{C}_5\text{H}_5\text{N})_2]\text{H}_2(\text{C}_5\text{H}_5\text{N})_2$, from an alcoholic solution of ferric chloride, pyridine, and lithium nitrate; brown aggregates of needles and prisms. By recrystallisation from alcohol, it reverts to (8).

(10) *Pyridinium-μ-dichloro-pentachlorotripyridinediferrate*,

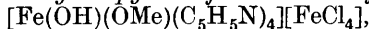
is obtained in orange crusts from an alcoholic solution of (8) with pyridine.

(11) *Hexapyridine-μ-dichlorodiferridi(tetrachloroferrate)*

is obtained from a dry alcoholic solution of (2) with pyridine. It forms irregular, six-sided leaflets or tablets, deep brown in colour, and when freshly prepared can be recrystallised unchanged from alcohol, ethyl acetate, or acetone. Its probable constitution is discussed at length and the conclusion is that it probably contains a complex kation containing pyridine combined with two $[\text{FeCl}_4]$ anions.

(12) *Dihydroxytetrapyridineferritetetrachloroferrate*,

garnet-red, thick crystals from an alcoholic solution of ferric chloride (1 mol.) and pyridine (10 mols.).

(13) *Hydroxymethoxytetrapyridineferritetetrachloroferrate*,

forms a heavy, yellow, crystalline powder when (11) is crystallised.

from methyl alcohol, or it can be prepared from its constituents in methyl alcohol.

(14) *Hydroxymethoxytetrapyridineferritetrathiocyanatoferrate* is constituted analogously to (13). It forms a heavy, reddish-black, crystalline powder.

(15) *Octapyridine- μ -dichlorodiferrichloride*, $[\text{Fe}_2\text{Cl}_2(\text{C}_5\text{H}_5\text{N})_8]\text{Cl}_4$, obtained from a solution of anhydrous ferric chloride in pyridine, forms deep red crystals, decomposed by alcohol.

The electrical conductivities of some of the compounds in alcohol were determined and confirmed, in the case of those compounds stable in alcohol, the constitutions given above. E. H. R.

Preparation of Hydrogenated N-Alkylpyridine-3-carboxylates. RICHARD WOLFFENSTEIN (D.R.-P. 340873; from *Chem. Zentr.*, 1921, iv, 1102).—N-Alkylhaloids of alkylpyridine-3-carboxylates are treated with metals and hydrogen haloids in the presence of non-hydrolysing solvents. For example, methyl pyridine-3-carboxylate-N-methochloride is dissolved in methyl alcohol. Tin is added and a current of hydrogen chloride is passed for three to four hours at 100° , whereby *methyl 1-methylhexahydro-pyridine-3-carboxylate* is formed as a liquid, b. p. $86-89^\circ/21.5$ mm. The 1-methochloride of methyl pyridine-3-carboxylate can also be reduced without warming by tin and hydrogen chloride, using formic acid as a solvent. *Ethyl pyridine-3-carboxylate-N-ethiodide* dissolved in alcohol may be similarly reduced by magnesium and hydrogen chloride. The products have therapeutic uses.

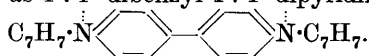
G. W. R.

Preparation of N-Alkylhaloids of Methyl Pyridine-3-carboxylate [Methyl Nicotinate]. RICHARD WOLFFENSTEIN (D.R.-P. 340874; from *Chem. Zentr.*, 1921, iv, 1102).—Methyl pyridine-3-carboxylate is treated with alkyl haloids. For example, methyl pyridine-3-carboxylate is heated at 100° under pressure with methyl bromide and methyl alcohol for forty-eight hours. After removal of methyl alcohol by distillation, the N-methobromide is obtained from the residue; it forms crystals, m. p. 71° . The N-methiodide forms light yellow crystals, m. p. 130° . The N-methochloride forms white crystals, m. p. 98° . The compounds have therapeutic uses.

G. W. R.

Free Ammonium Radicles. III. Existence of N-Benzylpyridinium. ERNST WEITZ and RICHARD LUDWIG (*Ber.*, 1922, 55, [B], 395—413).—In a previous communication (A., 1921, i, 804), Weitz, Nelken, and Ludwig have described the isolation of a red, crystalline substance which gives deep blue solutions in methyl and ethyl alcohols from 1:1'-dibenzyltetrahydro-4:4'-dipyridyl (cf. Hofmann, A., 1881, 921; Emmert, A., 1919, i, 455; 1920, i, 331), which they considered to be 1-benzylpyridinium. This conception has been found to require modification, since the product formed by the iodination of the blue solution, $\text{C}_{24}\text{H}_{22}\text{N}_2\text{I}_2$, short, red needles, m. p. 232° , has been converted into a sparingly soluble perchlorate, slender needles, m. p. 257° , which is not identical

with 1-benzylpyridinium perchlorate, as the melting points of the the compounds differ by about 160° . Also, it has now been found possible to prepare the crystalline iodide (see above) by titration of solutions of the radicle, preferably in acetone or chloroform, with iodine; the compound contains the halogen in completely ionisable form, but is distinguished from 1-benzylpyridinium iodide by its much smaller solubility in water. Each pyridine nucleus requires approximately one atom of iodine. Formation of the deep blue, oxidisable solution from the iodide is effected readily by zinc dust (preferably in the presence of alcohol or glacial acetic acid); under these conditions, 1-benzylpyridinium chloride is known to remain unchanged. The phenomena are thus closely analogous to those observed with benzylpyridinium (Weitz, Roth, and Nelken, A., 1921, i, 804), and the probability thus suggested that the radicle is a dipyridyl compound is confirmed by its production from 1:1'-dibenzyl-4:4'-dipyridinium dichloride and zinc dust; on the assumption, therefore, that the substance is a radicle, it must be regarded as 1:1'-dibenzyl-4:4'-dipyridinium,



(An alternative quinoid formula, $\text{C}_7\text{H}_7\text{N} \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \end{array} = \begin{array}{c} \diagup \quad \diagdown \\ \text{---} \quad \text{---} \\ \diagdown \quad \diagup \end{array} \text{N}\cdot\text{C}_7\text{H}_7$, is discussed which, although appearing rather less probable, cannot be discarded completely.) The new conception explains the necessity of the presence of oxygen for the production of the radicle from Hofmann's dibenzyltetrahydrodipyridyl. The ready removal of two atoms of hydrogen from the latter appears nearly as difficult to explain as is its oxidation by silver nitrate to the unimolecular pyridinium salt as recorded by Hofmann; this observation is confirmed, but, on the other hand, it is shown that the new radicle gives exclusively a dibenzylidipyridinium salt when treated with silver nitrate. In addition, it is found that the freshly-prepared solution of Hofmann's product is only moderately oxidisable and that only such solutions as have been heated in the absence of air are brownish-yellow and successively become immediately deep blue and ultimately colourless when treated gradually with air. Similarly, a cold, freshly-prepared solution of Hofmann's compound immediately decolorises iodine in the absence of air, a pale green coloration being developed which is discharged by further addition of the halogen; that portion of the product of the reaction which is soluble in water consists almost entirely of unimolecular *N*-benzylpyridinium iodide which contains only the merest trace of dipyridyl derivative. When, on the other hand, a solution of iodine is added gradually to a boiling solution of Hofmann's compound in the absence of air, a deep blue colour is developed which disappears on further addition of the halogen. The reaction is not smooth or quantitative. The product of the change, which is soluble in water, contains the iodides of dibenzylidipyridinium and of benzylpyridinium. The former is never produced except from solutions which have become blue, and therefore owes its origin to the formation of the radicle under the influence of halogen.

Since the formation of the di-iodide is invariably accompanied by that of the mono-iodide, it is clear that the original Hofmann's compound is converted only gradually in hot solution into the parent substance of the bimolecular radicle; the constitution of the latter and of Hofmann's compound is not yet definitely elucidated.

The authors' experience with benzylpyridinium indicates that, in spite of the results of determinations of the molecular weight, benzoylpyridinium (A., 1921, i, 804) is really a bimolecular product, particularly in view of its ready convertibility into 4 : 4'-dipyridyl.

1 : 1'-Diacetyltetrahydro-4 : 4'-dipyridyl (cf. Dimroth and Heene, this vol., i, 48) appears to resemble the benzyl derivative in requiring oxygen for the development of the blue colour in its solutions.

H. W.

Condensation of Acetophenone. III. C. GASTALDI (*Gazzetta*, 1921, **51**, ii, 289—306; cf. A., 1916, i, 31).—The hydrocarbon, $C_{25}H_{22}$, obtained by condensation of acetophenone under the agency of potassium hydroxide (A., 1900, i, 603; 1901, i, 604; 1904, i, 32) reacts with benzoyl chloride in presence of aluminium chloride, yielding 2 : 4 : 6-triphenylpyrylium chloride, $CPh \begin{smallmatrix} \text{CH} \cdot CPh \\ \text{CH} : CPh \end{smallmatrix} \gg O \cdot Cl$.

Similar pyrylium derivatives are obtained also in the same way from the homologous hydrocarbon, $C_{28}H_{28}$, obtained from *p*-tolyl methyl ketone, and from the interaction of either of these hydrocarbons with other acid chlorides; certain of the latter, however, fail to react in this way, and in no case is the reaction quantitative. Sublimed aluminium chloride, but not ferric chloride or zinc chloride, serves as condensing agent. As diluent, carbon disulphide gives the best results and nitrobenzene may be used, but light petroleum cannot be employed. The results obtained are explainable according to Delacré's suggestion that the hydrocarbon $C_{25}H_{22}$ is 1 : 3 : 5-triphenyl- $\Delta^{1:4}$ -cycloheptadiene (A., 1920, i, 165, 236).

The *hydrocarbon*, $C_{28}H_{28}$, crystallises in colourless cubes, m. p. 122° , and dissolves in concentrated sulphuric acid to a red solution showing green fluorescence.

2 : 4 : 6-Triphenylpyrylium chloride gives : (1) with nitric acid, the corresponding *nitrate*, $C_{23}H_{17}O \cdot NO_3$, golden-yellow needles, m. p. 149° (decomp.), (2) with sodium acetate, α -hydroxy- ϵ -keto- $\alpha\gamma\epsilon$ -triphenyl- $\Delta^{\alpha\gamma}$ -pentadiene, and (3) with ammonia, 2 : 4 : 6-triphenylpyridine.

4 : 6-Diphenyl-2-*p*-chlorophenylpyrylium chloride, obtained from the hydrocarbon $C_{25}H_{22}$ and *p*-chlorobenzoyl chloride (1) forms the *nitrate*, $CPh \begin{smallmatrix} \text{CH} \cdot C(C_6H_4Cl) \\ \text{CH} \text{---} CPh \end{smallmatrix} \gg O \cdot NO_3$, which crystallises in slender, yellow needles, m. p. 161° (decomp.), and dissolves in acetic acid, giving a solution showing green fluorescence and in concentrated sulphuric acid giving a non-fluorescent, orange-yellow solution; (2) when treated with ammonia solution, yields 4 : 6-diphenyl-2-*p*-chlorophenylpyridine, $N \begin{smallmatrix} C(C_6H_4Cl) \cdot CH \\ CPh \text{---} CH \end{smallmatrix} \gg CPh$, which crystallises

in colourless needles, m. p. 137°, and in concentrated sulphuric acid gives a solution showing blue fluorescence; (3) when treated with sodium acetate, gives the yellow, flocculent pseudo-base, which was not obtained crystalline.

4 : 6-Diphenyl-2-*p*-bromophenylpyridine, $N \left\langle \begin{array}{c} C(C_6H_4Br) \cdot CH \\ CPh \quad \quad \quad CH \end{array} \right\rangle CPh$, prepared from 4 : 6-diphenyl-2-*p*-bromophenylpyrylium chloride, forms colourless laminae, m. p. 154–155°, and yields a non-fluorescent solution in concentrated sulphuric acid.

4 : 6-Diphenyl-2-*p*-tolylpyrylium chloride, prepared from the hydrocarbon $C_{15}H_{22}$ and *p*-toluoyl chloride, (1) forms the *nitrate*, $CPh \left\langle \begin{array}{c} CH \cdot C(C_6H_4Me) \\ CH \quad \quad \quad CPh \end{array} \right\rangle O \cdot NO_3$, which crystallises in lustrous, orange-yellow laminae, m. p. 155° (decomp.), and in acetic acid gives a solution showing green fluorescence and in concentrated sulphuric acid an orange-yellow coloration showing faint green fluorescence; (2) with sodium acetate, gives α -hydroxy- ϵ -keto- $\alpha\gamma$ -diphenyl- ϵ -*p*-tolyl- $\Delta\gamma$ -pentadiene (cf. Dilthey, A., 1921, i, 188); (3) with ammonia solution yields 4 : 6-diphenyl-2-*p*-tolylpyridine, $C_{24}H_{19}N$, which crystallises in colourless needles, m. p. 111°, and in concentrated sulphuric acid solution shows blue fluorescence.

2-Phenyl-4 : 6-di-*p*-tolylpyrylium chloride, prepared by the interaction of the hydrocarbon $C_{28}H_{28}$ and benzoyl chloride, (1) yields the *ferric chloride* compound, $FeCl_4 \cdot O \left\langle \begin{array}{c} CPh \quad \quad \quad CH \\ C(C_6H_4Me) \cdot CH \end{array} \right\rangle C \cdot C_6H_4Me$, which crystallises in brownish-yellow needles, m. p. 234°; (2) is converted by ammonia solution into 2-phenyl-4 : 6-di-*p*-tolylpyridine, $C_{25}H_{21}N$, which forms colourless laminae, m. p. 138°, and in concentrated sulphuric acid solution exhibits blue fluorescence; (3) is converted by sodium acetate into the pseudo-base, which separates in pale yellow flocks, but undergoes almost immediate alteration.

2-*p*-Chlorophenyl-4 : 6-di-*p*-tolylpyrylium chloride, from the hydrocarbon $C_{28}H_{28}$ and *p*-chlorobenzoyl chloride, (1) yields the corresponding *nitrate*, $C_{25}H_{20}O_4NCl_4$, which crystallises in bundles of prisms, m. p. 190° (decomp.); (2) is converted by ammonia into 2-*p*-chlorophenyl-4 : 6-di-*p*-tolylpyridine, $C_{25}H_{20}NCl$, which forms colourless needles, m. p. 188°.

2 : 4 : 6-Tri-*p*-tolylpyridine, $C_{26}H_{23}N$, crystallises in long, colourless needles, m. p. 177°, and in concentrated sulphuric acid solution shows blue fluorescence.

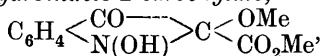
T. H. P.

The Halogenated Isatins. EUGÈNE GRANDMOUGIN (*Compt. rend.*, 1922, 174, 620–623).—The halogenated isatins may be prepared by oxidising the corresponding halogenated indigotins in acetic acid solution by chromic acid. The crude isatin is dissolved in warm dilute alkali to free it from unchanged indigotin and reprecipitated by acid. The following compounds are described: 5 : 7-Dichloroisatin, m. p. 223°, giving an *oxime*, m. p. 255° (decomp.), and a *phenylhydrazone*, m. p. 296–297°. 4 : 7-Dichloroisatin, m. p. 252°, and its *oxime*, m. p. 245° (decomp.), and

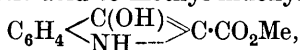
phenylhydrazone, m. p. 265°. 4-Chloro-5-bromoisatin, m. p. 273—274°, its *oxime*, m. p. 253—254° (decomp.), and *phenylhydrazone*, m. p. 278°. 5:7-Dibromoisatin, m. p. 250°, its *oxime*, m. p. 272° (decomp.), and *phenylhydrazone*, m. p. 297—298°. 4:5:7-Tri-bromoisatin, m. p. 257—258°. 4:5:6:7-Tetrachloroisatin, m. p. 294—295°, and its *phenylhydrazone*, m. p. 293°. The oximes and phenylhydrazones are in all cases β -substituted derivatives. The absorption of these compounds in the ultra-violet has been studied and some of the results are given, indicating that the absorption in the ultra-violet of these substituted derivatives is essentially of the same character as that of the parent substance. W. G.

Isatogens. GUSTAV HELLER and WERNER BOESSNECK (*Ber.*, 1922, 55, [B], 474—482).—Treatment of certain highly-coloured isatogens (cf. Pfeiffer, A., 1916, i, 327) with alcoholic hydrogen chloride has led to the formation of less intensely coloured compounds, which, according to Ruggli (A., 1919, i, 221), can only be formulated in Baeyer's original manner, $O < \begin{smallmatrix} N-C_6H_4 \\ | \\ CR \cdot CO \end{smallmatrix}$. Further investigation, however, has shown that they are additive compounds of the isatogen and the alcohol, $C_6H_4 < \begin{smallmatrix} CO \\ | \\ N(OH) \end{smallmatrix} > C < \begin{smallmatrix} OR \\ | \\ CO_2R \end{smallmatrix}$, and that they are also formed in the complete absence of halogen acid.

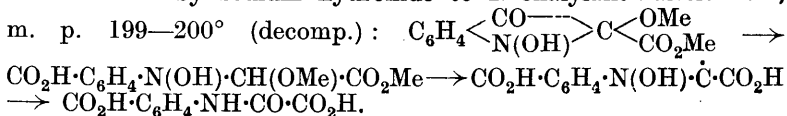
Methyl isatogenate is transformed by methyl alcoholic hydrogen chloride (1%) at the atmospheric temperature into *methyl 1-hydroxy-3-keto-2-methoxydihydroindole-2-carboxylate*,



pale, lemon-yellow crystals, m. p. 171° (decomp.), after previous darkening. In the presence of pyridine, it is converted by acetyl chloride into the *acetyl* derivative, almost colourless crystals, m. p. 95—96°, and by benzoyl chloride into the *benzoyl* compound, $C_{18}H_{15}O_6N$, colourless crystals, m. p. 141° (decomp.). It is reduced by zinc dust and acetic acid to methyl indoxylate,



which is obtained more readily from methyl isatogenate. Reduction of the two substances by zinc dust and acetic acid in the presence of methyl alcohol gives a *polymeride* of methyl indoxylate of unknown molecular weight, prisms, m. p. about 245° (decomp.) after darkening at 225°. The 1-hydroxy-ester is converted by hydroxylamine hydrochloride into the oxime of methyl isatogenate, m. p. 221°, from which the corresponding *acid*, $C_9H_6O_4N_2$, pale yellow crystals, m. p. 187° (decomp.), is obtained by hydrolysis with cold sodium hydroxide solution. The 1-hydroxy-compound is isomerised by sodium hydroxide to *N*-oxalylanthranilic acid, m. p. 199—200° (decomp.):



Ethyl isatogenate and ethyl alcoholic hydrogen chloride give *ethyl 1-hydroxy-3-keto-2-ethoxydihydroindole-2-carboxylate*, yellow prisms, m. p. 158—159°, with subsequent evolution of gas, after darkening at 150°; like ethyl isatogenate, it is converted by hydroxylamine hydrochloride into *ethyl isatogenate oxime*, yellowish-brown octahedra, m. p. 187° (decomp.). Ethyl isatogenate and methyl alcohol give *ethyl 1-hydroxy-3-keto-2-methoxydihydroindole-2-carboxylate*, pale yellow crystals, m. p. 142—143°, whereas methyl isatogenate and ethyl alcohol yield *methyl 1-hydroxy-3-keto-2-ethoxydihydroindole-2-carboxylate*, lemon-yellow crystals, m. p. 176°, with subsequent evolution of gas. Either compound is isomerised by sodium hydroxide to *N-oxalylanthranilic acid*. H. W.

Equilibrium in the System: Lithium Chloride-Quinoline. JAMES H. WALTON and CLARENCE R. WISE (*J. Amer. Chem. Soc.*, 1922, **44**, 103—104).—The solubility of lithium chloride in quinoline has been determined from 0° to 96°; measurements were not possible beyond this temperature, for the very long time required for saturation at high temperatures brought about a decomposition of the quinoline. The following solubilities in grams of lithium chloride per 100 grams of solvent are recorded: 0°, 0.1515; 25°, 0.3538; 40°, 0.6175; 45°, 1.0328; 50°, 1.1107; 56.4°, 1.1734; 67°, 1.2353; 75°, 0.8180; and 96°, 0.4588. The solid phase in equilibrium with the solution is $2C_9H_7N.LiCl$. This compound is very stable at all temperatures within the range measured. There is evidence of the formation of a second solid phase above 100°, but this was not investigated because of the decomposition of the quinoline. The solubility curve of lithium chloride is shaped like an irregular inverted U with the maximum at 67°. J. F. S.

The Three Aminotriphenylamines. JEAN PICCARD and RAY Q. BREWSTER (*J. Amer. Chem. Soc.*, 1921, **43**, 2630—2631).—*o*- and *m*-Nitrotriphenylamines (cf. Piccard and Larsen, A., 1917, i, 644) were reduced by adding them gradually in acetic acid solution to a mixture of zinc and alcohol. *o*-Aminotriphenylamine, m. p. 145°, gives an *acetyl* derivative, m. p. 130°. *m*-Aminotriphenylamine, m. p. 116°, gives a *hydrochloride* and an *acetyl* derivative, m. p. 167°.

Attempts to reduce the nitrotriphenylamines to their corresponding aminophenols by the electrolytic method were not successful. W. G.

Tetra-substituted Carbamides. T. J. ALBERT, jun. (U.S. Pat. 1393597).—Tetra-substituted carbamides, for example, diphenyldimethylcarbamide are prepared by treating a secondary amine, for example, monomethylaniline, with carbonyl chloride in the presence of an aqueous solution of a basic inorganic compound such as sodium carbonate capable of neutralising the hydrogen chloride which results from the reaction. The reaction is conducted at 95—99° and is complete in two hours. CHEMICAL ABSTRACTS.

Synthesis of Indigotin from Fumaric Acid and Aniline. G. C. BAILEY and R. S. POTTER (*J. Amer. Chem. Soc.*, 1922, **44**, 215—216).—Fumaric acid is brominated in acetic acid solution

and the resulting dibromosuccinic acid is converted into dianilino-succinic acid (cf. Reissert, A., 1893, i, 565). An equimolecular mixture of potassium and sodium hydroxides is dehydrated in a closed iron pot at 450° with stirring. Sodamide is then added and a stream of dry ammonia passed through the pot, and the sodium salt of dianilinosuccinic acid is slowly added, the mixture being kept at 230—240° for one and a half hours. The fused mass is dissolved in water and air is blown through. The yield of indigotin is 60·4% and its purity is 96·5%.

W. G.

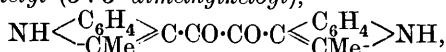
New Syntheses in the Indole Group. VIII. B. ODDO and G. SANNA (*Gazzetta*, 1921, 51, ii, 337—342).—It has been shown (A., 1911, i, 488; 1912, i, 721) that pyrrole, in the form of its magnesium derivative, reacts readily with chlorides of dibasic acids, giving pyrrole derivatives with a double ketonic function analogous to benzil, benzoylacetophenone, and diphenacyl. The indole and methylketole analogues of benzil have now been obtained.

The action of oxalyl chloride on magnesium indolyl bromide yields: (1) *Bis-1:3-indyl* (*bis-1:3-di-indoyl*) (annexed formula), which forms almost colourless, prismatic crystals, m. p. 200°; (2) principally *3:3-indyl* (*3:3-di-indoyl*),

$$\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C} \diagdown \\ \diagdown \text{N} \diagup \end{array} \begin{array}{c} \text{CO} \text{---} \text{CO} \\ \text{CH} \text{---} \text{CH} \end{array} \begin{array}{c} \diagup \text{C} \diagdown \\ \diagdown \text{N} \diagup \end{array} \text{C}_6\text{H}_4$$

$$\text{NH} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{CH} \diagup \end{array} \text{C} \cdot \text{CO} \cdot \text{CO} \cdot \text{C} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{CH} \diagup \end{array} \text{NH}$$
, which forms yellow needles or prismatic plates, contracting at about 200°, m. p. 235° (decomp.), and is resistant to the action of boiling alkali hydroxide solution, but yields indole-3-carboxylic acid when fused with potassium hydroxide; (3) a small proportion of *1:1-indyl* (*1:1-di-indoyl*), $\text{CH} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{CH} \diagup \end{array} \text{N} \cdot \text{CO} \cdot \text{CO} \cdot \text{N} \begin{array}{c} \diagup \text{C}_6\text{H}_4 \diagdown \\ \diagdown \text{CH} \diagup \end{array} \text{CH}$, which crystallises in colourless prisms, m. p. 218—220°, and yields indole when boiled with 10% potassium hydroxide solution.

3:3-Methylketyl (*3:3'-dimethylketoyl*),

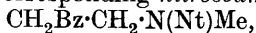


prepared by the action of oxalyl chloride on magnesiummethylketole, crystallises in colourless prisms, m. p. 256—257° (decomp.), and gives with phenylhydrazine a condensation product which crystallises in silky, yellow needles, m. p. 192°, and with *o*-phenylenediamine a condensation product, m. p. (crude) 149°.

T. H. P.

Transformations of a Secondary Keto-base. C. MANNICH and G. HELLNER (*Ber.*, 1922, 55, [B], 365—374).—Few secondary keto-bases have been prepared previously and their properties have been little studied. The comparatively ready availability of ω -methylaminopropiophenone (this vol., i, 351) has led the authors to make an extended study of its reactions.

ω -Methylaminopropiophenone hydrochloride is converted by nitrous acid into the corresponding *nitrosoamine*,



large, colourless, prismatic rods or needles, m. p. 66°, which is

reduced by zinc dust and acetic acid in methyl alcoholic solution to 3-phenyl-1-methylpyrazoline, $\text{NMe} \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \quad \diagup \\ \text{N} = \text{CPh} \end{smallmatrix}$, unctuous leaflets, m. p. 37° (hydrochloride, needles, m. p. 162°), the hydrazine, $\text{CH}_2\text{Bz} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{NH}_2$, being probably formed intermediately.

ω-Methylaminopropiophenone hydrochloride reacts normally with potassium cyanate, giving as-phenacylmethylmethylcarbamide, $\text{COPh} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{CO} \cdot \text{NH}_2$, colourless needles, m. p. $123-124^\circ$, which is insoluble in cold dilute acids, but readily soluble in solutions of alkali hydroxide, pointing thus to its existence in the enolic form, $\text{OH} \cdot \text{CPh} \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{NMe} \cdot \text{CO} \cdot \text{NH}_2$. It is converted slowly in alkaline solution, more rapidly by regulated treatment with warm dilute acid into 2-keto-4-phenyl-1-methyl-1 : 2 : 5 : 6-tetrahydropyrimidine, $\text{NMe} \begin{smallmatrix} \text{CO} - \text{N} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CPh}$, m. p. $152-154^\circ$, after previous softening. The latter is transformed rapidly by an excess of warm dilute mineral acid into a mixture of equivalent amounts of 2-keto-4-phenyl-1-methyl-1 : 2-dihydropyrimidine, $\text{NMe} \begin{smallmatrix} \text{CO} - \text{N} \\ \diagdown \quad \diagup \\ \text{CH} \cdot \text{CH} \end{smallmatrix} \text{CPh}$,

matted needles, m. p. 217° , and 2-keto-4-phenyl-1-methylhexahydropyrimidine, $\text{NMe} \begin{smallmatrix} \text{CO} - \text{NH} \\ \diagdown \quad \diagup \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CHPh}$, m. p. $115-116^\circ$, the phenomenon being thus similar to that observed by Knoevenagel and Fuchs in the case of dihydrolutidinedicarboxylic ester. The relationship of the di- and tetra-hydropyrimidine derivatives to the hexahydro-compound is placed beyond doubt by the observation that the latter is produced when either of the others is treated with hydrogen in the presence of palladised animal charcoal. The hexahydro-compound does not decolorise bromine. On the other hand, 2-keto-4-phenyl-1-methyl-1 : 2-dihydropyrimidine is converted smoothly by bromine in glacial acetic acid solution into 2-keto-4-phenyl-1-methyl-1 : 2-dihydropyrimidine 5 : 6-dibromide, $\text{NMe} \begin{smallmatrix} \text{CO} - \text{N} \\ \diagdown \quad \diagup \\ \text{CHBr} \cdot \text{CHBr} \end{smallmatrix} \text{CPh}$, pale yellow, lustrous leaflets, m. p. 260°

(decomp.). The tetrahydropyrimidine derivative is transformed by two molecular proportions of bromine in glacial acetic acid solution into a colourless, unstable crystalline substance, decomp. 260° , to which the constitution $\text{NMe} \begin{smallmatrix} \text{CO} - \text{NH} \\ \diagdown \quad \diagup \\ \text{CHBr} \cdot \text{CHBr} \end{smallmatrix} \text{CBrPh}$ is assigned; it is considered that the initial action of the bromine consists in the conversion of the tetra- to the di-hydro-derivative which then unites with a molecular proportion of hydrogen bromide and bromine with formation of the tribromide. The yellow dibromide readily loses hydrogen bromide under the action of sodium hydrogen carbonate, and passes into 6(15)-bromo-2-keto-4-phenyl-1-methyl-1 : 2-dihydropyrimidine, colourless, slender needles, m. p. 177° . This monobromide is converted by bromine in glacial acetic acid solution into a highly unstable, orange-coloured tetra-bromide, but the reaction appears to be complicated and not entirely due to simple addition of bromine.

As the salt of a secondary base, ω -methylaminopropiophenone hydrochloride is able to condense with formaldehyde and ketones or substances with reactive hydrogen atoms; thus with antipyrine it gives α -phenacylmethyl- α' -antipyrino-4-methylmethylaniline, $\text{CH}_2\text{Bz}\cdot\text{CH}_2\cdot\text{NMe}\cdot\text{CH}_2\cdot\text{C}\begin{smallmatrix} \text{CO}-\text{NPh} \\ \text{CMe}\cdot\text{NMe} \end{smallmatrix}$, thin, slender needles, m. p. 86° ; the corresponding hydrochloride has m. p. 164° . H. W.

Some Ketones of the Pyrazole Series. C. A. ROJAHN (*Ber.*, 1922, **55**, [B], 291—294).—It has been shown previously that very varying yields of ketones are obtained by the application of the Friedel-Crafts method to 5-chloro-1-phenyl-3-methylpyrazole (Michaelis and Rojahn, A., 1917, i, 480). The influence of substituents in the pyrazole ring on the reactivity of the hydrogen atom in position 4 with respect to the ketone synthesis has been investigated in greater detail, and it is found that only those chloropyrazoles which have an aryl group in position 1 yield ketones, whereas it is not very material whether the substituent in position 3 is an aryl or alkyl group. The synthesis cannot be effected with 5-pyrazolones which yield *O*- or *O'*- and *N*-benzoyl derivatives.

The following individual substances are described: 5-Chloro-4-benzoyl-1-*p*-tolyl-3-methylpyrazole, $\text{N}\begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{C}\cdot\text{Cl} \\ \text{CMe}\text{---}\text{C}\cdot\text{Bz} \end{smallmatrix}$ (from 5-chloro-1-*p*-tolyl-3-methylpyrazole, benzoyl chloride, and aluminium chloride in the presence of carbon disulphide), colourless, hexagonal plates, m. p. 70° . 5-Chloro-4-benzoyl-1:3-diphenylpyrazole (from 5-chloro-1:3-diphenylpyrazole, m. p. 56° instead of 49° recorded in the literature), needles, m. p. 127° , b. p. $340\text{---}345^\circ/25\text{ mm.}$ 5-Benzoxyl-1-benzoyl-3-methylpyrazole, $\text{N}\begin{smallmatrix} \text{NBz}\cdot\text{C}\cdot\text{OBz} \\ \text{CMe}\cdot\text{CH} \end{smallmatrix}$ (from 3-methyl-5-pyrazolone and benzoyl chloride in the presence of aluminium chloride or by the Schotten-Baumann method), long needles, m. p. 128° , which is converted by bromine in glacial acetic acid solution into 4-bromo-5-benzoxyl-1-benzoyl-3-methylpyrazole, long needles, m. p. 167° . 4-Phenyl-1-*p*-tolyl-3-methyldipyrazole, $\text{N}\begin{smallmatrix} \text{N}(\text{C}_6\text{H}_4\text{Me})\cdot\text{C}\cdot\text{NH} \\ \text{CMe}\text{---}\text{C}\cdot\text{CPh} \end{smallmatrix}\text{N}$ (from 5-chloro-4-benzoyl-1-*p*-tolyl-3-methylpyrazole and hydrazine hydrate at $160\text{---}175^\circ$), colourless, matted needles, m. p. 244° . 1:3:4-Triphenyldipyrazole, $\text{N}\begin{smallmatrix} \text{NPh}\cdot\text{C}\cdot\text{NH} \\ \text{CPh}\cdot\text{C}\cdot\text{CPh} \end{smallmatrix}\text{N}$, needles, m. p. 233° . H. W.

The Action of Diazomethane on the Ureides and Uric Acid. J. HERZIG (*Z. physiol. Chem.*, 1921, **117**, 13—27).—A number of ureides and uric acids were methylated with diazomethane. Alloxan yielded a syrupy substance, $\text{C}_4\text{N}_2\text{O}_3\text{Me}_2\cdot\text{OMe}$. From barbituric acid, a crystalline substance, $\text{NMe}\begin{smallmatrix} \text{CO}\text{---}\text{CH} \\ \text{CO}\cdot\text{NMe} \end{smallmatrix}\text{C}\cdot\text{OMe}$, m. p. $164\text{---}166^\circ$, was obtained. Diethylbarbituric acid yielded an oily substance,

$C_8H_{11}N_2O_3Me$, which, after several months, crystallised in needles, m. p. 33—36°. Phenylethylbarbituric acid gave a compound,

$C_{12}H_{10}O_3N_2Me_2$, a crystalline mass, m. p. 88—90°, dipropylbarbituric acid gave a crystalline compound, $C_{10}H_{14}O_3N_2Me_2$, m. p. 80—83°, uric acid gave a tetramethyl uric acid, $C_5O_3N_4Me_4$, the four methyl groups being attached to nitrogen. On treating barbituric acid with methyl sulphate in sodium hydroxide, a compound, $C_4H_2O_3N_2Me_2$, probably $CO<\begin{smallmatrix} NMe\cdot CO \\ NMe\cdot CO \end{smallmatrix}>CH_2$, m. p. 119—121°, was obtained.

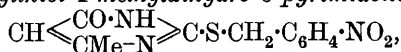
S. S. Z.

Pyrimidines from Alkylmalonic Esters and Aromatic Amidines. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1922, **44**, 361—366).—Alkyl malonic esters readily condense with aromatic amidines in the presence of sodium ethoxide, the monoalkylmalonic esters yielding insoluble yellow pyrimidine derivatives and the dialkyl esters giving soluble colourless derivatives. The colour of the derivatives from the monoalkyl esters is thought to be due to a tautomeric rearrangement to a compound of the structure $CR<\begin{smallmatrix} C(OH)\cdot N \\ C(OH):N \end{smallmatrix}>CR'$. With two exceptions, the 5-monoalkyl derivatives of pyrimidine all melt at above 300°, whereas the 5:5-dialkyl derivatives melt considerably below 300°. The pyrimidine derivatives described are all analogous to 4:6-diketo-2-phenyl-5:5-diethyltetrahydropyrimidine and are:

Substituents.			Substituents.		
5-Carbon.	2-Carbon.	M. p.	5-Carbon.	2-Carbon.	M. p.
	Methyl	>300°	Ethyl	<i>p</i> -Tolyl	>300°
Phenyl	Methyl	>300°	Ethyl	<i>p</i> -Ethoxyphenyl	>300°
Benzyl	Methyl	>300°	Dimethyl	Phenyl	184°
	Phenyl	>300°	Diethyl	Phenyl	207°
Methyl	Phenyl	>300°	Dipropyl	Phenyl	164°
Ethyl	Phenyl	>300°	Dibutyl	Phenyl	144°
Allyl	Phenyl	288—289°	Dibenzyl	Phenyl	234°
Butyl	Phenyl	296—297°	Diethyl	<i>p</i> -Tolyl	181°
<i>iso</i> Amyl	Phenyl	>300°	Diethyl	<i>p</i> -Ethoxyphenyl	165°
Benzyl	Phenyl	>300°	Diethyl	β -Naphthyl	178°
Dimethyl	Phenyl	263°			

W. G.

Pyrimidines. XCI. Alkylation of 2-Thiolpyrimidines. WILLIAM JOHN HORN (*J. Amer. Chem. Soc.*, 1921, **43**, 2603—2611).—Experiments are described showing further abnormalities in the alkylation of 2-thiolpyrimidines (cf. Johnson and Haggard, A., 1915, i, 88; Johnson and Moran, 1916, i, 78). A study has now been made of the alkylation of 2-*p*-nitrobenzylthiol-4-methyl-dihydro-6-pyrimidone. With methyl iodide substitution in the 1-position first occurs, and then this compound apparently forms an additive product with another molecule of methyl iodide. With ethyl bromide or allyl bromide, however, the action is quite different, oxygen ethers being formed in each case and there is no indication of substitution of the alkyl groups on a nitrogen atom of the ring.

2-p-Nitrobenzylthiol-4-methyldihydro-6-pyrimidone,

m. p. 220°, is obtained by the action of *p*-nitrobenzyl chloride on the sodium salt of 2-thio-4-methyluracil. When treated with the calculated amount of methyl iodide in the presence of sodium methoxide, it yields 2-*p*-nitrobenzylthiol-1:4-dimethyldihydro-6-pyrimidone, $\text{CH} \begin{array}{c} \text{CO} \cdot \text{NMe} \\ \diagup \quad \diagdown \\ \text{CMe} - \text{N} \end{array} \text{C} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, m. p. 136°, which is hydrolysed by hydrochloric acid, giving 1:4-dimethyluracil and *p*-nitrobenzylmercaptan, m. p. 58°. By further alkylation, this dimethyl derivative gave an additive compound, some of which was also isolated from the products of the first alkylation. Its constitution is apparently $\text{CH} \begin{array}{c} \text{Cl}(\text{OMe}) \cdot \text{NMe} \\ \diagup \quad \diagdown \\ \text{CMe} - \text{N} \end{array} \text{C} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, and on hydrolysis it gives 1:4-dimethyluracil and *p*-nitrobenzyl disulphide, m. p. 126.5°, the latter being formed by oxidation due to the presence of a trace of free iodine.

With ethyl bromide the sodium salt of 2-*p*-nitrobenzylthiol-4-methyldihydro-6-pyrimidone gives 6-ethoxy-2-*p*-nitrobenzylthiol-4-methylpyrimidine, $\text{CH} \begin{array}{c} \text{C}(\text{OEt}) \cdot \text{N} \\ \diagup \quad \diagdown \\ \text{CMe} - \text{N} \end{array} \text{C} \cdot \text{S} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, m. p. 104°; on hydrolysis, this yields 4-methyluracil. In a similar manner with allyl bromide, 6-allyloxy-2-*p*-nitrobenzylthiol-4-methylpyrimidine, m. p. 77–78°, is obtained.

Strakosch's observation (*Ber.*, 1872, 5, 698) giving the m. p. 140° for *p*-nitrobenzyl mercaptan is incorrect (see above) and a repetition of his work did not yield any of this mercaptan. W. G.

Colouring Matters from 1:2:4:5-Tetrahydroxybenzene and Related Substances. DHIRENDRA NATH MUKERJI (*T.*, 1922, 121, 545–552).

The Cyanine Dyes. IV. Cyanine Dyes of the Benzothiazole Series. WILLIAM HOBSON MILLS (*T.*, 1922, 121, 455–466).

Ring Closure with Hydrazinedicarbonamides containing Sulphur. II. Thiourazole. F. ARNDT, E. MILDE, and F. TSCHENSCHER (*Ber.*, 1922, 55, [B], 341–356; cf. Arndt and Milde, *A.*, 1921, i, 813).—Further investigation has established the general validity of the rule that ring closure with hydrazinedicarbonamides containing sulphur takes place in neutral or acid media by means of the sulphur atom, with formation of thiodiazoles, whereas in alkaline solution it occurs through the nitrogen atom, thus giving triazoles.

The hydrazide, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$, loses successively aniline, ammonia, and hydrogen sulphide when boiled with sodium hydroxide solution. The first change constitutes the main reaction and leads to the production of thiourazole, $\text{NH} \begin{array}{c} \text{CO} \cdot \text{NH} \\ \diagup \quad \diagdown \\ \text{CS} - \text{NH} \end{array}$, small, colourless crystals, m. p. 206° (decomp.). The substance is most

conveniently isolated from the products of the reaction as the *monosodium* salt (the trihydrate and anhydrous substance are described) from which free thiourazole is readily obtained by addition of acid. Elimination of ammonia gives 4-*phenylthiourazole*, $\text{NPh} \begin{smallmatrix} \text{CO} \cdot \text{NH} \\ \text{CS} \cdot \text{NH} \end{smallmatrix}$ (see later), but the product derived by

loss of hydrogen sulphide has not been isolated in this connexion. The constitution of thiourazole is established by the formation of a dark yellow *tri-silver* salt, $\text{C}_2\text{ON}_3\text{SAg}_3$, by its oxidation by iodine in alcoholic solution to *thiourazole disulphide*, $\begin{smallmatrix} \text{NH} \cdot \text{N} \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > \text{C} \cdot \text{S} \cdot \text{S} \cdot \text{C} < \begin{smallmatrix} \text{N} \cdot \text{NH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$,

colourless, lustrous needles, m. p. 246° (decomp.) (the *dihydrate* is also described), and by the conversion of its monosodium salt by means of methyl sulphate into thiourazole methyl ether,

$\text{NH} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{SMe}) \cdot \text{N} \end{smallmatrix}$, colourless, anhydrous plates, m. p. $192\text{--}193^\circ$.

The substance described by Freund (A., 1894, i, 97; 1895, i, 400) as thiourazole is actually iminothiodiazolone, $\text{S} < \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{NH}) \cdot \text{NH} \end{smallmatrix}$ (cf. Busch and Schmidt, A., 1913, i, 907; Busch and Lotz, A., 1915, i, 317).

[With FRL. BIELICH.]—Thiourazole is more conveniently prepared by the action of boiling sodium hydroxide solution on the *hydrazide*, $\text{SMe} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{CS} \cdot \text{NH}_2$; the latter, a colourless, crystalline powder, m. p. 208° (decomp.), is obtained by the action of methyl chlorothioformate on thiosemicarbazide in warm aqueous solution.

3-*Imino-4-phenylurazole*, $\text{NPh} \begin{smallmatrix} \text{CO} \text{---} \text{NH} \\ \text{C}(\text{NH}) \cdot \text{NH} \end{smallmatrix}$, colourless, lustrous leaflets, m. p. $231\text{--}232^\circ$, is obtained readily and exclusively by the action of boiling alkali hydroxide on *phenylhydrazothiodicarbonamide S-methyl ether*, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{NH} \cdot \text{C}(\text{NH}) \cdot \text{SMe}$, colourless, silky needles, m. p. indefinite 147° (decomp.).

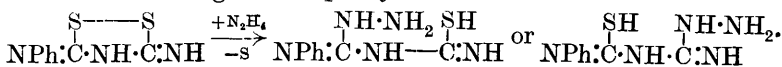
The *hydrazide*, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, small, lustrous needles, m. p. 198° , is prepared by the action of semicarbazide hydrochloride on phenylthiocarbimide in aqueous alcoholic solution; it is converted by boiling alkali hydroxide solution almost exclusively into 4-phenylthiourazole (see above), long, coarse, colourless prisms ($+1\text{H}_2\text{O}$), m. p. (anhydrous) 196° . 4-*Phenylthiourazole disulphide*, needles, m. p. $284\text{--}285^\circ$, is most conveniently prepared by the oxidation of 4-phenylthiourazole with iodine in alcoholic solution. 4-*Phenylthiourazole methyl ether* crystallises in colourless, lustrous needles, m. p. $207\text{--}208^\circ$. The hydrazide, $\text{NHPh} \cdot \text{CS} \cdot \text{NH} \cdot \text{NH} \cdot \text{CO} \cdot \text{NH}_2$, is transformed by methyl sulphate and sodium hydroxide into the corresponding *S-methyl ether* which could not be obtained in the crystalline form; it is converted by boiling hydrochloric acid into phenylthiourazole methyl ether and by boiling sodium hydroxide solution into *anilinourazole*, $\text{NH} \begin{smallmatrix} \text{C}(\text{NPh}) \cdot \text{NH} \\ \text{CO} \text{---} \text{NH} \end{smallmatrix}$, small, colourless, anhydrous crystals, m. p. 238° .

The *hydrazide*, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2$, lustrous leaflets, m. p. 180° , is prepared from thiosemicarbazide and phenylthiocarbimide in aqueous-alcoholic solution. It is converted by boiling alkali hydroxide solutions with loss of ammonia and hydrogen sulphide into 4-phenyldithiourazole, $\text{NPh}\begin{smallmatrix} \text{CS}\cdot\text{NH} \\ \text{CS}\cdot\text{NH} \end{smallmatrix}$, colourless, coarse crystals, m. p. 216° (decomp.) (the substance described previously in the literature as 4-phenyldithiourazole is anilinothiodiazoethiol), and 3-imino-4-phenylthiourazole, m. p. $267\text{--}268^\circ$ (the *monohydrate*, colourless needles, is also described). Both substances are acidic, but can be largely separated from one another with the aid of sodium carbonate solution, in which practically only phenyldithiourazole is soluble. The latter substance is transformed by methyl sulphate in dilute ammoniacal solution into 4-phenyldithiourazole

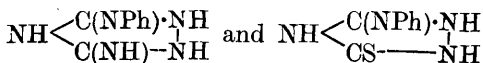
dimethyl ether, $\text{NPh}\begin{smallmatrix} \text{C}(\text{SMe})\cdot\text{N} \\ \text{C}(\text{SMe})\cdot\text{N} \end{smallmatrix}$, long, lustrous needles, m. p. $132\text{--}5^\circ$ (the corresponding *nitrate* has m. p. 141°); it is oxidised by potassium ferricyanide in the presence of sodium hydroxide or by an alcoholic solution of iodine to a mixture of *products*, one of which, yellow crystals, m. p. 228° , gave analytical results in agreement with the formula $\text{C}_{16}\text{H}_{12}\text{N}_6\text{S}_4$. 3-Imino-4-phenylthiourazole is converted by methyl sulphate and sodium hydroxide into the corresponding *methyl ether*, m. p. 168° (the *hydrate*, $2\text{C}_9\text{H}_{10}\text{N}_4\text{S}_2\text{H}_2\text{O}$, silky needles, is also described); it behaves somewhat anomalously when oxidised, since it is stable towards iodine in alcoholic solution, but is affected by potassium ferricyanide in the presence of ammonia or sodium hydroxide; probably, however, a disulphide is not thereby formed, since the same phenomena are observed with the methyl ether.

H. W.

Disulphides with Neighbouring Single and Multiple Linkings. Syntheses of Triazoles and Thiodiazoles. EMIL FROMM, with ERICH KAYSER, KARL BRIEGLEB, and ERICH FÖHRENBACH (*Annalen*, 1922, **426**, 313—345).—The course followed by the reaction between bases and unsaturated disulphides of the type $\text{X}:\text{CR}:\text{S}\cdot\text{S}:\text{CR}:\text{Y}$ is, in general, that expressed by the equation $\text{X}:\text{CR}:\text{S}\cdot\text{S}:\text{CR}:\text{Y} + \text{NH}_2\text{Ph} \rightarrow \text{X}:\text{CR}:\text{SH} + \text{NHPh}:\text{CR}:\text{Y} + \text{S}$. The present paper shows that the reactions between hydrazines and similar disulphides are of an analogous kind and may be utilised for the synthesis of triazoles and thiodiazoles. For instance, phenyldithiobiuret may react with hydrazine in two ways, eliminating one atom of sulphur and yielding either aminophenylguanidinothiurea or aminoguanidinophenylthiurea:



The former can pass into a triazole by elimination of either H_2S or NH_3 , but the latter can give only the first of the two following substances:



3-amino-5-anilino-1 : 2 : 4-triazole and 3-thio-5-anilino-1 : 2 : 4-triazole.

The principal product is actually 3-thio-5-anilino-1 : 2 : 4-triazole, which separates from hot water in needles, m. p. 268°. This shows that the main product of the initial ring-scission is the aminophenylguanidinothiurea. The by-products obtained are 3-amino-5-anilino-1 : 2 : 4-triazole, which has m. p. 77° and gives a *monobenzoyl* derivative of m. p. 142°, the *salt*, m. p. 70°, of the aminoanilino-1 : 2 : 4-triazole (basic constituent) with the thioanilino-1 : 2 : 4-triazole (acid constituent), and *aminoguanidinophenylthiurea*, which has m. p. 155° and yields a *benzylidene* derivative crystallising in yellow needles, m. p. 223°. The thioanilino-1 : 2 : 4-triazole gives a *dibenzoyl* derivative (yellow needles, m. p. 130°), and on treatment with benzyl chloride and alkali yields 5-anilino-3-benzylthiol-1 : 2 : 4-triazole, which has m. p. 168° and gives a *dibenzoyl* derivative, m. p. 108°. On oxidation by means of ferric chloride, the thioanilino-1 : 2 : 4-triazole gives a yellow *disulphide*, $S_2\left(C\begin{smallmatrix} \text{N}\cdot\text{N} \\ \text{NH} \end{smallmatrix}\right)_2$, m. p. 225°, which undergoes fission by means of sodium hydroxide, giving 3-hydroxy-5-anilino-1 : 2 : 4-triazole, m. p. 169° (the *dibenzoyl* derivative has m. p. 166°), and 3-thio-5-anilino-1 : 2 : 4-triazole. Aniline effects a similar fission, the products being the same thioanilino-1 : 2 : 4-triazole and 3 : 5-dianilino-1 : 2 : 4-triazole, which is conveniently isolated in the form of its *dibenzoyl* derivative, m. p. 88°.

The action of phenylhydrazine on perthiocyanic acid has already been investigated by Fromm and Schneider (A., 1906, i, 714) and has been shown to proceed in directions analogous to the reactions described above, the products being 3 : 5-dithio-1-phenyl-1 : 2 : 4-triazole and 3-amino-5-thio-1-phenyl-1 : 2 : 4-triazole. The former compound is now subjected to a closer investigation with the view of establishing its constitution quite definitely. On methylation by methyl iodide and sodium hydroxide, it forms 3 : 5-dimethylthiol-1-phenyl-1 : 2 : 4-triazole, filamentous needles, m. p. 73·5°, which on oxidation by permanganate yields 3 : 5-dimethyl-disulphon-1-phenyl-1 : 2 : 4-triazole, filamentous needles, m. p. 182°, together with a substance, $C_{10}H_{11}O_2N_3S_2$, m. p. 104·5°, which may be either a monosulphone or a disulphoxide. The disulphone is unstable towards alkalis and loses one sulphone group, yielding 5-hydroxy-3-methylsulphone-1-phenyl-1 : 2 : 4-triazole, m. p. 206°, identical with the substance obtained on oxidising Acree's 5-hydroxy-3-methylthiol-1-phenyl-1 : 2 : 4-triazole (A., 1904, i, 351) by means of permanganate. 5-Hydroxy-3-methylsulphone-1-phenyl-1 : 2 : 4-triazole can be methylated by means of its silver salt, giving 5-methoxy-3-methylsulphone-1-phenyl-1 : 2 : 4-triazole, which separates from alcohol in fine needles, m. p. 206°. The disulphone, in contrast to its behaviour towards alkalis, is very stable towards acids, and can be nitrated with the formation of 3 : 5-dimethylsulphone-1-nitrophenyl-1 : 2 : 4-triazole, m. p. 238°, which with alkalis is converted into a substance, 5-hydroxy-3-methylsulphone-1-nitrophenyl-1 : 2 : 4-triazole, m. p. 234°, identical with the product obtained on directly nitrating hydroxymethylsulphonephenyltriazole.

Some derivatives of 3-amino-5-thio-1-phenyl-1 : 2 : 4-triazole are described also. 3-Amino-5-methylthiol-1-phenyltriazole, needles, m. p. 148°, is obtained with the help of methyl iodide and alkali; on benzylation in the presence of pyridine, it yields 3-benzoyl-amino-5-methylthiol-1-phenyl-1 : 2 : 4-triazole, m. p. 141·5°, which may also be obtained by methylating Fromm and Sturm's 5-thiol-3-benzoylamino-1-phenyl-1 : 2 : 4-triazole (A., 1913, i, 204). A dibenzoyl derivative, m. p. 152°, is formed when 3-amino-5-methylthiol-1-phenyltriazole is heated with benzoyl chloride until hydrogen chloride is no longer evolved.

The simplest members of the series to which the above substances belong are 3 : 5-dithiol-1 : 2 : 4-triazole, $\text{NH} \begin{smallmatrix} \text{C}(\text{SH})\text{:N} \\ \text{C}(\text{SH})\text{:N} \end{smallmatrix}$, and 5-amino-

3-thiol-1 : 2 : 4-triazole, $\text{NH} \begin{smallmatrix} \text{C}(\text{SH})=\text{N} \\ \text{C}(\text{NH}_2)\text{:N} \end{smallmatrix}$, which are both obtained

as their hydrazine salts when hydrazine hydrate is allowed to react with perthiocyanic acid. They may be separated by taking advantage of the fact that the monothiol compound is the weaker acid and is liberated in the free condition when an aqueous solution of its hydrazine salt is evaporated. The hydrazine salt of the dithiol compound is stable in these circumstances, but may be decomposed by means of mineral acids or by benzaldehyde. 5-Amino-3-thiol-1 : 2 : 4-triazole separates from water in small, white needles, m. p. 298° (decomp.); 3 : 5-dithiol-1 : 2 : 4-triazole, m. p. 196° (decomp.), has strongly reducing properties; it first reddens blue litmus paper and then bleaches it, and quickly reduces iodine, ferric chloride, and ferricyanide; it gives a yellow lead salt, $\text{C}_2\text{HN}_3\text{S}_2\text{Pb}$, and a hydrazine salt, $\text{C}_2\text{H}_7\text{N}_5\text{S}_2$, m. p. 268° (decomp.). On benzylation by the Schotten-Baumann method, aminothioltriazole gives 5-imino-3-thion-2 : 4-dibenzoyl-1 : 2 : 4-triazole, yellow crystals, m. p. 178°, whilst the dithioltriazole yields 3 : 5-dithion-1 : 2 : 4-tribenzoyl-1 : 2 : 4-triazole, m. p. 171°, which on treatment with benzyl chloride and sodium hydroxide gives 3 : 5-dibenzylthiol-1 : 2 : 4-triazole, m. p. 112° (its hydrochloride has m. p. 157°), the product of the direct benzylation of dithioltriazole. The dibenzyl compound, on benzylation by the Schotten-Baumann method, yields 4-benzoyl-3 : 5-dibenzylthiol-1 : 2 : 4-triazole, which forms fine, white needles, m. p. 91°. The tribenzoate is readily hydrolysed by alkalis, all three benzoyl groups being eliminated. All these reactions are in harmony with the constitutions assigned to the original condensation products.

An investigation of the substances, $\text{C}_2\text{H}_3\text{N}_3\text{S}_2$ and $\text{C}_2\text{H}_4\text{N}_4\text{S}$, obtained by Freund and Imgart (A., 1895, i, 400) from hydrazodicarbondithioamide leads the present authors to the conclusion that these substances are not triazoles, but thiodiazoles, $\text{S} \begin{smallmatrix} \text{CS}—\text{NH} \\ \text{C}(\text{NH})\text{:NH} \end{smallmatrix}$

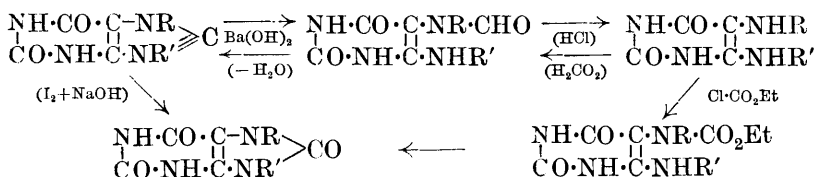
and $\text{S} \begin{smallmatrix} \text{C}(\text{NH}_2)\text{:N} \\ \text{C}(\text{NH}_2)\text{:N} \end{smallmatrix}$, isomeric, therefore, with the substances obtained

from perthiocyanic acid and hydrazine. 5-Amino-3-thion-4 : 1 : 2-thiodiazole forms a lead salt, $\text{C}_4\text{H}_4\text{N}_6\text{S}_2\text{Pb}$, and on benzylation gives 5-amino-3-thion-2 : 5-dibenzoyl-4 : 1 : 2-thiodiazole, m. p. 224°;

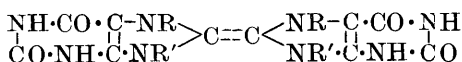
the corresponding uric acids. They are more strongly basic than the uric acids and are characterised by forming sparingly soluble salts with the acid HI_3 . A convenient method of preparation consists in oxidising by means of iodine a solution of the sodium salt of the 7 : 9-dialkyl-8-thiouric acid, rendered alkaline by sodium hydrogen carbonate; usually the periodide of the deoxyuric acid is precipitated. Nitrous acid also converts the thiouric acid into the deoxyuric acid.

The deoxyuric acids are very stable substances; in acid and in alkaline solution they are remarkably resistant to oxidising and reducing agents. However, the product obtained by the action of chlorine water gives the murexide test with ammonia, and the periodide when heated with sodium hydroxide decomposes, with the formation of a moderate quantity of the corresponding dialkyluric acid, from which it appears that the residue, $\text{NH}\cdot\text{CO}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\text{NR} > \text{C} < \text{CO}\cdot\text{NH}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\text{NR}'$, must exist in the deoxyuric acid. With aqueous barium hydroxide hydrolysis occurs; the product is a formyldialkyldiaminouracil, from which the formyl group may be eliminated with the aid of hydrochloric acid. The free dialkyldiaminouracil may be re-formylated, using formic acid, and the formyl compound dehydrated with the formation of the original deoxyuric acid. If the dialkyldiaminouracil is treated with chloroformic ester, a urethane is produced, from which the uric acid may be prepared by the usual means.

These reactions are represented as follows :



The constitution suggested for the deoxyuric acids is a remarkable one, inasmuch as it involves a quinquivalent nitrogen and the presence of a triple linking in a ring, but it appears not to be without analogy. Possibly the above formula should be changed to $\text{NH}\cdot\text{CO}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\text{NR} \equiv \text{C} < \text{CO}\cdot\text{NH}\cdot\overset{\text{H}}{\underset{\text{H}}{\text{C}}}\cdot\text{NR}'$, but the formula



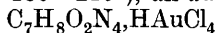
is out of the question by reason of the molecular weight and on obvious chemical grounds.

C. K. I.

7 : 9-Dialkyldeoxyuric Acids. II. 7 : 9-Dimethyldeoxyuric Acid. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1922, 426, 246—263; cf. preceding abstract).—7 : 9-Dimethyl-8-thio- ψ -uric acid is readily prepared from 7-methyluramil and methylthiocarbimide. It separates from warm water in four-sided prisms, m. p. 224°

(corr.; decomp.), after sintering at 215° . A small amount of 7:9-dimethyl-8-thiouric acid is formed as a by-product in this condensation, and may be obtained in good yield from the ψ -uric acid by boiling with 10% hydrochloric acid. It forms needles which dissolve in about 600 parts of boiling water and melt with decomposition at 362° .

7:9-Dimethyldeoxyuric acid may be prepared from the thiouric acid by either of the general methods previously described. It is soluble in about 4 parts of boiling water, from which it separates in needles which decompose at 385° . It has the stability and general properties characteristic of its class (preceding abstract) and forms a *hydrochloride* (decomp. $345\text{--}350^{\circ}$), a *perchlorate* (decomp. 270°), an *acid sulphate* (decomp. 265°), a *nitrate* (decomp. 205°), an *iodide* (decomp. 350°), a *periodide*, $\text{C}_7\text{H}_8\text{O}_2\text{N}_4\cdot\text{HI}_3$, dark brown needles (decomp. $180\text{--}210^{\circ}$), an *aurichloride*,



(decomp. $286\text{--}296^{\circ}$), a *platinichloride*, and an *additive* product with silver nitrate (? $2\text{C}_7\text{H}_8\text{O}_2\text{N}_4\cdot\text{AgNO}_3$). 7:9-Dimethyldeoxyuric acid is converted by heating with sulphur into 7:9-dimethyl-8-thiouric acid, and by iodine and alkali hydroxides into 7:9-dimethyluric acid. 6-Methylamino-5-formylmethylaminouracil (decomp. 385°) can be crystallised from about 20 parts of boiling water, or from acetic acid, but in the latter case $2\text{CH}_3\cdot\text{CO}_2\text{H}$ is retained. 5:6-Dimethyldiaminouracil crystallises from acetic acid (with $2\text{CH}_3\cdot\text{CO}_2\text{H}$) as rhombic plates, m. p. 380° (decomp.), and gives a *hydrochloride* which decomposes at 261° . The *methyl carbamate* obtained from 5:6-dimethyldiaminouracil and methyl chloroformate, dissolves in 60 parts of boiling water and decomposes at 343° . The *ethyl* ester is soluble in 10 parts of boiling water and decomposes at 325° . C. K. I.

7:9-Dialkyldeoxyuric Acids. III. 7-Methyl-9-ethyldeoxyuric Acid. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1922, 426, 264—269; cf. preceding abstracts).—7-Methyl-9-ethyl-8-thio- ψ -uric acid, prepared from 7-methyluramil and ethylthiocarbimide, forms hexagonal tablets, decomp. 206° (corr.). The *thiouric acid* dissolves in about 400 parts of boiling water, from which it separates in silky needles, decomp. 359° . 7-Methyl-9-ethyldeoxyuric acid crystallises with $2\text{H}_2\text{O}$ as leaflets, decomp. 325° (corr.), and gives a *hydrochloride*, decomp. $277\text{--}278^{\circ}$ (corr.); an *iodide*, decomp. 254° (corr.); a *periodide*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\cdot\text{HI}_3$, decomp. 215° (corr.); an *aurichloride*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\cdot\text{HAuCl}_4$, decomp. 190° , and a complex salt with silver nitrate. All these compounds are similar to the lower homologues previously described. C. K. I.

7:9-Dialkyldeoxyuric Acids. IV. 9-Methyl-7-ethyldeoxyuric Acid. HEINRICH BILTZ and DOROTHEA HEIDRICH (*Annalen*, 1922, 426, 269—283; cf. preceding abstracts).—9-Methyl-7-ethyl-8-thio- ψ -uric acid, leaflets, m. p. 212° (decomp.), is difficult to isolate owing to the ease with which it undergoes conversion into 9-methyl-7-ethyl-8-thiouric acid, silky filamentous crystals, decomp. 344° (corr.). 9-Methyl-7-ethyldeoxyuric acid, separates

from water with $2\text{H}_2\text{O}$ in rectangular leaflets, decomp. 340° (corr.), and gives a *hydrochloride*, decomp. 263° (corr.); an *iodide*, decomp. 251° (corr.); a *periodide*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{HI}_2$, decomp. $215\text{--}222^\circ$ (corr.); a *periodide*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{HI}_3$, decomp. $230\text{--}235^\circ$ (corr.); a *perchlorate*, decomp. 238° (corr.); a *nitrate*, decomp. 194° (corr.); an *aurichloride*, decomp. 239° (corr.), and a complex salt with potassium tri-iodide, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{S}_3\text{KI}_3$, decomp. 242° (corr.). 6-Methylamino-5-formylethylaminouracil, best obtained by using lime-water in place of baryta, forms hexagonal crystals, decomp. 262° , and is extremely soluble in water. 6-Methylamino-5-ethylaminouracil, forms long needles, m. p. 235° (decomp.), gives a *hydrochloride*, $\text{C}_7\text{H}_{12}\text{O}_2\text{N}_4\text{HCl}$, decomp. 280° (corr.), and a *methyl carbamate*, m. p. 326° (decomp.), on condensation with methyl chloroformate. 9-Methyl-7-ethyluric acid, forms small, lancet-like leaflets, m. p. 355° (corr., decomp.), and on treatment with chlorine and water yields 4:5-dihydroxy-9-methyl-7-ethyl-4:5-dihydrouric acid, which crystallises as small elongated prisms, m. p. 240° (decomp., corr.). 4-Hydroxy-5-methoxy-9-methyl-7-ethyl-4:5-dihydrouric acid, m. p. 131° (corr.), and 4-hydroxy-5-ethoxy-9-methyl-7-ethyl-4:5-dihydrouric acid, m. p. 193° , are prepared from the uric acid by means of chlorine and methyl or ethyl alcohol.

C. K. I.

7:9-Dialkyldeoxyuric Acids. V. 1:7:9-Trimethyldeoxyuric Acid. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1922, 426, 283—290; cf. preceding abstracts).—1:7:9-Trimethyl-8-thio- ψ -uric acid is readily prepared by condensation of 1:7-dimethyluramil with methylthiocarbimide. It forms small, thick crystals, decomp. 185° , and on heating with hydrochloric acid passes into 1:7:9-trimethyl-8-thiouric acid, m. p. 317° (corr.), which may also be obtained from 7:9-dimethylthiouric acid by methylation with the help of methyl sulphate.

1:7:9-Trimethyldeoxyuric acid separates from water in small, rhombic leaflets, with $1\text{H}_2\text{O}$, m. p. 348° (corr., decomp.), and forms a *hydrochloride*, filamentous needles, decomp. 231° (corr.), an *iodide*, glistening, rectangular leaflets, decomp. 249° (corr.), a *periodide*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{HI}_3$, sinters at 208° , a *nitrate*, sinters at 125° , and an *aurichloride*, $\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4\text{HAuCl}_4$, needles, decomp. 267° (corr.). 6-Methylamino-5-formylmethylamino-3-methyluracil, forms rectangular tablets which sinter at 267° and evolve water vapour, leaving a residue consisting of 1:7:9-trimethyldeoxyuric acid. C. K. I.

7:9-Dialkyldeoxyuric Acids. VI. 1:3:7:9-Tetramethyldeoxyuric Acid. HEINRICH BILTZ and DOROTHEA HEIDRICH (*Annalen*, 1922, 426, 290—299; cf. preceding abstracts).—1:3:7:9-Tetramethyl- ψ -uric acid, decomp. 165° (corr.), is prepared from 1:3:7-trimethyluramil and methylthiocarbimide, or, alternatively, from 7:9-dimethyl-8-thio- ψ -uric acid by methylation with methyl sulphate. It passes very easily into 1:3:7:9-tetramethylthiouric acid, which forms fine needles, m. p. $255\text{--}258^\circ$ (decomp., corr.). Methylation of 1:3:7-trimethyl-8-thiouric acid by means of methyl sulphate and sodium hydroxide leads to the

formation of the 8-methylthiol ether, m. p. 179—180° (corr.), which appears to possess no tendency to pass into the isomeric C-methyl derivative.

1 : 3 : 7 : 9-Tetramethyldeoxyuric acid, m. p. 282° (corr.), forms a hydrochloride, m. p. 110—115° (corr.), a perchlorate, decomp. 237° (corr.), an iodide, decomp. 238° (corr.), and a periodide, $C_9H_{12}O_2N_4HI_3$, m. p. 195° (corr.), and on hydrolysis by barium hydroxide yields 6-methylamino-5-formylmethylamino-1 : 3-dimethyluracil, which separates from alcohol as small, elongated prisms, decomp. 259—260° (corr.). 5 : 6-Dimethylamino-1 : 3-dimethyluracil, decomp. 290° (corr.), is unstable in the presence of air and moisture. It forms a hydrochloride, prisms, decomp. 278° (corr.). These compounds are related like their analogues previously described.

C. K. I.

7 : 9-Dialkyldeoxyuric Acids. VII. 7 : 9-Diethyldeoxyuric Acid. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1921, **426**, 299—305; cf. preceding abstracts).—7 : 9-Diethyl-8-thio- ψ -uric acid (prepared from 7-ethylramil and ethylthiocarbimide), forms leaflets, decomp. 208° (corr.). 7 : 9-Diethyl-8-thiouric acid, decomp. 340—369°, is sparingly soluble in boiling water, and does not give the murexide reaction. 7 : 9-Diethyldeoxyuric acid separates with $1H_2O$ from water as rectangular leaflets, decomp. 305—307°, and forms an iodide, rectangular leaflets, m. p. 262° (corr., decomp.), a periodide, $C_9H_{12}O_2N_4HI_2$, brown needles, m. p. 225° (corr., decomp.), and an aurichloride, $C_9H_{12}O_2N_4HAuCl_4$, decomp. 180—190°. 6-Ethylamino-5-formylethylaminouracil, forms needles which decompose at 268° (corr.), eliminating water and leaving a residue consisting of the original deoxyuric acid.

C. K. I.

9-Methyl-8-iodo- $\Delta^{7:8}$ -isoxanthine. HEINRICH BILTZ and HANS BÜLOW (*Annalen*, 1922, **426**, 306—312; cf. preceding abstracts).—The sulphur atom in 9-methyl-8-thiouric acid is removed by iodine and sodium hydrogen carbonate, the product being a polyiodide of 8-iodo-9-methyl- $\Delta^{7:8}$ -isoxanthine, which is obtained in the free state on subsequent reduction by sulphurous acid. It separates from 800—900 parts of hot water in short, thick crystals which begin to lose iodine at 280°. It forms an ammonium salt, $C_6H_4O_2N_4I \cdot NH_4 \cdot 2H_2O$, and a di-iodide, $C_6H_5O_2N_4I_2$, and on reduction by means of stannous chloride gives 9-methyl- $\Delta^{7:8}$ -isoxanthine, which is conveniently isolated in the form of its stannichloride, $(C_6H_6O_2N_4)_2 \cdot H_2SnCl_4$.

Methylation of 9-methyl-8-thiouric acid by means of methyl sulphate and potassium hydroxide leads to the formation of 8-methylthiol-9-methyl- $\Delta^{7:8}$ -isoxanthine, which forms fine needles or four-sided leaflets, decomp. 335° (corr.).

C. K. I.

Oxonium Salts of Azo-substances. F. KEHRMANN and R. VAN DER LAAR (*Ber.*, 1922, **55**, [B], 511—512).—*p*-Azoanisole unites slowly with acid-free methyl sulphate at 55—60°, yielding violet crystals which dissolve in water; addition of perchloric acid to the aqueous solution precipitates the corresponding perchlorate,

$C_{15}H_{17}N_2ClO_6$, dark red leaflets with a violet, metallic glance, from which the *platinichloride*, $(C_{15}H_{17}O_2N_2Cl)_2PtCl_4$, is obtained as a tile-red, crystalline powder. The constitution of the perchlorate is in all probability represented by the formula $OMe \cdot C_6H_4 \cdot NMe(ClO_4) \cdot N \cdot C_6H_4 \cdot OMe$; the oxonium formula, $OMe \cdot C_6H_4 \cdot N \cdot N \cdot C_6H_4 \cdot OMe_2 \cdot ClO_4$, is improbable, but the quinonoid expression, $OMe \cdot C_6H_4 \cdot NMe \cdot N \cdot C_6H_4 \cdot O < \overset{Me}{\underset{ClO_4}{C}}$, is not disproved. *p*-Azophenetole gives precisely similar salts. H. W.

Preparation of *o*-Hydroxyazo-colouring Matters. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (F.P. 22347; from *Chem. Zentr.*, 1921, iv, 1067—1068).—Diazotised anthranilic acid is combined with pyrazolones containing a hydroxyl group in the aryl portion of the molecule, or diazotised aromatic amines which do not contain a hydroxyl or carboxyl group in the ortho-position to the amino-group are combined with pyrazolones containing a hydroxyl or carboxyl group in the aryl portion of the molecule. Colouring matters are obtained:—From *o*-diazotised anthranilic acid and 1-5'-sulpho-2'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid, $CO_2H \cdot C_6H_2(SO_3H)(OH) \cdot C_3N_2H_2O$ (from 5-sulpho-2-hydroxy-1-hydrazinobenzene-3-carboxylic acid and ethyl acetoacetate). From diazotised chloroanthranilic acid ($NH_2 : CO_2H : Cl = 1 : 2 : 4$) and 1-5'-chloro-3'-sulpho-2-hydroxyphenyl-3-methyl-5-pyrazolone (from 5-chloro-3-sulpho-2-hydroxy-1-hydrazinobenzene and ethyl acetoacetate). From diazotised sulphoanthranilic acid ($NH_2 : CO_2H : SO_3H = 1 : 2 : 5$) and 1-5'-nitro-2'-hydroxyphenyl-3-methyl-5-pyrazolone (from 5-nitro-2-hydroxy-1-hydrazinobenzene and ethyl acetoacetate). From diazotised sulphoanthranilic acid and 1-4'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. From diazotised sulphanilic acid and 1-4'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. From diazobenzene and 1-5'-chloro-2'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. From *m*-diazobenzoic acid and 1-5'-sulpho-1'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. From 1-diazonaphthalene-5-sulphonic acid and 1-4'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. 5-Chloro-2-hydroxy-1-phenylhydrazine-3-carboxylic acid (obtained by reduction of diazotised 4-chloro-2-amino-1-hydroxybenzene-6-carboxylic acid) gives with ethyl acetoacetate 1 : 5'-chloro-2'-hydroxyphenyl-3-methyl-5-pyrazolone-3'-carboxylic acid. Most of the compounds obtained are fast yellow dyes. G. W. R.

The Preparation of Optically Active Hydrazines. II. The Preparation of *dl-p*-sec.-Butylphenylhydrazine. The Resolution of *dl-p*-sec.-Butylaniline. J. W. E. GLATTFELD and EDGAR WERTHEIM (*J. Amer. Chem. Soc.*, 1921, **43**, 2682—2687; cf. A., 1921, i, 63).—*dl-p*-sec.-Butylaniline was obtained by reducing *dl-p*-nitro-sec.-butylbenzene with tin and hydrochloric acid. It has b. p. 112°/11 mm., and gives an acetyl derivative, m. p. 125—126° (cf. Reilly and Hickinbottom, T., 1920, **117**, 120). The racemic butylaniline was resolved into its optically active components by converting it into its camphorsulphonates and separating these by
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recrystallisation first from ether and then from a mixture of ethyl acetate and acetone. The l-p-sec.-*butylaniline* has b. p. 116·5—118°/15 mm. and gives an *acetyl* derivative, m. p. 123—124°; $[\alpha]_D^{25} + 0·9301^\circ$. d-p-sec.-*Butylaniline* has b. p. 123—125°/20 mm.; $[\alpha]_D^{25} + 0·26^\circ$.

dl-p-sec.-*Butylaniline* was diazotised and the resulting product poured into a cold solution of sodium sulphite, giving a rich red solution. This was reduced by zinc and acetic acid and ultimately dl-p-sec.-*butylphenylhydrazine* was isolated having b. p. 155—157°/18 mm. and giving a *hydrochloride*, a *sodium sulphonate*, and a crystalline *derivative* with d-galactose, m. p. 152—155°. Attempts to reduce the active butylanilines in a similar way were not successful. W. G.

The Coagulation of Protein by Sunlight. ELRID GORDON YOUNG (*Proc. Roy. Soc.*, 1922, [B], 93, 235—248).—Sunlight or the arc light when freed from ultra-violet and infra-red rays can effect coagulation of serum-albumin and ovalbumin when these have been recrystallised several times. The process consists of two separate reactions, (1) denaturation, (2) flocculation. During the primary reaction there is an increase of viscosity and specific rotation and a decrease of surface tension, and at the same time a convergence of the reaction of the solution towards neutrality independent of its initial P_H . Serum-albumin is much more easily affected than ovalbumin. The rôle of light is similar to that of heat—catalysis of the primary reaction. Addition of certain substances, for instance potassium thiocyanate or alcohol, accelerate the reaction. H. K.

Deaminoproteins. J. HERZIG and HANS LIEB (*Z. physiol. Chem.*, 1921, 117, 1—12).—Deaminoglutin, deamino-ovalbumin, deaminocasein, and deaminogliadin yield, when treated by the Van Slyke and Sørensen methods, approximately the same amount of amino-nitrogen as the respective proteins from which they are derived. S. S. Z.

Ultramicroscopic Investigation of Casein. B. BLEYER and R. SEIDL (*Kolloid Z.*, 1922, 30, 117—118).—An ultramicroscopic examination and comparison of calciumcasein and paracasein and of acid casein and acid paracasein. In the case of the calcium derivatives, it is shown that the Brownian movement of the paracasein compound is twice as rapid as that of the casein calcium compound. The individual particles of the paracasein compound are always smaller than those of the casein compound. This indicates that the viscosity of paracasein solutions will be considerably smaller and the electrical conductivity larger than in corresponding solutions of casein, a result which confirms the work of Laqueur and Sackur. It also supports Van Slyke's view that the molecular weight of paracasein is only half that of casein. The acid derivatives were prepared by shaking 1 gram of casein or paracasein with 100 c.c. of N/100 hydrochloric, sulphuric, lactic, or acetic acid. On examination in the luminous beam, it is found

that the particles are much larger than in the case of the calcium derivatives. As in the case of the calcium derivative, the casein particles are in more rapid motion than the corresponding paracasein particles. The lactic acid casein and hydrochloric acid casein particles are in the most rapid motion, but in all cases except lactic acid the velocity decreased markedly after keeping for twenty-four hours. The acid caseinates are shown to be adsorption complexes and not true chemical compounds. J. F. S.

Crystallisation of Hæmoglobin. G. AMANTEA and C. KRZYSZKOWSKY (*Arch. Fisiol.*, 1920, **18**, 87—92; from *Chem. Zentr.*, 1921, iii, 1324).—Crystallisation of hæmoglobin from the blood of many animals can easily be effected if hæmolysis is produced by saponaria-saponin (not, however, with human blood and blood of frogs and toads). The hæmoglobin of nucleated corpuscles is crystallised with difficulty. Addition of gum arabic to red corpuscles may induce the formation of hæmoglobin crystals. G. W. R.

Pigment Metabolism. I. FROMHOLDT and NERSESSOV (*Biochem. Z.*, 1921, **125**, 149—152).—Bilirubin prepared from a number of different sources and analysed by Pregl's method for carbon and hydrogen, and nitrogen by that of Kjeldahl, gave values in agreement with the accepted formula. H. K.

The "Coupled" Nucleic Acid from the Pancreas. II. EINAR HAMMARSTEN and ERIK JORPES (*Z. physiol. Chem.*, 1922, **118**, 224—232).—The nucleic acid from the pancreas previously described by Hammarsten yields guanylic acid and a substance which consists of a pentose and most probably of only one purine base, namely, adenine, on alkaline hydrolysis. In the authors' opinion, this reaction is characteristic of a nucleic acid resembling yeast-nucleic acid. S. S. Z.

The Isoelectric Point of Collagen. ARTHUR W. THOMAS and MARGARET W. KELLY (*J. Amer. Chem. Soc.*, 1922, **44**, 195—201).—The swelling method of determining the isoelectric point of American hide powder as the source of collagen is applicable only for the purpose of locating the approximate isoelectric region when solutions of widely differing hydrogen-ion concentrations are employed, and consequently large swelling differences are obtained. The dye method gives more consistent results, the values of p_{11} at the isoelectric point varying from 4.6 to 5.4, with an average of 5.0. The results indicate that hide substance, generally referred to as collagen, is a mixture of proteins rather than one simple protein. The isoelectric points of a number of different proteins, as reported in the literature, are tabulated. W. G.

The Significance of the Isoelectric Point for the Preparation of Ash-free Gelatin. JACQUES LOEB (*J. Amer. Chem. Soc.*, 1922, **44**, 213—215; cf. A., 1919, i, 295, 296, 418; ii, 14, 399, 497).—A reply to Smith (cf. A., 1921, i, 749). W. G.

The Drying and Swelling of Gelatin. S. E. SHEPPARD and F. A. ELLIOTT (*J. Amer. Chem. Soc.*, 1922, **44**, 373—379).—A preliminary note in which the authors consider the behaviour of

gelatin in "leaf" form and in cubes on ordinary "forced" drying and subsequent swelling. They conclude that the "case-hardening" effect, in particular as initiated at edges and corners, is responsible for two important phenomena in the hydration-dehydration cycle of gelatin jellies. The first, noted with "leaf" gelatin, is that the greatest shrinking and subsequent swelling takes place perpendicularly to the largest evaporating surface (cf. Shreve, A., 1919, i, 228). The second is the apparent influence of the original concentration of the gelatin jelly on its swelling limit subsequent to drying. This they regard as due to the initial case-hardening, which preserves an approximate "skin extension" corresponding with the original figure. On this basis, any structure is not inherent in the gelatin, but is an environmental impress, a strain structure in the original mass.

W. G.

Swelling and Gelation of Gelatin. ROBERT H. BOGUE (*J. Ind. Eng. Chem.*, 1922, **14**, 32—35).—When gelatin sols and gels are treated with sodium silicates of varying composition, the swelling and the viscosity increase with a decrease in the silica content and appear to be dependent on the p_H value, as this increases constantly with increase of the ratio $Na_2O : SiO_2$. The swelling and viscosity reach their maximum at p_H 8.5, and decrease slightly at higher values; the jelly consistence, however, is solid at p_H values between 4.7 and 8.0, but becomes soft at 8.5 and is liquid at 9.0.

W. P. S.

Movement of Pepsin in Agar-agar Gels with and without Protein. C. A. PEKELHARING (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **24**, 269—279).—Pepsin (A., 1902, i, 411) from the gastric mucosa of pigs diffuses more rapidly in agar-agar gels containing proteins than in similar gels to which no protein has been added or which contain mixed amino-acids. The movement of pepsin through gels containing protein is held to be due to alternate combination of the enzyme with the protein substrate and decomposition of the substrate with liberation of the enzyme. This view is supported by the fact that in gels specially purified from nitrogenous substances, diffusion of pepsin is slower than in ordinary agar-agar gels.

G. W. R.

Uniformity in Invertase Action. J. M. NELSON and DAVID I. HITCHCOCK (*J. Amer. Chem. Soc.*, 1921, **43**, 2632—2655).—From a consideration of the results of Nelson and Vosburgh (cf. A., 1917, ii, 252) and new data recorded, it is shown that all preparations of yeast invertase are not alike in their action, but that some of them are abnormal in allowing the hydrolysis of sucrose to slow more than others after the first 20% of the inversion. The following empirical equation has been deduced, which fits the experimental data for the hydrolysis of sucrose by normal invertase over an extreme range of invertase concentration of 12 : 1.

$$t = 1/n [\log 100/(100-p) + 0.002642p - 0.000008860p^2 - 0.0000001034p^3]$$

where t is the time, p the percentage of sucrose inverted and n is a

constant which is proportional to the amount of active invertase present. It is shown that the hydrolysis-time curves for normal invertase are of the same shape for these different invertase concentrations and can be made to superimpose if the time scale be multiplied by the proper constant. The hydrolysis curve with normal invertase has the same shape at temperatures varying from 15° to 35° , and at hydrogen-ion concentrations from 4.0×10^{-5} to 3.2×10^{-7} .

One abnormal invertase preparation could be rendered normal by the addition of boiled normal invertase or of $0.1M$ -sodium chloride, but another was not affected by such treatment. Further dialysis or partial inactivation by heating or by submission to ultra-violet light did not render normal invertase preparations abnormal.

W. G.

The Law of Action of Saccharase : Velocity of Hydrolysis and Reaction of the Medium. H. COLIN and (MLLE) A. CHAUDUN

(*Compt. rend.*, 1922, **174**, 218—220; cf. A., 1918, i, 414; ii, 357).—In extension of the view that the inversion of sucrose by saccharase is a catalytic action in which the catalyst transitorily unites with the substance which it decomposes, the velocity of formation of the intermediate compound being infinitely great with respect to the velocity of decomposition, it is suggested that there is a weight, a , of sucrose which corresponds with a volume, n , of a given saccharase solution. It is shown that this, like the velocity of inversion, varies with the reaction of the medium, the value of a being smaller the greater is the acidity of the medium. Thus the addition of acid may be considered as causing a diminution of the amount of enzyme coming into action, and when the diminution of velocity due to this cause becomes greater than the increase in velocity due to the greater instability of the complex, the variation of the velocity becomes negative, that is, the velocity of inversion diminishes.

W. G.

The Inversion of Sucrose by Saccharase. (MLLE) ANDRÉE CHAUDUN (*J. fabr. sucre*, 1921, **62**, No. 39).—The rate of inversion of sucrose by saccharase was studied. To a sucrose solution of known strength, a known amount of saccharase was added. At fifteen minute intervals the amount of invert-sugar formed was estimated in an aliquot part of the solution. When the enzyme was used in excess the rate of inversion decreased from the start, the values found agreeing with the law of Wilhelmy, $x=a(1-e^{-kt})$, where x is the weight of sucrose inverted during the time t , a the initial concentration of sucrose, and e and k are constants. When the sucrose was used in excess and the solution was not more than 10% in strength, the rate of inversion remained constant until a point B was reached where the sucrose and enzyme were present in equivalent amounts, then decreased according to the above law. In more concentrated solutions, a very slight decrease in the rate of inversion was noticed before the point B was reached. Other investigators have ascribed this to a supposed reversibility of the reaction, but it is here considered to be due to the hindering

of the reaction by the increase in viscosity as the inversion progresses.

CHEMICAL ABSTRACTS.

Inhibition Phenomena in Amylases. II. URBAN OLSSON (*Z. physiol. Chem.*, 1921, **117**, 91—145).—The optimum reaction for the action of a sample of ptyalin in the presence of sodium chloride and sodium acetate was found to be $P_H=6.4$. Malt diastase is inactivated more readily than ptyalin. Iodine and fluorine ions have no inactivating influence on malt diastase. Ferric chloride in low concentration activates, in higher concentrations inactivates malt diastase. On dialysing ptyalin, an activator is removed which consists chiefly of salts the presence of which is necessary for the usual diastatic action. The action of various inhibiting reagents is given. It is suggested that the inactivating capacity of some of the heavy metals might be utilised as a means of detecting very small traces of these metals.

S. S. Z.

Emulsin. BURCKHARDT HELFERICH (*Z. physiol. Chem.*, 1921, **117**, 159—171).—A satisfactory method for preparing emulsin from the kernel of the plum is to mill the stones, extract the paste with water under toluene for nine weeks, filter, and precipitate with 95% alcohol. Prolonged extraction and precipitation from dilute solution conduce to more potent preparations. The enzyme can be purified by dialysis. The conditions for the quantitative estimation of the activity of β -glucosidases is also described.

S. S. Z.

Emulsin. RICHARD WILLSTÄTTER and WILHELM CSÁNYI (*Z. physiol. Chem.*, 1921, **117**, 172—200).—The optimum reaction for the hydrolysis of amygdalin by emulsin lies in the neighbourhood of neutrality; that of lactose and raffinose more on the acid side. Emulsin preparations kept for about six months showed considerable loss of activity. From the difference of the quotients (a) of the hydrolysis of β -methylglucoside, lactose, and raffinose from that of amygdalin, (b) of the hydrolysis of lactose from that of prunasin, (c) of the hydrolysis of β -glucoside from that of prunasin by various preparations from sweet and bitter almonds and apricot kernels, it was concluded that the emulsin reactions were of the nature of independent enzyme reactions, and that the preparations were a mixture of numerous enzymes capable of degrading glucosides and polyoses.

S. S. Z.

Castor Bean Lipase, its Preparation and some of its Properties. D. E. HALEY and J. F. LYMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 2664—2670).—An active lipase preparation is best obtained from castor beans by extracting the crushed, hull-free beans with light petroleum. Lipase zymogen is activated by acid, but the active enzyme is unstable and is rapidly destroyed in an acid medium in the absence of fats. In the presence of fats, the enzyme shows much greater stability. The zymogen form appears to be somewhat soluble in fats or in a mixture of fat and ethyl ether, but is insoluble in ether alone. The optimum hydrogen-ion concentration for castor bean lipase is 1×10^{-5} . As the acidity

increases above this point, the lipolytic activity falls and stops entirely at a concentration of about 1×10^{-3} . The hydrolysis of hard fats by the castor bean lipase in the presence of water is accelerated by the addition of light petroleum. Similarly, the hydrolysis of oils is somewhat hastened. W. G.

The Importance of the Medium in the Study of Catalase. I. UBALDO SAMMARTINO (*Biochem. Z.*, 1921, **126**, 179—188).—Experiments on the evolution of oxygen from hydrogen peroxide under the influence of a dilute solution of blood and addition of a vitamin solution, for example, extract of yeast, show that a mercury surface and addition of sodium hydrogen carbonate greatly influence the reaction velocity. Using the Van Slyke apparatus to avoid mercury, the presence of the vitamin solution, whether the reaction of the medium be faintly alkaline or made definitely alkaline by addition of sodium hydrogen carbonate or sodium hydroxide solution, has a strong accelerating influence on the evolution of oxygen. H. K.

Influence of Different Chemicals, of Kations and Anions, and of Mixtures of Electrolytes, on the Ureolitic Power of Urease. D. H. WESTER (*Pharm. Weekblad*, 1922, **59**, 173—190; *Biochem. Z.*, 1922, **128**, 279).—The enzyme was obtained by extraction with equal volumes of water and glycerol of the seeds of soja and canavalia beans, the solutions being stable. The course of the reaction was followed by titration of the ammonium carbonate formed, using *N*/10-acid and methyl-orange.

Tannin, iodine, and copper sulphate retard the action; chloroform, however, does not, and thymol, mercuric chloride, and oil of mustard have practically no effect in concentrations sufficient to inhibit bacterial growth. Alcohols also have only slight retarding effects. Of the common kations, Ca^{++} and Ba^{++} have relatively great effect, K^+ least; Mg^{++} is irregular. Of the anions, Cl' , Br' , and NO_3' have almost equal effects, I' greater and SO_4'' less. Mixtures of electrolytes exert almost the same effect as would be exerted by that which has the strongest effect if it were present alone. S. I. L.

Organo-derivatives of Thallium. V. The Preparation of Thallium Diaryl Salts. ARCHIBALD EDWIN GODDARD and DOROTHY GODDARD (*T.*, 1922, **121**, 482—488).

Sodium 2-Nitro-4-hydroxymercuriphenoxide. J. F. SCHAMBERG, G. W. RAIZISS, and J. A. KOLMER (U.S. Pat. 1390972).—Sodium 2-nitro-4-hydroxymercuriphenoxide is formed when *o*-nitrophenol and aqueous sodium hydroxide react with an excess of mercuric acetate in dilute aqueous solution containing a little acetic acid at a temperature which is gradually raised from 50° to 80° . The product is soluble in hot water, has a brick-red colour, and possesses antiseptic and therapeutic properties.

CHEMICAL ABSTRACTS.

Physiological Chemistry.

Respiratory Metabolism and Toxic Glycæmia. A. BORNSTEIN and ELISABETH MÜLLER (*Biochem. Z.*, 1921, **126**, 64—76).—Experiments on dogs and man indicate that injections of pilocarpine cause an immediate increase in the respiratory coefficient. This is attributed to combustion of sugar. Adrenaline, however, although it forms sugar from glycogen, does not bring about increased sugar combustion. H. K.

The Degradation Products of Cholesterol in the Animal Organs. (Substances Associated with Cholesterol in the Blood.) I. LIFSCHÜTZ (*Z. physiol. Chem.*, 1921, **117**, 201—211).—Some derivatives of cholesterol are associated with it in the unsaponifiable fraction of fat in the blood. Some of these substances are precipitated by digitonin, whilst others are not. The chemical properties of both fractions are given. S. S. Z.

The Chemical Nature and the Transformation of the Fat of the Blood. I. LIFSCHÜTZ (*Z. physiol. Chem.*, 1921, **117**, 212—217).—On oxidation of the blood fat the relative proportion of the unsaponifiable matter increases whilst the ratio of crystalline cholesterol to cholesterol oxidation products diminishes. S. S. Z.

The Uric Acid of Human Blood. J. LUCIEN MORRIS and A. GARRARD MACLEOD (*J. Biol. Chem.*, 1922, **50**, 65—75).—Certain discrepancies between the results obtained in the estimation of uric acid in human blood by the authors' method (this vol., ii, 328) and by that of Folin and Wu (*A.*, 1919, ii, 308) lead to the suggestion that there are two forms of uric acid present in human blood. E. S.

Blood Enzymes. I. Occurrence of Maltase in Mammalian Blood. ARTHUR COMPTON (*Biochem. J.*, 1921, **15**, 681—686).—Maltase is present in the blood-serum of the pig, dog, goat, sheep, rat, horse, and ox, and is absent from that of the cat, guinea-pig, rabbit, and man. The pig is particularly rich in the enzyme. Some variation occurs in different individuals belonging to the same species, especially in the case of the dog. W. O. K.

The Ferment Numbers of Blood. I. Quantitative Estimation of Catalase, Protease, Peroxydase, and Esterase in a Drop of Blood. A. BACH and SOPHIE ZUBKOWA (*Biochem. Z.*, 1921, **125**, 283—291).—The blood solution used for the estimations is prepared by measuring 0.02 c.c. of blood by means of a capillary pipette and adding to it 20 c.c. of water. For the estimation of catalase and protease, use is made of the observation that the action of catalase on hydrogen peroxide falls off with rise of temperature, due to the action of the protease on the catalase, so that the catalase number is the number of milligrams of hydrogen peroxide

decomposed by 0.001 c.c. of blood at 17°, and the protease number is the difference between the catalase numbers determined at 17° and 37°. In man, the catalase number varies between 14 and 18, and the protease number between 3 and 5.

As evidence for the existence of a peroxydase in blood, it is found that when blood is diluted 1000-fold, it accelerates the action of hydrogen peroxide on guaiacol, but is inactive when heated. The peroxydase number is the quantity of guaiacol in thousandths of a milligram oxidised by 0.001 c.c. of blood in presence of hydrogen peroxide. The guaiacol is determined colorimetrically. For estimation of esterase, use is made of the observation that guaiacol esters are not attacked by peroxydase except in the presence of esterase and the esterase number of the blood is the number in thousandths of a milligram of guaiacol eliminated from guaiacol esters by 0.001 c.c. of blood.

H. K.

The Fermentative Properties of Blood. V. Appearance of Ferments in Blood after Various Operations. LUDWIG PINCUSSEN (*Biochem. Z.*, 1921, **126**, 93—96).—By transplantation of tissues or by interfering with the normal mechanism of the kidney of rabbits and dogs, the author finds evidence of the presence in the sera of specific proteolytic ferments. The results are in general complicated.

H. K.

Blood Clotting. IV. B. STUBER and A. FUNCK (*Biochem. Z.*, 1921, **126**, 142—146).—Fibrinogen in 6% sodium chloride solution is precipitated by kations in the order $\text{Cs} > \text{K} > \text{Na} > \text{Li} > \text{Rb}$. Dialysed fibrinogen dissolved in sodium hydroxide or hydrochloric acid of various strengths is precipitated by alcohol when the alkali or acid concentration is above 0.05*N*, but there is no precipitation between the range 0.05*N* to 0.005*N*. Dialysed salt-free fibrinogen has an isoelectric point at P_H 5.0. In acid solution, fibrinogen is precipitated by anions in the order $\text{SO}_4 > \text{citrate} > \text{acetate} > \text{Cl} > \text{NO}_3, \text{Br} > \text{I} > \text{CNS}$. In alkaline solution, the bivalent kations are effective in the order $\text{Ba} > \text{Sr} > \text{Ca} > \text{Mg}$.

H. K.

Coagulation of the Blood. I. Some Physico-chemical Aspects of Coagulation. JOHN WILLIAM PICKERING and JAMES ARTHUR HEWITT (*Biochem. J.*, 1921, **15**, 710—724).—The authors attempt to bring the facts known about the clotting of the blood into connexion with physico-chemical concepts. Alcohol precipitates a greater quantity of gelatin from solution when added slowly than when added all at once. This effect may help to explain the delay in coagulation following slow injection of tissue extracts or of synthetic colloids. In fact, a negative phase (delayed coagulation) can be obtained in vitro by adding tissue extract slowly to unsalted birds' blood. The authors suggest that the injected colloids combine with the fibrinogen, and that there is no necessity for assuming the existence of antithrombin. In the same way, the slow disintegration of the platelets of the normal circulating blood helps it to maintain its fluidity. There is no conclusive evidence that the liver produces an anti-coagulant.

Blood surrounded by paraffin exhibits an intermediate reversible phase in the formation of a clot. A gel is first formed, which dissolves in tap water. This phase lasts for only a few minutes in mammalian blood, but for a day or two in frogs' blood. At 37°, birds' blood clots rapidly in clean glass vessels without the addition of tissue extract.

It is suggested that coagulation phenomena are largely physical and colloidal in nature, and that the effect of foreign substances may be due largely to surface effects and to the electrical charges of the particles concerned.

W. O. K.

Solubility of Carbon Monoxide in Serum and Plasma.

H. R. O'BRIEN and W. L. PARKER (*J. Biol. Chem.*, 1922, **50**, 289—300).—The solubility of carbon monoxide is practically the same in ox, sheep, and human serum and in ox plasma, and is about three-quarters of its solubility in water.

E. S.

Relation between the Viscosity of Blood and the Ratio of Uric Acid in Serum to that in Whole Blood. ROUZAUD and THIÉRY (*Compt. rend. soc. biol.*, 1921, **85**, 962—964; from *Physiol. Abstr.*, 1922, **6**, 626).—The viscosity of blood, which depends on the number of red cells, determines the distribution of uric acid between plasma and corpuscles. In patients with excessively viscous blood, the serum contains proportionally less uric acid than in patients with less viscous blood; in the latter, whether anæmic or hydræmic, the amount of uric acid in the serum may occasionally exceed that in the whole blood.

E. S.

Relation between Viscosity and the Ratio of Cholesterol in Serum to that in Whole Blood. ROUZAUD and THIÉRY (*Compt. rend. soc. biol.*, 1921, **85**, 964—965; from *Physiol. Abstr.*, 1922, **6**, 627).—The ratio of cholesterol in the serum to that in whole blood varies directly with the viscosity. There is a larger fraction of cholesterol in the serum when the blood is rich, than when it is poor, in red cells. This is considered to be of importance in cases of hypercholesterinæmia.

E. S.

The Action of Salvarsan on the Serum of Animals and on Blood-cells in Vitro. J. L. KRITSCHESVSKY (*Biochem. Z.*, 1921, **126**, 11—20).—Salvarsan in acid and in alkaline solution causes a pronounced decrease in the degree of dispersity of colloids, as is shown by its behaviour towards serum. Corpuscles of various species are strongly agglutinated to various degrees, depending on the species. The hæmolytic action of salvarsan is inhibited by serum.

H. K.

Influence of Temperature on Hypotonic Hæmolysis.

A. JARISCH (*Pflüger's Archiv*, 1921, **192**, 255—271; from *Physiol. Abstr.*, 1922, **6**, 625).—The resistance of the red cells to hæmolysis increases with rise of temperature between 0° and 45° to 50°, but then very rapidly falls off as temperatures are reached which are themselves capable of causing hæmolysis. Different animals vary in the sensitiveness to temperature influence on hypotonic hæmolysis; the differences are explained as dependent on different

phosphate content of the corpuscles, low phosphate content corresponding with a small temperature effect. By adding phosphate buffer mixtures to ox blood, the phosphate content of which is small, the temperature effect could be intensified. Sodium sulphate and sodium tartrate had no such effects. The phosphates probably act by keeping the hydrogen-ion concentration constant, so that with rise of temperature the concentration of hydroxyl ions increases. If the latter is kept constant by adding ammonium salts, the effect of temperature is diminished. E. S.

Basal Metabolism in Menstruation. MARION O. P. WILTSHIRE (*Lancet*, 1921, 201, 388—389).—Basal metabolism is not appreciably affected by menstruation. A. A. E.

Paradoxical Behaviour of the Sugar Metabolism on Simultaneous Administration of Pilocarpine and Adrenaline ("Dissimilatory Reversal"). R. VOGEL and A. BORNSTEIN (*Biochem. Z.*, 1921, 126, 56—63).—In the dog both adrenaline and pilocarpine cause an increase of blood-sugar. The simultaneous injection of both causes no change in the normal blood-sugar content. The mechanism of the two glycaemias is supposed therefore to be different. H. K.

The Metabolism of Carbohydrates. II. On the Possible Occurrence of Stereochemical Changes in Equilibrated Solutions of Reducing Sugars Introduced into the Circulation. JAMES ARTHUR HEWITT and DAVID HENRIQUES DE SOUZA (*Biochem. J.*, 1921, 15, 667—671; cf. A., 1920, i, 508, 648).—From estimates of the optical rotation of the urine of rabbits or dogs after the intravenous injection of equilibrated solutions of dextrose, *d*-fructose, or *d*-galactose, it is concluded that the equilibrium of these sugars is unaltered as a result of their passage through the body and that no stereochemical changes take place.

The polarimetric estimations of the sugar in the urine do not agree with Bertrand estimations, and so the former method may give fallacious results if uncontrolled. W. O. K.

Influence of Radiation on Nucleic Acid Metabolism. LUDWIG PINCUSSEN and KATE MOMFERRATOS-FLORES (*Biochem. Z.*, 1921, 126, 86—92).—Exposure to Röntgen rays increases the katabolism of purine derivatives as shown in rabbits by increased oxalic acid excretion and as shown in vitro by a change of optical rotation. H. K.

Accessory Food Factors. II. Importance of Water-soluble Extractives. RICHARD GRALKA and HANS ARON (*Biochem. Z.*, 1921, 126, 147—152; cf. A., 1921, i, 475).—Experiments on rats indicate that a lack of fat-soluble vitamin is borne much better if copious water-soluble extractives, as, for example, of carrots and bran, be added. H. K.

Chemistry of Blood and Spinal Fluid. GRETE EGERER-SEHAM and C. E. NIXON (*Arch. Int. Med.*, 1921, 28, 561—585).—About one hundred spinal fluids were analysed with the following

results: Sugar (Myers-Bailey method), 0.045—0.095, average 0.069% in normal individuals; approximately the same in cases of syphilis, tabes, brain tumour, neurasthenia, arteriosclerosis, and other diseases; slightly increased in dementia paralytica and hysteria; decreased in tuberculous and epidemic meningitis and increased in diabetes with increase in blood-sugar; ratio of spinal fluid-sugar to blood-sugar variable in all groups. Creatinine, 0.45—2.20 mg. per 100 c.c. in patients without renal disease; ratio to blood creatinine very variable. Urea, 9.87 mg. per 100 c.c. or 62% of that in blood, both values slightly increased in cerebrospinal syphilis. Titration to bromocresol-purple, 2.11—2.63, average 2.49 c.c. 0.1N HCl per 100 c.c. normal, practically the same in pathological cases except in acidosis and a few unexplained cases. Carbon dioxide capacity 46.5—61.7, average 53.1% normal, decreased in acidosis and few other cases; lipase present only in 2 out of 26 cases; trypsin, absent in all; diastase 22% of blood diastase, variations unrelated to sugar-content of fluid; d 1.0086.

CHEMICAL ABSTRACTS.

The Action of Potassium and Calcium Ions on the Surviving Human Stomach. OTTO TEZNER and MAX TUROLT (*Z. ges. exp. Med.*, 1921, **24**, 1—10).—The addition of calcium to Ringer solution inhibits stomach contractions. The inhibition is overcome by acetylcholine and barium chloride, but not by nicotine, and is probably due to stimulation of the sympathetic. The action of adrenaline is more marked in calcium-rich than in normal Ringer solution. The addition of potassium to Ringer solution increases automatic muscular action; this action is increased by papaverine, but not by atropine; with large doses it is increased up to muscle cramp. In addition to the action on the muscle, there is probably also a stimulation of the nerve-endings due to injury of the vasoconstrictors. Potassium behaves in every respect similarly to barium even in its antagonism to calcium. The addition of potassium does not affect the action of acetylcholine, but decreases adrenaline action. Calcium-free media produce a reduction of stomach motility, owing to diminished vagus sensitivity.

CHEMICAL ABSTRACTS.

Relation of Histamine to Intestinal Intoxication. I. Presence of Histamine in the Human Intestine. JONATHAN MEAKINS and CHARLES ROBERT HARRINGTON (*J. Pharm. exp. Ther.*, 1922, **18**, 455—465).—Histamine was demonstrated in minute concentration in the human cæcum and transverse colon, but could not be detected in faeces possibly owing to oxidation during passage through the large intestine. The formation of histidine does not seem to depend on intestinal obstruction, and the amount present is too small to account for intestinal intoxication. G. B.

Pharmacology of Selenium and Tellurium. III. The Action of their Acids on the Organs of the Circulation. GEORG JOACHIMOGLU and W. HIROSE (*Biochem. Z.*, 1921, **125**, 5—11).—On the isolated frog's heart, sodium tellurite is at least

two hundred times as toxic as sodium tellurate, and sodium selenite at least one hundred times as toxic as sodium selenate. The selenite is also much more toxic than the tellurite. The heart musculature has a reducing effect on the first three salts mentioned. On the rabbit's blood-pressure, sodium selenite and tellurite have a more powerful depressor action than sodium selenate and tellurate.

H. K.

Microchemical Recognition of Urea in the Kidney by means of Xanthidrol. H. STÜBEL (*Anat. Anz.*, 1921, **54**, 236—239).—Xanthidrol combines with urea to give insoluble crystalline dioxanthylurea. By means of this reaction the presence of urea can be demonstrated in tissue. The tissue is immersed in small pieces in a 6% solution of xanthidrol and acetic acid for six to twelve hours, washed in absolute alcohol for forty-eight hours, with repeated renewal of alcohol, the tissue cleared in xylene, embedded in paraffin, and treated as other histological preparations.

CHEMICAL ABSTRACTS.

Secretin. I. and II. C. VAN EWYK and M. TENNENBAUM (*Biochem. Z.*, 1921, **125**, 238—245; 246—252).—I. Popielski's observation on the stimulating effect of histamine on the flow of pancreatic juice in a Pavlov dog is confirmed. Tyramine, glycine, alanine, and glutamic acid are without action. By heating histidine at 300°, an active stimulant was obtained which gave a picrate identified as histamine picrate. The amino-acids formed on hydrolysis of casein, when heated at 280° or 300° give an active substance, in all probability histamine.

II. The artificial secretin produced by the hydrolysis of spinach has no action on the blood pressure of the rabbit or on the isolated uterus of the guinea-pig, and is therefore not to be identified with histamine.

H. K.

Chemical Composition of the Thyroid Gland. EDGARD ZUNZ (*Arch. internat. Physiol.*, **16**, 288—306; from *Chem. Zentr.*, 1921, iii, 1329).—The mean weight of thyroid glands examined was 26 to 30 grams. The moisture content was 75—76%. On the material dried at 105°, the following results were obtained: nitrogen, 13.82%; ash, 3.53%; phosphorus, 0.55%; iodine, 0.2293%. (See also Zunz, *Arch. internat. Physiol.*, 1921, **15**, 459.)

G. W. R.

Spleen and Digestion. W. MOLLOW (*Z. physiol. Chem.*, 1921, **117**, 218—239).—Splenectomy did not affect the digestion of dogs with gastric and duodenal fistulas.

S. S. Z.

The Pituitary Active Principles and Histamine. H. H. DALE and H. W. DUDLEY (*J. Pharm. expt. Ther.*, 1921, **18**, 27—42).—Contrary to the suggestion of Abel and Nagayama (*ibid.*, 1920, **15**, 347), the pituitary activity on the isolated uterus is almost completely destroyed by boiling with 0.5% hydrochloric acid. So little histamine is present in the gland, that its chemical identification is impracticable, and there seems no reason for

suggesting a relation between histamine and the specific action of pituitary extracts. The oxytocic principle (acting on the uterus) is slowly destroyed by erepsin, but not by papain (cf. *Ann. Reports*, 1920, 17, 172). G. B.

Pressure of Carbon Dioxide or Swelling of Protein as the Cause of Muscle Contraction. OTTO FÜRTH (*Biochem. Z.*, 1921, 126, 55).—The author, in reply to Wacker (*ibid.*, 1921, 120, 284), reaffirms his position. H. K.

Osmotic Behaviour of Frog's Muscle, Deficient in Water and Poisoned by Glycerol, and on the Shrinkage of Muscle Protein. PAUL DUX and ARTUR LÖW (*Biochem. Z.*, 1921, 125, 222—237).—The muscles of frogs which have lost 20% of their weight by drying, when placed in physiological saline solution, swell more rapidly and eventually lose weight more rapidly than normal muscle. The muscles of frogs which have been poisoned by glycerol show a still sharper rise and fall, the muscles of such frogs being about one-fifth the weight of normal muscle. This very steep rise is partly due to accumulation of lactic acid in the tissue robbed of water. The results are held to support Fürth's hypothesis of muscle contraction. H. K.

The Interconversion of Carbohydrate and Lactic Acid in Muscle. DOROTHY LILIAN FOSTER and DOROTHY MARY MOYLE (*Biochem. J.*, 1921, 15, 672—680).—This paper confirms various recent investigations on the function of lactic acid in the muscle. Exhaustive stimulation results in a minimum lactic acid content. During recovery in oxygen after fatigue, there is an increase in carbohydrate content and a corresponding decrease in lactic acid, confirming Meyerhof's work in support of the view that the lactic acid formed during the first stage of excitation is partly reconverted back into carbohydrate during recovery. In chopped muscle, the decrease in carbohydrate is quite parallel to the increase in lactic acid and does not lag behind it as found by Parnas. Chopped muscle is able, not only to break down hexosephosphate, but also to synthesise it from dextrose and phosphate. W. O. K.

The Distribution of Carnosine in the Animal Kingdom. WINIFRED MARY CLIFFORD (*Biochem. J.*, 1921, 15, 725—735).—Using the colorimetric method previously described by the author (*A.*, 1921, ii, 604), quantitative estimations have been made of the carnosine (β -alanylhistidine) in the muscles of a large variety of animals. It appears to be completely absent from the flesh of certain fishes, birds, and reptiles, but is present in all mammals so far examined, the highest figure being obtained in the case of the bull, the fresh muscle of which contains more than 1%. In some cases (for example, salmon) the colour is not developed properly owing apparently to the presence of some inhibitory substance, and in such cases the observations were controlled by precipitating and isolating the carnosine. W. O. K.

The Rôle of Inorganic Salts in the Functions of the Cell.

S. G. ZONDEK (*Ber. deut. Pharm. Ges.*, 1922, **32**, 7—15).—The inorganic salts in the living cell play an important part in the chemical mechanism by means of which it performs its functions. Apart from their functioning as catalysts, as, for example, iron as an oxygen carrier in hæmoglobin, attention is directed to the influence exerted by the ions, particularly the kations, on the cell colloids, including protoplasm. The determining factor in this case is not osmotic pressure, but the actual valency of the ions. Both univalent and multivalent kations alone inhibit the living functions, but if both are present together in suitable proportions, as, for example, sodium or potassium, and calcium as in Ringer's solution, then the poisonous action is removed (cf. this vol., i, 296). This antagonistic action of uni- and bi-valent kations is observable in the higher organisms, so, for example, sodium salts, and still more pronouncedly potassium salts, lead to a stoppage of an isolated frog's heart with relaxation of the muscles, whilst calcium salts lead also to a stoppage with contracted muscles. With a mixture of the two ions the heart's action remains normal. These phenomena are attributable to the physico-chemical influence which the respective ions exert on the colloidal state of the cell protoplasm.

G. F. M.

The Function of the Vitamins in the Chemistry of the Cell.

W. R. HESS (*Z. physiol. Chem.*, 1921, **117**, 284—308).—The diminution in the respiratory function of polyneuritic pigeons can be demonstrated in vitro to be due to the decrease in the various tissues of the enzymes associated with respiration. The polyneuritic condition in birds can also be induced by inhibiting the respiratory functions of the tissues with hydrogen cyanide. Birds kept on a diet of polished rice were shown to be more susceptible to potassium cyanide intoxication than normal birds. S. S. Z.

Mode of Action of Potassium on Isolated Organs.

A. J. CLARK (*J. Pharm. expt. Ther.*, 1922, **18**, 423—447).—Rubidium acts as a perfect and caesium as an imperfect substitute for potassium in all the isolated tissues examined (chiefly rabbit's auricle, frog's heart, uterus, intestine). Thorium and uranium do not act as substitutes to potassium, but act as irritants to the frog's heart and will induce automatic beats in hearts arrested by lack of potassium (cf. Zwaardemaker, A., 1917, i, 70, 105, 241; 1918, ii, 182; *Ann. Reports*, 1919, **16**, 148; Loeb, A., 1921, i, 145; Peters, A., 1921, i, 144).

G. B.

Copper in Tumours and Normal Tissues.

CHARLES POWELL WHITE (*Lancet*, 1921, **201**, 701—703).—Copper was found to be present in all the animal and vegetable tissues examined, and to exist to a greater extent in degenerating tumours than in those which are not degenerated. The suggestion is made that copper may be of physiological importance in the higher animals and plants.

A. A. E.

New Observations on the Venom of Ants. ROBERT STUMPER (*Compt. rend.*, 1922, **174**, 413—415; cf. *ibid.*, 1922, **174**, 66).—The amount of formic acid in the venom from the ant, *Formica rufa*, varied from 21.35 to 72.8%. Formic acid is invariably found in the *Camponotinae*, but the *Myrmicinae* and the *Dolichoderinae* practically do not secrete this acid. The toxic action of the venom of the *Camponotinae* is due to formic acid and there are two distinct actions, namely, a corrosive action due to the concentration of the acid and the toxic action proper, due to an injurious influence of the formate ion on the nervous system. W. G.

An Organic Constituent of the Tube of *Mesochætopterus taylora*. POTTS. C. BERKELEY (*J. Biol. Chem.*, 1922, **50**, 113—120).—By extracting the tubes of *Mesochætopterus taylora*, a polychæte worm, with warm 2% sodium carbonate, a furfuraldehyde-yielding substance is obtained which resembles chondroitin-sulphuric acid. On hydrolysis, it yields sulphuric acid, a volatile organic acid, a hexosamine which is probably galactosamine, and probably glycuronic acid. E. S.

Origin of Milk Fat, and its Relation to the Metabolism of Phosphorus. EDMOND JOHN SHEEHY (*Biochem. J.*, 1921, **15**, 703—709).—Carbohydrate and fat are equally efficient in the food of the cow for the production of milk fat. This indicates that the immediate source of the milk fat is some compound which can be produced from fat or from sugar, and may be a phosphatide. There is no parallelism between the quantity of phosphoric acid and of fat or caseinogen in milk, but this may be due to the inorganic phosphorus being partly returned to the blood from the mammary gland. W. O. K.

The Diastatic Action of Cow's Milk towards Various Starches. FERDINAND WELZMÜLLER (*Biochem. Z.*, 1921, **125**, 179—186).—The diastatic action of cows' milk was determined at various temperatures on a number of varieties of starch. The results show that a diastase is present in cows' milk with an optimum temperature of 37°. This, together with its different behaviour towards a variety of starches, indicates a difference between the diastase of cows' milk and other diastatic ferments. H. K.

Ambard's Urea Constant. ALFRED LUBLIN (*Biochem. Z.*, 1921, **125**, 187—201).—Experiments on the excretion of urea and urine in man in normal and pathological cases do not support Ambard's laws (*Compt. rend. Soc. Biol.*, 1910). H. K.

Influence of Lecithin on the Excretion of Veronal. C. BACHEM (*Biochem. Z.*, 1921, **126**, 117—119).—After subcutaneous injection into rabbits of a mixture of lecithin and sodium veronal, the excretion of veronal in the urine is the same as when sodium veronal is injected alone. If, however, the lecithin be given intravenously and the sodium veronal subcutaneously, the excretion of veronal decreases by 33 to 50%. H. K.

Urochrome as a Derivative of Chlorophyll. HERBERT ELDON ROAF (*Biochem. J.*, 1921, **15**, 687—688).—Consumption of green plant pigment (chlorophyll) increases the output of urochrome in the urine, whereas with carotene there is no such increase.
W. O. K.

Alcaptonuria and its Metabolism. R. B. GIBSON and C. P. HOWARD (*Arch. Int. Med.*, 1921, **28**, 632—637).—In a case of alcaptonuria, high values were obtained for ammoniacal nitrogen, uric acid nitrogen, and undetermined nitrogen, whilst the urea-nitrogen value was low. The excretion of sulphur appeared to be normal.
CHEMICAL ABSTRACTS.

Inflammation. I. Influence of Chemicals on the Chemotaxis of Leucocytes in Vitro. ELIZABETH P. WOLF (*J. Expt. Med.*, 1921, **34**, 375—396).—The calcium ion is the only inorganic ion which is found to be of itself positively chemotactic; the chemotaxis exhibited by magnesium and sodium salts is dependent on the negative ions. Sodium phosphates, morphine, amino-acids, and amines are positively, and all potassium salts negatively chemotactic; examples are also given of substances which act synergistically as regards chemotaxis. Although tyramine, for example, is an exception to the rule, it is suggested that the longer the carbon chain, the greater is the degree of chemotaxis. The conditions of the test appear markedly to influence the character of the results.
CHEMICAL ABSTRACTS.

The Total Non-protein Nitrogen Constituents of the Blood in Chronic Nephritis with Hypertension. J. LISLE WILLIAMS (*Arch. Int. Med.*, 1921, **28**, 426—433; cf. *ibid.*, 1921, **27**, 748).—In chronic nephritis with hypertension, there is a retention of nitrogenous products in the blood and a diminished ability to excrete phenolsulphonaphthalein. The changes from the normal in these respects parallel the renal involvement but bear no definite relation to the increase in blood pressure. In cardiac insufficiency, without definite nephritis, there is a slight retention of nitrogenous products, particularly uric acid. Improvement in the cardiac condition is followed by a partial or complete return to the normal non-protein nitrogen of the blood. The presence of albumin and casts in the urine is not necessarily diagnostic of nephritis nor is their absence necessarily indicative of the non-existence of such disease.
CHEMICAL ABSTRACTS.

Blood Chemistry in Puerperal Infection. PAUL COUINAUD and RENÉ CLOGNE (*Rev. mensuelle gynécol. et obstét.*, 1921, **3**, 265—274).—In puerperal infection, blood urea is increased in proportion to the severity of the infection; the residual nitrogen of the blood is increased; in the urine, Lantzenberg's coefficient is increased, and the amount of urinary acetone is augmented as compared with values obtained in a normal puerperium.
CHEMICAL ABSTRACTS.

Tetany. H. ELIAS and E. A. SPIEGEL (*Wiener Arch. Inn. Med.*, 1921, **2**, 447—460).—The phosphorus content of the blood serum

is increased in tetany. The increase in total phosphorus depends on an increase in inorganic phosphorus, whilst the lipid phosphorus shows no characteristic change. In general, the phosphorus content shows a greater increase in the more severe cases of tetany. The change in phosphorus content cannot be attributed to increased muscular activity. A disturbance of phosphorus metabolism appears to be an important symptom of tetany, and is perhaps also an important factor in its occurrence.

CHEMICAL ABSTRACTS.

Pharmacology of Carbon Oxysulphide. RICHARD FISCHER (*Biochem. Z.*, 1921, **125**, 12—24).—The action of carbon oxysulphide was investigated on frogs and rabbits and on blood *in vitro*. The gas is unstable and readily forms hydrogen sulphide. The frog is relatively resistant, an atmosphere containing 4.5% of the gas causing death in one hour. In the case of the rabbit, inhalation of air containing less than 1% of the gas leads to death. In both cases death is due to respiratory failure. There is no apparent change in the blood *in vivo*; but *in vitro*, blood treated with carbon oxysulphide shows the absorption bands of thiohæmoglobin.

H. K.

[Physiological] Action of Dimethyl Telluride Dihaloids. DOUGLAS V. COW and W. E. DIXON (*J. Physiol.*, 1922, **56**, 42—52).—The stereoisomeric dimethyl telluride dichlorides, TeMe_2Cl_2 , described by Vernon (T., 1920, **107**, 86, 889) behave quite differently when injected intravenously into cats, dogs, or rabbits. The α - or *trans*-compound is relatively inactive, the β - or *cis*-compound is a powerful stimulant of the spinal medulla and specifically excites the adrenal gland to excrete adrenaline; hence it causes rise of blood pressure and other effects. This new type of the effect of stereochemical arrangement on physiological action is considered to be due to the intramolecular strain of the β -chloride. Ultimately both compounds are excreted in the breath as dimethyl telluride.

G. B.

Influence of Intravenous Sugar Injections on the Excretion of Lactic Acid, on the Blood-sugar, and on the White Blood-corpuscles. WACŁAW MORACZEWSKI and EGON LINDNER (*Biochem. Z.*, 1921, **125**, 49—68).—The authors have examined the effect of the administration of dextrose or lævulose orally or intravenously on the blood-sugar, the urinary content of lactic acid, phosphoric acid, and sugars, the body temperature, and the corpuscular content (red and white) of the blood, both in the case of normal persons and in pathological cases. The effect of simultaneous administration of adrenaline and phloridzin was also examined, and the effect of injections of salvarsan, dextrin, deuto-albumose, etc. In general, the results vary from case to case. There is no apparent relation between phosphate excretion and lactic acid excretion, and although injection of dextrose produces little effect, lævulose causes a large increase of lactic acid in the

urine, a rise of body temperature of 3° , and a decrease of leucocytes. Phloridzin and adrenaline increase the lactic acid excretion. H. K.

Behaviour of Oxalic Acid in the Animal Body. LUDWIG PINCUSSEN (*Biochem. Z.*, 1921, **126**, 82—85).—About four-fifths of the oxalic acid injected subcutaneously as sodium salt into rabbits appears in the urine. This quantity shows a slight decrease when the animal is exposed to light in the presence of an activator (eosin or dichloroanthracenedisulphonic acid). H. K.

The Behaviour of some Cyclic Compounds in the Human and Animal Organisms. ERICH SCHEMPF (*Z. physiol. Chem.*, 1921, **117**, 41—47).—Phenylacetic acid administered as the sodium salt to a cat was excreted in the urine as phenaceturic acid. The same compound given subcutaneously to a hen was excreted as a substance which did not quite agree with the properties of phenacetornithuric acid which Totani identified in similar circumstances. The sodium salt of *o*-nitrophenylacetic acid was excreted as the unchanged acid in the case of a man and a dog, as was also found to be the case with the *p*-nitro-compound except that a few decigrams of hippuric acid were also found in the human urine. Phenylbromoacetic acid in the case of man and dog was excreted as mandelic acid, whilst α -thiophenic acid was recovered in the urine in both cases as thiophenuric acid. A human patient who received pyromucic acid per os excreted it in the urine as pyromycuric and hippuric acids. S. S. Z.

Action of Adrenaline on the Blood-sugar. GÉZA PETÉNYI and HEINRICH LAX (*Biochem. Z.*, 1921, **125**, 272—282).—In man at all ages, subcutaneous administration of adrenaline produces a hyperglycæmia followed by a state of hypoglycæmia. In tetany, the behaviour is slightly different. The normal dextrose content shows greater variations and after adrenaline the hyperglycæmia is smaller and the hypoglycæmia more pronounced and protracted than in normal persons. H. K.

Physiological Action of N-Methylhistamine and of Tetrahydropyrido-3 : 4-iminazole ("Iminazoleisopiperidin" of Fränkel) [1 : 3 : 5-Benztriazole]. H. H. DALE and H. W. DUDLEY (*J. Pharm. expt. Ther.*, 1921, **18**, 103—110).—4- β -Methylaminoethylglyoxaline (*N*-methylhistamine), prepared by Fargher and Pyman (*T.*, 1921, **119**, 734), has 1/200 of the activity of histamine on the blood pressure and 1/80 of the activity of the uterus. The base prepared by Fränkel and Zeimer (*A.*, 1920, **i**, 882) by condensing histamine with methylal by no means exceeds the latter base in activity, as was claimed by its discoverers, but has only 1/1500 of the activity of histamine on uterine muscle, and practically none on the blood pressure. The dihydrochloride melts at $276\text{--}278^{\circ}$, and not at 253° as stated by Fränkel and Zeimer, whose preparation must have been seriously contaminated with histamine. G. B.

Pigment Metabolism. II. FROMHOLDT and NERSESSOV (*Biochem. Z.*, 1921, **125**, 153—157).—Bilirubin in quantities above 0.1 gram is lethal when injected intravenously into rabbits and causes excretion of albumin. With dogs and rabbits, repeated injection of bilirubin leads to urobilinuria and in the case of dogs bilirubin appears in the urine. H. K.

The Influence of Treatment with Alkali or Bromine on the Physiological Activity and Foaming Capacity of some Saponaceous Substances. ERNST SIEBURG and FRANZ BACHMANN (*Biochem. Z.*, 1921, **126**, 130—141).—The biological activity of five saponaceous substances, cyclamin, digitonin, saponin pur. alb., Quillaia saponin, and Guaiak saponin, were compared before and after treatment with alkali or with bromine. As a rule, such treatment results in a depression of activity as exemplified by the property of foaming, by precipitation of cholesterol, by hæmolysis of corpuscles, by toxicity on the frog's heart, and by the toxicity on tadpoles. There is no close parallelism between these properties, except in the action on the frog's heart and the toxicity on tadpoles. H. K.

Distribution of Chloride and Water after Poisoning with Mercuric Chloride. A. BORNSTEIN and JOH. KERB (*Biochem. Z.*, 1921, **126**, 120—129).—A comparison is made of the chloride and water-content of the blood, kidneys, liver, lungs, brain, intestine, muscles, skin, and skeleton of normal rats, and rats which have received, subcutaneously, either sodium chloride, sodium chloride and mercuric chloride, or cantharidin. There is no parallelism between water and chloride retention. For the ashing of animal tissues the Hoppe-Seyler-Thierfelder method can be shortened by stronger ignition in a muffle furnace without loss of chloride. H. K.

Chemotherapy of Antimony. Comparison of Antimony Tartrates with Organic Compounds of Antimony. ROBERT GEORGE FARGHER and WILLIAM HERBERT GRAY (*J. Pharm. expt. Ther.*, 1921, **18**, 341—360).—The toxicity to mice of a number of salts of antimonyltartaric acid and of phenyl-, of *m*-acetylaminophenyl-, and of *p*-bromophenyl-stibinic acids has been determined. The paper contains a review of the literature of the chemotherapy of antimony, and describes a method for estimating antimony in organic compounds. G. B.

Effect of Hydrogen-ion Concentration on the Toxicity of Alkaloids for *Paramæcium*. MARIAN M. CRANE (*J. Pharm. expt. Ther.*, 1921, **18**, 319—339).—The limits of P_H within which *Paramæcium* can live for twenty-four hours are 5—9.6. The effect of P_H on the toxicity of alkaloids varies with the dissociation constant of the latter, and the results seem to indicate that only the free undissociated base is toxic. Thus a change in P_H scarcely influences the toxicity of quinoline, whereas with strychnine and piperidine, which have a much higher dissociation constant, the toxicity at P_H 5.9 is twenty-five times as great as at P_H 8.0. G. B.

Chemistry of Vegetable Physiology and Agriculture.

The Determination of Alkalinity in Culture Media. L. MICHAELIS (*Z. Immun.* 1921, **32**, 194—203).—A colorimetric method is described which indicates the p_H of culture media in a simple and rapid manner. The method differs from that of Clark and Lubs in that an indicator with a single change in colour, from colourless to yellow, is used. The reagent is a solution of 0.3 gram of *m*-nitrophenol in 100 c.c. of distilled water.

CHEMICAL ABSTRACTS.

The Ionisation Constants of Glycerophosphoric Acid and their Use as Buffers, especially in Culture Media. R. R. MELLONS, S. F. ACREE, P. M. AVERY, and E. A. SLAGLE (*J. Infect. Dis.*, 1921, **29**, 1—6).—Disodium glycerophosphate is a solvent for some salts of calcium and magnesium and perhaps other metals, and when used in proper concentration prevents much of the objectionable precipitation of phosphates on the alkaline side of neutrality. This property suggests its employment in culture media, in the washing of agar, in the precipitation of casein, and for the study of the effect of the calcium and magnesium ions on the growth of various organisms. The fact that the ionisation constants of the glycerophosphates are substantially the same as those of the non-glycerolated phosphates makes possible a substitution of these salts as buffers, owing to their stability in the lower alkaline ranges where, for example, an initial p_H of 8 has been maintained in broth after autoclaving.

CHEMICAL ABSTRACTS.

Extracellular Bacterial Proteases. K. G. DERNBY (*Biochem. Z.*, 1921, **126**, 105—108).—Bacteria were grown in a nutrient broth, then filtered through paper and a Chamberland candle. The sterile filtrate was examined for proteolytic activity by liquefaction of gelatin or hydrolysis of Witte's peptone. Tubercle bacilli, various pneumococci, various streptococci, staphylococci, and tetanus bacilli gave negative results. Active bacilli were *Bacillus subtilis*, *B. pyocyaneus*, *B. proteus*, *B. prodigiosus*, *B. sporogenes*, and *B. histolyticus*. These were active within the range P_H 4 to 9 with an optimum zone of 6 to 7.

H. K.

Endo's Reaction, Biology of *Bacillus coli*. O. FERNÁNDEZ and T. GARMENDIA (*Anal. Fis. Quím.*, 1921, **19**, 313—319).—The red colour produced by *Bacillus coli* in Endo's medium (bouillon, with agar containing lactose, magenta, and sodium sulphite) is probably produced, not by acetaldehyde, but by lower acids of the fatty series. The production of acetaldehyde by the agency of *B. coli* was studied, using different modifications of Endo's medium and estimating the acetaldehyde produced by weighing as its *p*-nitrophenylhydrazone. Increase in the amount of lactose or sodium sulphite and substitution of lactose and sodium sulphite by dextrose and sodium phosphate respectively did not result in

any marked increases in the amount of acetaldehyde produced. With mannitol and sodium sulphite, however, increased amounts of acetaldehyde were obtained. The maximum production of acetaldehyde was obtained, using a medium containing alanine, lactose, sodium chloride, and sodium sulphite. G. W. R.

Theory of Disinfection in the Light of the Meyer-Overton Lipoid Theory. P. G. F. VERMAST (*Biochem. Z.*, 1921, **125**, 106—148).—Experiments conducted with *Bacillus coli* show that in acid or neutral media disinfection with benzoic acid depends on the concentration of the undissociated acid. The benzoic acid anion and the hydrogen-ion concentration of the solution can undergo considerable variation without affecting the disinfection value, provided that the concentration of undissociated acid remains the same. The results with benzoic and salicylic acids confirm the Meyer-Overton theory in neutral and acid media if the distribution coefficient be based on the concentration of undissociated acid. In alkaline media, the disinfection value is not apparently in agreement with the theory. H. K.

Proteinogenous Amines. XII. The Production of Histamine and other Iminazoles from Histidine by the Action of Micro-organisms. MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1922, **50**, 131—191).—A study was made of the action of a large number of micro-organisms on histidine, using the standard medium previously employed (A., 1919, i, 611). The results are presented in tabular form. In a few cases, evidence was obtained which suggested the rupture of the iminazole ring with the probable production of a triamino-carboxylic acid. Addition of leucine to the medium facilitated the growth of all the organisms, and, in those cases where decarboxylation occurred, increased the rate of production of histamine. The effect on *Bacillus coli cystitis* of additions of other amino-acids was also investigated. Alanine, leucine, arginine, glycine, and peptone augmented both the growth of the organism and the rate of production of histamine; tyrosine increased growth alone; glutamic acid and tryptophan increased growth, but diminished the yield of histamine; whilst cystine retarded growth and almost prevented the formation of histamine. E. S.

Pharmacology of Selenium and Tellurium. II. Action of their Acids on Diphtheria Bacilli. GEORG JOACHIMOGLU and W. HIROSE (*Biochem. Z.*, 1921, **125**, 1—4).—The growth of diphtheria bacilli is inhibited by the oxy-acids of tellurium and selenium. The active concentrations of tellurium and selenium are, for tellurites 1 : 420, for tellurates 1 : 125, for selenites 1 : 1160, and for selenates 1 : 666. Diphtheria bacilli are much less sensitive than bacilli of the typhus-coli group, which latter are killed at dilutions of tellurium four hundred times the above. H. K.

Fermentation of *i*-Inositol. JAMES ARTHUR HEWITT and DOROTHY BEATTY STEABEN (*Biochem. J.*, 1921, **15**, 665—666).—The main products of the fermentation of inositol by *Bacillus*

lactis aerogenes are ethyl alcohol, acetic acid, succinic acid, and carbon dioxide, and small quantities of lactic acid and formic acid. Dextrose apparently is not an intermediate product.

W. O. K.

The Culture of *Bacillus pyocyaneus* on Definite Artificial Media. A. GORIS and A. LIOT (*Compt. rend.*, 1922, **174**, 575—578; cf. *ibid.*, 1921, **172**, 1622).—It has previously been shown that the ammonium salts of dibasic acids can serve as nutrients for *B. pyocyaneus*. It is now shown that the corresponding amides cannot serve as nutrients. Amino-acids may serve as nutrients for the bacillus provided that they have first been neutralised by sodium hydroxide, but, in general, they are less effective than the ammonium salts of the dibasic acids, particularly when they are used without the addition of mineral salts. The nutritive value of a given amino-acid depends, not only on the presence of one or more amino-groups, but also on the structure of the chain to which these groups are linked.

W. G.

The Production of Hydrocyanic Acid by *Bacillus pyocyaneus*. F. A. PATTY (*J. Infect. Dis.*, 1921, **29**, 73—81).—The optimum reaction for the production of hydrogen cyanide by most strains of *B. pyocyaneus* is p_H 5·4 to 5·8. The thiocyanate colorimetric method of estimating minute quantities of hydrogen cyanide is a satisfactory one, but control tests must be made, because in protein media there is sufficient thiocyanate formed on distillation to give a positive reaction. Oxygen is necessary for the production of hydrogen cyanide by *B. pyocyaneus*. Hydrogen cyanide is not produced by a filterable extra-cellular enzyme. Pigmentation, gelatin liquefaction, and hydrogen cyanide production, although independent functions, show a close relationship. Whole egg-broth is the most favourable medium for hydrogen cyanide production, but synthetic medium is second, indicating that a favourable synthetic medium may be devised. Contaminating organisms which do not produce hydrogen cyanide appear to be slightly inhibitive of its production. *B. pyocyaneus* does produce a measurable amount in the animal body. There is a marked variation among the different strains of *B. pyocyaneus* as regards the amount of hydrogen cyanide production.

CHEMICAL ABSTRACTS.

Trehalose Fermentation in the Differentiation of the Paratyphoid-enteritidis Group. S. A. KOSER (*J. Infect. Dis.*, 1921, **29**, 67—72).—*Bacillus suispestifer* is unable to attack trehalose, whereas *B. paratyphosus*, *B. schottmulleri*, the animal para B subgroup, and *B. enteritidis* ferment it with the production of acid and gas. Furthermore, it is possible to differentiate by cultural methods the *B. schottmulleri* strains from the closely allied animal para B group, hitherto separable only by serological means. This has been accomplished by employing small amounts of a serum-water medium containing 0·5% trehalose and 1% Andrade indicator. In this medium, the animal para B strains produce a red coagulum after three to four days' incubation, whilst the *B. schottmulleri*

cultures present a light pink or colourless coagulum. This separation parallels the differentiation of these two groups by agglutinin absorption tests. *B. enteritidis* is similar in its reaction to the animal para B cultures and in contrast to *B. schottmulleri*.

CHEMICAL ABSTRACTS.

The Relation between Bacteria, Spores, and Formaldehyde.

E. HAILER (*Biochem. Z.*, 1921, **125**, 69—83).—Anthrax spores and vegetative bacterial forms, for example, paratyphus bacilli and staphylococci, were treated with formaldehyde solution followed by sodium sulphite solution. In the case of the spores, the sodium sulphite inhibits the toxic action of the formaldehyde the greater its concentration, provided that the formaldehyde has not been allowed to act too long. The results are interpreted on the theory that the formaldehyde forms an additive product with the amino-groups which is decomposed by sulphite, but prolonged action of formaldehyde gives rise to an irreversible complex, $-N=CH_2$. The results with bacteria are less simple.

H. K.

The Bactericidal After-effect of Formaldehyde Solutions.

E. HAILER (*Biochem. Z.*, 1921, **125**, 84—96).—The toxic action of formaldehyde continues after removal of anthrax spores or vegetative bacilli from the solutions if there be no nutrient material present. In the case of the spores, this after-effect is the more pronounced the drier the spores become, owing to loss of water and therefore increased formaldehyde concentration.

H. K.

Yeast Protein. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **118**, 304—306).—Yeast protein on hydrolysis yielded histidine 2.97%, arginine 3.15%, lysine 3.63%.

S. S. Z.

Stimulants of Alcoholic Sugar Fission. VIII. CARL NEUBERG and MARTA SANDBERG (*Biochem. Z.*, 1921, **125**, 202—219).—Purines, their complex derivatives, or their degradation products accelerate the fermentation of dextrose by living yeast-cells just as they stimulate the action of press juice (this vol., i, 306). Caffeine and alloxan, however, retard the action of living yeast cells.

H. K.

Stimulants of Alcoholic Sugar Fission. IX. CARL NEUBERG and MARTA SANDBERG (*Biochem. Z.*, 1921, **126**, 153—178).—With few exceptions, a large number of substances, belonging to very varied groups, have a stimulating influence on the action of living yeast and in some cases on press juice. The groups examined were, bitter substances, bile acids (sodium salts inhibit), various varieties of charcoal, saponins, cystin and its derivatives.

H. K.

Proteinogenous Amines. XIII. The Electronic Interpretation of certain Biochemical Phenomena. MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1922, **50**, 193—233).—Electronic formulæ for a number of organic compounds are deduced from their known chemical properties. From a consideration of these formulæ, the authors conclude that the decarb-

oxylation of pyruvic acid by yeast is a purely hydrolytic process, although no attempt is made to explain the mechanism of the action. Only those acids which contain quadruply positive carboxyl groups appear to be readily decarboxylated by yeast. Further, it is pointed out that, on the assumption that a quadruply negative carbon atom is only oxidised with difficulty, the behaviour of, at any rate, a number of acids in the animal body is readily explained by their electronic formulæ. E. S.

Vitamins. II. Acceleration of Fermentation by Extracts of Animal Organs. SIGMUND FRÄNKEL and JOSEF HAGER (*Biochem. Z.*, 1921, **126**, 189—226).—The water-soluble extract of the alcoholic extract of a large number (31) of animal tissues was tested in its action on the evolution of carbon dioxide in yeast fermentation. All extracts except that of the bone marrow had a strong accelerating influence. H. K.

Vitamins. III. Acceleration of Fermentation by Extracts of Plants and the Action of Choline and Aminoethyl Alcohol on Fermentation. SIGMUND FRÄNKEL and ALBERT SCHARF (*Biochem. Z.*, 1921, **126**, 227—264).—The water-soluble portion of an alcoholic extract of a large number of grains and vegetables was examined in its action on yeast fermentation. Vegetable roots and grains were feebly active, leaves of vegetables were more active, but leek-like vegetables most active. Extract of celery and of yolk of eggs were very active, but both choline and aminoethyl alcohol were inhibitory. H. K.

Vitamins. IV. The Adsorption of Vitamins. SIGMUND FRÄNKEL and ALBERT SCHARF (*Biochem. Z.*, 1921, **126**, 265—268).—Using a purified water-soluble vitamin preparation from yeast (A., 1921, ii, 228), the authors have examined the adsorption of vitamin as determined by its accelerating influence on yeast fermentation, by Fuller's earth, kaolin, and alumina. Kaolin adsorbs it completely, Fuller's earth slightly less, and alumina not at all. H. K.

Vitamins. V. Further Experiments on the Chemistry of Vitamins. SIGMUND FRÄNKEL and ALBERT SCHARF (*Biochem. Z.*, 1921, **126**, 269—280; cf. A., 1921, ii, 228).—Further experiments are described on attempts to isolate the water-soluble vitamin from yeast and rice polishings. By examining the activity of preparations of vitamin on yeast fermentation, the vitamin was found in the mercuric chloride precipitate (choline fraction). In the case of rice polishings, the filtrate from the mercury precipitate was found inactive, the precipitate active but containing choline (isolated as platinum salt), which was inhibitory. From 2.5 kilos. of dry yeast, the choline fraction was freed from choline by precipitation as platinum salt and the active substance precipitated from the filtrate by aqueous mercuric chloride. A small yield of very active substance giving no carbohydrate reaction with Molisch's reagent was obtained. It contained N 4.75% (Pregl). H. K.

The Distribution of Urease in Plants. A. KIESEL and TROITZKI (*Z. physiol. Chem.*, 1922, **118**, 247—253).—Drying and autolysis diminish the urease activity of *Aspergillus niger*. This activity increases in the seeds and fruits of plants on ripening. Leaves contain more urease than stems and roots. On germination, the urease content increases, but the content of the enzyme diminishes again as the reserve material of the seeds is exhausted.

S. S. Z.

The Invertase of *Mucor racemosus*. S. KOSTYTSCHEV and P. ELIASBERG (*Z. physiol. Chem.*, 1922, **118**, 233—235).—*Mucor racemosus*— contains, whilst *Mucor racemosus*+ does not contain, invertase.

S. S. Z.

Enantiomorphism of Matter, Pasteur's Theory, and Life. S. CONDELLI (*Gazzetta*, 1921, **51**, ii, 309—324).—The author has subjected various racemic acids and amino-acids in nutrient solutions to the action of different bacteria and moulds. The results obtained are briefly as follows.

Both optically active malic acids are destroyed by the bacillus of fowl cholera, even at the ordinary temperature. With a solution containing the two enantiomorphous tartaric acids and dextrose, *Saccharomyces Pastorianus II* (Hansen) attacks only the sugar; doubt hence arises as to the affinity between the spacial configurations of an enzyme and the enantiomorph it preferably attacks. In the case of fermentations by yeasts in acid media, the influence of the acid appears to be solely due to the acidity it produces. Results similar to those obtained with the bacillus of fowl cholera are given by *Bacillus Fitzianus* in presence of a racemate. In the action of various schizomycetes on glyceric acid, the degree to which one of the two enantiomorphs is selected in preference to the other varies with the different organisms from a minimum to a maximum, the pure lævorotatory acid being left when *B. Fitzianus* is employed; these results confirm that of Frankland and Frew (T., 1891, **59**, 96) and not that of Lewkowitsch (A., 1883, 1124).

Penicillium glaucum acts on the sweet dextrorotatory asparagine in preference to the natural insipid lævorotatory enantiomorph. The bacillus of fowl cholera attacks lævorotatory in preference to the dextrorotatory aspartic acid, although the latter is derivable from *d*-asparagine; the acid function appears to influence the choice in this case. With tyrosine, two different moulds exhibit slight selection, in one case for the one and in the other for the other isomeride; tyrosine is not attacked by the bacillus of fowl cholera. *P. glaucum* acts on *l*-leucine more rapidly than on the dextro-isomeride (cf. Schulze and Bosshard, *Z. physiol. Chem.*, 1892, **9**, 100).

The author contests the view that asymmetry is a characteristic of life.

T. H. P.

The Physiology of the "Polyamyloses." I. HANS PRINGSHEIM and KARL O. MÜLLER (*Z. physiol. Chem.*, 1922, **118**, 236—240).—*Spirogyra dubia* which was previously freed from starch

was allowed to act on various substances with the purpose of ascertaining whether starch could be formed from them. Glycerol, dextrose, lævulose, galactose, maltose, and cellobiose gave positive results. No starch was formed from the "polyamyloses."

S. S. Z.

An Indicatory Method for Evaluating the Vitality of Seeds by a Biochemical Method. ANTONIN NĚMEC and FRANTIŠEK DUCHOŇ (*Compt. rend.*, 1922, **174**, 632—634; cf. this vol., i, 94).—The catalase activity of the seed is measured by determining the amount of oxygen liberated under definite conditions from hydrogen peroxide by a known weight of the seed previously ground to powder. Results with numerous different species show that the volume of oxygen liberated increases steadily with the germinative capacity of the seed, the curve showing their relationship being a smooth one.

W. G.

The Alleged Development of Hydrogen Peroxide in Carbon Dioxide Assimilation. HANS MOLISCH (*Biochem. Z.*, 1921, **125**, 257—261).—The author was unable to confirm the production of hydrogen peroxide in the assimilation of carbon dioxide by plants as described by Kleinstück (A., 1918, ii, 107).

H. K.

Energy Exchange in Carbon Assimilation by Green Cells. C. MÜLLER and O. WARBURG (*Ber. Physikal.-Techn. Reichsanst.*, 1920; from *Chem. Zentr.*, 1921, iii, 1205).—The utilisation of energy in the assimilation of carbon by *Chlorella vulgaris* in a nutrient solution saturated with 4% of carbon dioxide was studied for different wave-lengths. The percentage utilisation of energy in different parts of the spectrum was as follows: red (600—710 μ) 14%; yellowish-red (600—650 μ) 20%; orange (570—610 μ) 23%; yellow (550—590 μ) 21%; green (510—550 μ) 15%; blue (445—500 μ) 13%.

G. W. R.

Hydrogen-ion Concentration of Plant Cells. W. R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1922, **16**, 414—434).—A summary is given of earlier work on the reaction of plant cells and of the experimental methods used. Observations are recorded of the hydrogen-ion concentrations of a large number of plants. Varying reactions are found under differing cultural conditions and in different parts of the same plant. The values recorded range from P_H 1.4 to P_H 8. The P_H value in any tissue is generally near to but rather less than the optimum for the characteristic enzyme at ordinary temperatures, which ensures that the enzyme is not destroyed at higher temperatures which may be experienced. Diethyl-red is recommended as a reagent for microchemical work.

G. W. R.

The Variation in the Manganese Content of Leaves with Age. GABRIEL BERTRAND and (MME) M. ROSENBLATT (*Compt. rend.*, 1922, **174**, 491—493; cf. A., 1921, i, 759; Jadin and Astruc, A., 1913, i, 948).—The plants examined may be divided into four groups according to the manner of the variation of the manganese

content of their leaves with age, but there are certain species which fall between two groups. In the first two groups, the manganese content of the leaves is at a maximum at the commencement of the leaf formation and then diminishes with age, the rate of diminution differing with the group. In the third group, the manganese content increases very rapidly with age to a maximum and then diminishes. In the fourth group, the manganese content increases continuously with age. W. G.

Action of Soluble Lead Salts on Plants. EUGÈNE BONNET (*Compt. rend.*, 1922, **174**, 488—491).—Lead salts exert an unfavourable influence on the growth of plants, their effect being most marked in the curtailment of root development and to some extent of stem development. The plants absorb lead and the metal is found entirely in the roots. W. G.

The Presence of Ornithine in Plants. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **118**, 254—266).—So far, experiments to prove the presence of ornithine in plants have yielded negative results; it appeared possible that this might be due to the reagents employed. Experiments on the precipitation of ornithine by phosphotungstic acid, silicotungstic acid, tungstic acid, phosphomolybdic acid, Staněk's reagents, potassium bismuth iodide, potassium mercury iodide, and cadmium chloride show that they would fail to precipitate the small amounts of ornithine likely to be present in plant extracts. S. S. Z.

The Glutencasein of Buckwheat. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **118**, 301—303).—The glutencasein of buckwheat was found to yield on hydrolysis histidine 0·84%, arginine 7·13%, and lysine 1·48%. S. S. Z.

***Digitalis purpurea* Growing Wild on the Uplands of Desulo (Sardinia).** R. BINAGHI (*Gazzetta*, 1921, **51**, ii, 284—288).—The *Digitalis purpurea* growing wild at Desulo contains sufficient digitoxin to render it of medicinal value. The best method of extraction on a large scale is that given by Nativelle (A., 1875, 276), and Fromme's modification of Keller's method serves well for the rapid estimation of the content of digitoxin. T. H. P.

The Formation of Anthocyanin Pigments. RAOUL COMBES (*Compt. rend.*, 1922, **174**, 240—242; cf. A., 1909, ii, 420).—A reply to Jonesco (this vol., i, 97), in which the author considers that the materials taken by Jonesco for γ -pyrone pigments were only tannins and that, in consequence, his conclusions were false. W. G.

The Hydrocyanic Acid Question. VII. *Cornus sanguinea*. L. ROSENTHALER (*Schweitz. Apoth. Zeit.*, 1921, **59**, 465—469; from *Chem. Zentr.*, 1921, iii, 1247).—The leaves of *Cornus sanguinea*, L., do not contain hydrocyanic acid. The very rare occurrence of hydrocyanic acid and saponin together in the same plant suggests that there is no correlation between the occurrence of these substances. G. W. R.

Variations in the Chemical Composition of Fucaceæ. L. LAPICQUE and L. EMERIQUE (*Compt. rend. soc. biol.*, 1921, **85**, 172—175; from *Physiol. Abstr.*, 1922, **6**, 645).—The composition of Laminaræ shows an annual periodicity, the carbohydrate increasing in the summer and the ash constituents decreasing. *Fucus serratus* is similar, except that in June it contains a large quantity of mineral matter. *F. vesiculosus* exhibits a minimum of soluble ash constituents in June. *F. platycarpus* has a higher ash content. The analytical results are tabulated. E. S.

Western Sneezeweed (*Helenium hoopesii*) as a Poisonous Plant. C. DWIGHT MARSH, A. B. CLAWSON, JAMES F. COUCH, and HADLEIGH MARSH (*U.S. Dept. Agr. Bull.*, 1921, No. **947**, 1—46).—*H. hoopesii* contains a glucoside, *dugaldin*, which is poisonous to cattle. Dugaldin is a bitter, white, amorphous solid which forms a sparingly soluble, relatively slightly toxic compound with tannic acid. Helenic acid, the active principle of *H. autumnale*, does not occur in *H. hoopesii*, nor do alkaloids, toxic saponins, or hydrogen cyanide. CHEMICAL ABSTRACTS.

The Colouring Matter of the Scarlet Pelargonium. GEOFFREY SAUNDERS CURREY (T., 1922, **121**, 319—323).

Lignin as it Occurs in Wood. PETER KLASON (*Ber.*, 1922, **55**, [B], 455—456).—Fagerlind and Klason (*Schriften Vereins Zellstoff. Papier Chemiker*, **2**) have described the isolation of lignin from pine wood by repeated alternate extractions of the wood with boiling water and alcohol containing a small quantity of acetic acid. Re-examination of the product proves that it contains water which had been overlooked and, after the necessary corrections thus involved the analytical data are found to agree excellently with those calculated for lignin (A., 1920, i, 821). The substance gives the usual lignin reactions. As far as can be observed by reason of the colour of the solutions, lignin and lignosulphonic acid are optically inactive. H. W.

The Colouring Matter of Red Roses. GEOFFREY CURREY (*Proc. Roy. Soc.*, 1922, [B], **93**, 194—197).—An examination of the petals of the deep red rose "George Dickson" has shown the presence of the anthocyanin pigment cyanin (A., 1915, i, 282) to the extent of 10% of the dried petals. An unidentified yellow sap pigment is also present. It yields an anthocyanin on reduction. H. K.

The Enzymic Degradation of Arginine in Plants. II. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **118**, 267—276).—The presence of arginase has been established in ergot (*Secale cornutum*) and in *Vicia sativa* by demonstrating the formation of ornithine from arginine. Ammonia was also formed in the reaction. Traces of ornithine are evidently also produced by *Angelica silvestris* and *Trifolium pratense*. S. S. Z.

The Action of Arginase on Agmatine and Tetramethylen-diguanidine. The Specificity of Enzymes. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **118**, 284—300).—The action of

Aspergillus niger, *Secale cornutum*, *Agaricus campestris*, *Vicia sativa*, *Lupinus albus* and *Trifolium pratense* on agmatine and tetramethylenediguanidine has been studied. Agmatine is not decomposed by these organisms, whilst tetramethylenediguanidine is only acted on by *Aspergillus niger* with the formation of agmatine. S. S. Z.

The Tryptophan Content of Important Foodstuffs. TOSHIO IDE (*Z. expt. Med.*, 1921, **24**, 166—207).—The tryptophan content of cereals was estimated indirectly from that of the three seed components (sodium chloride-soluble protein, alkali-soluble protein, and alcohol-soluble protein), Fürth and Nobel's method being employed. The figure for maize is about half that for wheat, rye, barley, oats, and rice, but great individual variations were observed. In the case of legumes, a 10% sodium chloride extract of the proteins of the different flours yielded relatively high results (more than 0.5%) which were unaffected by removal of the germ. The direct method showed that raw white of egg protein contains 2.56%, and dried white of egg 3.18%, greater hydrolysis taking place when the latter is dissolved, whilst raw and dried yolk both contain about 2.45%. Cow's milk gave results between 0.068 and 0.094%, whereas human milk yields a higher figure. The proteins of cheese contain 2.48% of tryptophan; of unsweetened condensed milk, 2.28%; of sweetened condensed milk, 2.35%; and of dried milk, 2.71%.

CHEMICAL ABSTRACTS.

The Chemical Composition of Maize Oil. WALTER F. BAUGHMAN and GEORGE S. JAMIESON (*J. Amer. Chem. Soc.*, 1921, **43**, 2696—2702).—The sample of maize oil examined had d_{20}^{25} 0.9185; n_D^{20} 1.4717; iodine number (Hanus), 117.2; saponification number, 187.3; unsaponifiable matter, 1.7%; saturated acids, 11.2%; unsaturated acids, 82.5%. Detailed analysis showed its composition to be as follows: Glycerides of oleic acid 45.4%, of linoleic acid 40.9%, of palmitic acid 7.7%, of stearic acid 3.5%, of arachidic acid 0.4%, of lignoceric acid 0.2%, and 1.7% of unsaponifiable matter, total 99.8%. There was no evidence of the presence of any hypogæic acid (cf. Leathes, "The Fats," 1910).

W. G.

Nitrogen Compounds in Lucerne Hay. HARRY G. MILLER (*J. Amer. Chem. Soc.*, 1921, **43**, 2656—2663).—Non-protein nitrogenous compounds to the extent of about 28% of the total nitrogen were easily extracted with hot water from lucerne hay regardless of the fineness of the hay. Alkali hydroxides extracted more protein from the finely ground than from the coarse material. Such protein extracted by dilute alkali had a nitrogen content of 13.0% and contained the basic amino-acids arginine, histidine, lysine, and cystine. As compared with the seed (cf. A., 1921, i, 486), the leaf protein contained smaller amounts of arginine and amide nitrogen and this may account for the difference in the total nitrogen of the two proteins.

The purine fraction contained 3.2% of the total nitrogen, and a

crystalline salt corresponding with the hypoxanthine silver salt was isolated. W. G.

The Manganese Content of Potatoes. G. BODE and K. HEMBD (*Biochem. Z.*, 1921, **124**, 84—89).—The manganese content of twenty varieties of potatoes grown without addition of fertilisers containing manganese was determined colorimetrically as permanganate by Marshall's method (A., 1901, ii, 350) and simultaneously the silica and phosphate content. The mean manganese content of 1.4 mg. per 100 grams of dried material does not show any extreme variations. There is no parallelism between the manganese content and the silica or phosphate content or with the content of protein or starch, the melanin number, or yield of tubers. H. K.

Composition of Wild Beetroots. E. SAILLARD (*Compt. rend.*, 1922, **174**, 411—412).—The wild beetroots from Finisterre which were analysed were found to contain higher percentages of dry matter, insoluble marc, total nitrogen, mineral matter, chlorine, sodium, magnesium, and phosphoric acid than the cultivated varieties. Their sugar content varied from 14 to 20%, but their juice, as a source of sugar, was rather impure. W. G.

Progressive Disappearance of Free Sulphurous Acid in a Preserved Apple Juice. WARCOLLIER and LE MOAL (*Compt. rend.*, 1922, **174**, 634—637).—The sulphited juices examined were made from rotten apples, and the conversion of free added sulphurous acid into combined acid was investigated. It was found to be due to the action of oxidising enzymes present in the moulds of the juice. These enzymes formed, at the expense of the sugars and pectins of the juice, substances having aldehydic or ketonic structure, which fixed the sulphurous acid. At the same time, there was a marked increase in the acidity of the medium. Such juices should not, in consequence, be used for preserving and sweetening cider. W. G.

Copper Sprays. G. VILLEDIEU and (MME) G. VILLEDIEU (*Compt. rend.*, 1922, **174**, 707—709; cf. A., 1920, i, 704).—It has previously been shown that the traces of copper which can be dissolved by the rain from the deposits on the leaves of plants could not prevent the germination of the zoospores of mildew. It is now shown that a 2% solution of sodium sulphate or a 1.5% solution of sodium or potassium chloride completely prevents the bursting of the conidia of phytophthora. A similar result is obtained by using a saturated solution of calcium sulphate. The authors consider that the anticryptogamic power of copper sprays may be explained as due to the presence of these alkali or calcium salts, without considering the possible conversion of the copper into a soluble form. W. G.

Relation of the Hydrogen-ion Concentration of the Soil to Plant Distribution. W. R. G. ATKINS (*Nature*, 1921, **108**, 80—81; cf. following abstract).—Wherry's (*Proc. Acad. Nat. Sci. Philadelphia*, 1920, 113) observation that the distribution of a

species is closely related to the p_H of the soil, has been tested and found applicable to the distribution of a number of plants in India and the British Isles, the limiting p_H values being given in each case. Although plants may survive, or even thrive, in cultivation outside their normal limits, yet in free competition with their neighbours, a sufficiently great divergence from the normal p_H value for the species is always a deciding factor. A. A. E.

Relation of the Hydrogen-ion Concentration of the Soil to Plant Distribution. NORMAN M. COMBER (*Nature*, 1921, **108**, 146—147; cf. preceding abstract).—In view of the fact that some plants which are usually very susceptible to acidity will thrive in certain soils of p_H 4—5, and will show no response to liming, it is inferred that the effect of the hydrogen-ion concentration of the soil on plants is indirect, and that there is some ulterior factor, the fluctuations of which are commonly, but not invariably, accompanied by fluctuations of hydrogen-ion concentration. For instance, in mineral soils variations in the concentrations of certain multivalent ions, particularly aluminium ions, will roughly correspond with variations in the hydrogen-ion concentration.

A. A. E.

Chemistry of the Oxidation of Sulphur to Sulphuric Acid by Micro-organisms, and Transformation of Insoluble Phosphates into Soluble Forms. SELMAN A. WAKSMAN and JACOB S. JOFFE (*J. Biol. Chem.*, 1922, **50**, 35—45).—The sulphuric acid produced in the soil by sulphur oxidising bacteria converts insoluble into soluble phosphates (cf. Lipman, McLean, and Lint, A., 1916, i, 784). Using cultures of the organism in a liquid medium to which tricalcium phosphate has been added, it is shown that the acidity of the medium increases to about P_H 2.8, at which value it remains constant until all the phosphate has been converted into a soluble form. E. S.

Practical Significance of the Organic Carbon : Nitrogen Ratio in Soils. J. W. READ (*Soil Sci.*, 1921, **12**, 491—495).—The results of analyses are recorded showing the carbon : nitrogen ratio and crop yields of a number of soils. In general, the lower ratios are associated with low percentages of organic matter, but no correlation between the ratio and crop yields is apparent.

A. G. P.

Nitrification in Acid Soils. R. E. STEPHENSON (*Iowa Expt. Sta., Research Bull.*, 1920, **58**, 331—349).—Nitrification may take place in acid soils. The addition of lime produced no measurable effect on the nitrification of the original soil nitrogen, but it caused a marked increase in the nitrification of ammonium sulphate added to the soil. Although very large amounts of lime may increase the nitrifying power of a soil, only that necessary to neutralise the most active acids (as shown by an estimation of the lime requirement) is essential for adequate nitrification and maximum crop production.

CHEMICAL ABSTRACTS.

Organic Chemistry.

Natural System of Carbon Compounds. I. General Statement of Mendeléev's Law on the Numerical Relationships between Primary, Tertiary, and Quaternary Carbon Atoms. HERMAN DECKER (*Helv. Chim. Acta*, 1922, 5, 201—205).—If qu represents the number of quaternary, te that of the tertiary, and pr that of the primary carbon atoms in the hydrocarbon C_nH_{2n+p} , $pr-p=2qu+te$, or the relation between pr , te , and qu in every homologous series is determined by the series-constant p . For compounds composed entirely of benzene nuclei, the expression becomes $-p=2qu+te$. If the number of the nuclei be R^{ar} , $R^{ar}=qu/2+1$, or the number of nuclei exceeds by one the number of quaternary carbon atoms. J. K.

The Action of Nitrosyl Chloride on Normal Heptane. E. V. LYNN and O. HILTON (*J. Amer. Chem. Soc.*, 1922, 44, 645—648).—In confirmation of previous work (A., 1919, i, 245), it is shown that nitrosyl chloride reacts with normal heptane in sunlight, giving di-*n*-propylnitrosomethane, which suffers rearrangement with formation of dipropyl ketoxime. When distilled with steam, the oxime decomposes, giving the ketone and hydroxylamine. W. G.

A New Heptane: Trimethylisopropylmethane [$\beta\beta\gamma$ -Trimethylbutane]. G. CHAVANNE and B. LEJEUNE (*Bull. Soc. chim. Belg.*, 1922, 31, 98—102).— $\beta\beta\gamma$ -Trimethylbutane is prepared from pinacol by the action of magnesium methyl iodide. The additive compound is decomposed by dilute acetic acid, yielding pentamethylethanol [$\beta\gamma\gamma$ -trimethylbutan- β -ol] (cf. Henry, A., 1906, i, 477). This, on dehydration with *p*-toluenesulphonic acid, is converted into a heptylene, $\beta\gamma\gamma$ -trimethyl- Δ^2 -butylene, $CMe_3\cdot CMe\cdot CH_2$, which, when treated in acetic acid solution with hydrogen in presence of platinum black, yields the heptane, a liquid of camphor-like odour, b. p. $80.75^\circ/760$ mm., m. p. -25° , d_4^{15} 0.6945, d_4^{20} 0.7065, n_a^{15} 1.3903, n_D^{15} 1.3923, n_B^{15} 1.3971, n_γ^{15} 1.4008. The following constants were determined for the heptylene: d_4^{15} 0.7101, d_4^{20} 0.7235, n_a^{15} 1.4032, n_D^{15} 1.4059, n_B^{15} 1.4119, n_γ^{15} 1.4164. H. J. E.

The Influence of the Elements of the Oxygen Group on Paraffin Wax. H. SIEBENECK (*Petroleum*, 1922, 18, 281—286).—Paraffin wax is fairly readily attacked by air or oxygen if the gas is bubbled through the material heated at about 135° . After ten hours, acid vapours are evolved, and after twenty-two hours the product remaining contains from 30—40% of saponifiable substances, according to whether pure oxygen or air is used. By continuing the experiment, a product containing 52.65% of saponi-

fiable substances was obtained having an acid value 59.03 and an ester value 93.91, corresponding with about 30% of free and 70% of esterified acids. The acids belong to the acetic acid series, lower members of which series are also present in the volatile portion of the product of oxidation together with water, amounting in all to about 7% of the paraffin employed. When paraffin wax is heated with sulphur, evolution of hydrogen sulphide commences at 150°, and at 230° this gas is liberated freely together with carbon disulphide. After seventy-two hours' treatment at this temperature, a brownish-black, fatty mass remained, from which, after extraction with carbon disulphide and then with ether, an amorphous, black substance was isolated containing only a negligible percentage of hydrogen and having a composition agreeing closely with the formula $(C_5S)_x$. The substance is indifferent to alkalis and organic solvents, but is attacked by concentrated sulphuric and nitric acids. Similar dehydrogenation of the paraffin was observed under the action of selenium and tellurium, but higher temperatures (300—370°) were necessary, and no product corresponding with the sulphurised paraffin could be isolated. The presence of small quantities of sulphur or selenium apparently completely inhibited the action of oxygen on the paraffin.

G. F. M.

Chemical Reactions Induced by the Silent Discharge. I. Ethylene and Nitrogen. II. Benzene and Carbon Dioxide.

SUSUMU MIYAMOTO (*J. Chem. Soc. Japan*, 1922, **43**, 21—48).—

I. A mixture of 1 volume of ethylene and 2 volumes of nitrogen was submitted to the electric field given by an alternating current of 10,000 volts and 50 cycles, in an apparatus cooled with water. The following substances were isolated: (1) A nitrile, $C_{18}H_{31} \cdot CN$, a light yellow liquid having a stimulating odour, b. p. 82—85°/10 mm., the hydrolysis of which gave an oily acid, $C_{18}H_{31} \cdot CO_2H$, and a silver salt, $C_{18}H_{31} \cdot CO_2Ag$, a yellow precipitate, m. p. 100° (approx., decomp.). (2) An amine, $C_{20}H_{38}N_4O_2$, which formed the following salts: *platinichloride*, yellow crystals, darkening at about 150°, *aurichloride*, yellow crystals, darkening at about 180°; *picrate*, yellow crystals, melting and darkening at about 170°. (3) The substances $C_{11}H_{20}O$, b. p. 58—65°/11 mm.; $C_{12}H_{22}O$, b. p. 73—79°/11 mm.; $C_{13}H_{24}O$, b. p. 87—93°/11 mm.; a mixture of $C_{15}H_{28}O$ and $C_{15}H_{28}O_2$, b. p. 97—103°/11 mm.; and $C_{18}H_{34}O$, b. p. 112—115°/11 mm.; these are presumed to be produced by the oxidising action of air on the unsaturated hydrocarbons, $C_{10}H_{20}$, $C_{12}H_{22}$, $C_{13}H_{24}$, $C_{15}H_{28}$, and $C_{18}H_{34}$, respectively, formed initially. (4) A substance, $(C_{22}H_{34}O_2)_n$, a yellow powder, which does not decompose at 300°, (5) hydrogen cyanide, (6) acetylene, (7) hydrogen, and (8) ethane; the last two gases and a compound, $C_{16}H_{32}N_4$, have been isolated by Berthelot in the same reaction (A., 1899, i, 657).

II. When a mixture of carbon dioxide and benzene vapour was passed through the apparatus under like conditions, the phenol, $(C_{10}H_{10}O_3)_3$, a yellow powder, decomposing and darkening at about 100°, was isolated.

K. K.

Photochemical Studies. XIII. Photopolymerisation of Vinyl Chloride and the Problem of Caoutchouc. JOH. PLOTNIKOW (*Z. wiss. Photochem.*, 1922, **21**, 117—134; cf. A., 1921, ii, 146).—Solutions of vinyl chloride in 99% ethyl alcohol, acetone, carbon disulphide, benzene, methyl alcohol, ethyl ether, toluene, and carbon tetrachloride have been subjected to ultra-violet light for periods of six hours at temperatures between 25.2° and 15.2°. In all solvents except benzene and carbon disulphide, a polymerisation occurs easily when the extreme ultra-violet is used, and a white, amorphous compound separates. In the case of carbon disulphide, there is no action, and with benzene an oily product is formed. In the normal action, the chlorine atom acts as an internal catalyst. The process has a temperature coefficient 1.03. Of all the solvents employed, methyl alcohol and ethyl alcohol are the most suitable. Salts of manganese, cobalt, nickel, copper, and vanadium act catalytically in the sense that they cause the reaction to take place in visible light. Carbon tetrachloride accelerates the reaction in ultra-violet light. Uranyl salts are the strongest catalysts, and a process for the preparation of the product by the action of sunlight in the presence of uranyl salts has been worked out and will be published later in the patent literature. The product of the reaction is described as a pure white, light powder resembling rice powder, which is slightly soluble in acetone, methyl alcohol, and ethyl alcohol, more soluble in benzene, chlorobenzene, carbon tetrachloride, and carbon disulphide, and very soluble in phenyl acetate. It separates from the solvents, in which it is fairly soluble, as an elastic film which loses its elasticity on keeping. By suitably mixing with vaselin, aniline, balsam of Peru, and similar substances, waxes, jellies, and solid elastic masses may be obtained.

J. F. S.

The System Water-Ethyl Alcohol-Carbon Disulphide. Miscibility of the Three Components in Different Proportions and some Practical Applications. N. SCHOORL and (MLLE) A. REGENBOGEN (*Rec. trav. chim.*, 1922, **41**, 125—134).—The diagram is given of the ternary system showing the limits of homogeneous mixtures at temperatures of 0°, 10°, 20°, 40°, 60°, and 80°, also diagrams for binary mixtures of ethyl alcohol and carbon disulphide showing critical temperatures at which separation takes place. The results are applicable to the estimation of the water content of alcohol, especially for high percentages of the latter, by the determination of the temperature of homogeneous mixing of two volumes of the alcohol with five volumes of carbon disulphide.

H. J. E.

The Composition of the Residue on Distillation of Crude Glycerin. E. LEWIS (*J. Soc. Chem. Ind.*, 1922, **41**, 97—100T).—An average sample of glycerin residues contained 19.56% of diglycerol (or polyglycerols). The polymerised glycerols are produced from glycerol under the influence of heat and pressure, and their formation is accelerated by the presence of alkaline salts, and by such catalysts as iodine and bromine. No simple means was found

for depolymerising these substances and recovering the glycerol, as even when a certain amount of depolymerisation was effected by means of high pressures at various temperatures further polymerisation occurred on distilling the mixture owing to the salts present. In addition, a considerable proportion of the depolymerised product was converted during the process into glyceric acid, glyceraldehyde, and a hexose sugar. Pure diglycerol was prepared by heating glycerol for two hours at 210° with 0.05% of iodine. On distillation in a vacuum, an 85% yield of a water-white, viscous, and very hygroscopic fluid, b. p. $257-260^{\circ}/30$ mm., $d_{20}^{20}=1.3215$, $d_{30}^{30}=1.3183$, was obtained.

During the investigation, the b. p. of anhydrous and aqueous solutions of glycerol were determined at 760 mm. pressure, the following being selected from the results recorded: 100% glycerol 290° , 99% 225.5° , 98% 196.0° , 95% 160° , 90% 137.5° , 80% 121.5° , 50% 106.0° , 10% 101.0° . The specific gravities of mixtures of glycerol with diglycerol, and with water in various proportions, were also determined and the results are recorded in tabular form.

G. F. M.

The Constitution of Glycerides from the Point of View of the Co-ordination Theory. AD. GRÜN (*Oesterr. Chem. Ztg.*, 1922, 25, 37—38).—In reply to Klimont, it is pointed out that the hypothesis of the existence of glycerides in the two forms, $R\cdot CO_2R_1$ and $R\cdot C\begin{smallmatrix} O \\ \diagup \end{smallmatrix}R_1$, is not advanced solely with the object of explaining the double melting point of certain glycerides, but mainly to account for their unusual reactivity, which frequently resembles that of salts except in the greater slowness of reaction. Reasons are advanced for considering the isolation of co-ordination forms less probable in the cases of methyl and ethyl esters than of glycerides. The author does not consider that dimorphism adequately explains the occurrence of glycerides in forms with different melting points, and regards the dimorphism as the outward expression of difference in internal structure.

H. W.

Production and Reactions of $\beta\beta'$ -Dichlorodiethyl Sulphide. FREDERICK GEORGE MANN and WILLIAM JACKSON POPE (*T.*, 1922, 121, 594—603).

Preparation of Esters of Dihydroxydiethyl Sulphide. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (*Brit. Pat.* 154907).—The esters are obtained by the interaction of organic acids or their anhydrides and dihydroxydiethyl sulphide. Thus, *diacetoxydiethyl sulphide* is prepared by slowly dropping 5 parts of dihydroxydiethyl sulphide on to 6 parts of acetic anhydride heated at 120° . It is a stable, mobile liquid, b. p. $142-150^{\circ}/12$ mm. The corresponding diformyl compound boils at $130-137^{\circ}/7$ mm.

G. F. M.

Sesqui-mustard Gas or Bis- β -chloroethyl Ether of Ethylene Dithioglycol. RAPHAEL ROSEN and E. EMMET REID (*J. Amer. Chem. Soc.*, 1922, 44, 634—636).—The work recorded is

in complete agreement with that of Bennett (T., 1921, **119**, 418, 1860), except in so far as the melting point of ethylene bis- β -hydroxyethyl sulphide is concerned. In a footnote the authors state that their product was probably impure. W. G.

A Homologue of Ethylene Sulphide : Trimethylethylene [β -Methyl- Δ^{β} -butylene] Sulphide. G. CALINGAERT (*Bull. Soc. chim. Belg.*, 1922, **31**, 109—111; cf. Delépine, A., 1920, i, 526; 1921, i, 156).— β -Methyl- Δ^{β} -butylene dibromide is transformed into the corresponding dithiocyanate and this is shaken in the cold with sodium sulphide solution, the product being distilled with steam. β -Methyl- Δ^{β} -butylene sulphide so obtained is a mobile, colourless liquid, b. p. 145—150°, d_4^{20} 0.927. H. J. E.

The Action of Selenium Monochloride on Propylene, Butylene, and Amylene. C. E. BOORD and F. F. COPE (*J. Amer. Chem. Soc.*, 1922, **44**, 395—401).—The action between ethylene and selenium monochloride resulting in the formation of $\beta\beta'$ -dichlorodiethyl selenide dichloride (cf. Bauser, Gibson, and Pope, T., 1920, **117**, 1453) really takes place in two stages: $2C_2H_4 + Se_2Cl_2 = (C_2H_4Cl)_2Se + Se$; and $(C_2H_4Cl)_2Se + Se_2Cl_2 = (C_2H_4Cl)_2SeCl_2 + 2Se$. The action may be stopped at the first stage by adding the selenium monochloride to the ethylene. These two stages have been obtained with propylene, butylene, and amylenes, but with the last two it is not easy to complete the second stage. The compounds described are $\beta\beta'$ -dichlorodipropyl selenide, b. p. 134°/10 mm., and its dichloride, m. p. 81°; $\beta\beta'$ -dichlorodibutyl selenide, b. p. 138°/8 mm., and its dichloride; $\beta\beta'$ -dichlorodiamyl selenide, b. p. 158°/10 mm., and its dichloride. These results are taken as further evidence in favour of the unsymmetrical structure, $Se:SeCl_2$, for selenium monochloride. W. G.

Action of Carbon Disulphide on Mercuric Acetate. A. BERNARDI and G. ROSSI (*Gazzetta*, 1922, **52**, i, 139—140).—The action of carbon disulphide on cold, saturated mercuric acetate solution, even in the dark, proceeds according to the equation: $CS_2 + 2(CH_3 \cdot CO_2)_2Hg + H_2O = S(Hg \cdot CO_2 \cdot CH_3)_2 + COS + 2CH_3 \cdot CO_2H$. The compound, $S(Hg \cdot CO_2 \cdot CH_3)_2$, forms a crust of white, silky needles, begins to decompose without melting at 215°, appears to be insoluble in all solvents, is decomposed by hot mineral acids, and yields mercuric sulphide when treated with either water or sodium thiosulphate. T. H. P.

Mangani-acetates and -benzoates. R. F. WEINLAND and GEORG FISCHER (*Z. anorg. Chem.*, 1921, **120**, 161—180).—Complex salts derived from ferric and chromic acetates have been described, particularly those containing pyridine in the complex kation, for example, $[Cr(OAc)_6Py_3(OH)_2]I_3$ (A., 1910, i, 503) and $[Fe_4(OAc)_6Py_3O]Cl_4$ (A., 1913, i, 644). Derivatives of manganic acetate have now been prepared containing pyridine in the complex kation. These are more nearly related to the iron than to the chromium compounds, and appear to contain four atoms of

metal in the inner complex. They are generally brown in colour, are decomposed by water, and are soluble in alcohol.

Perchlorates. $[\text{Mn}_4(\text{OAc})_6\text{Py}_{4.5}(\text{OH})_2](\text{OAc})_3\cdot\text{ClO}_4$, long, narrow, rectangular tablets; $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_3](\text{OAc})_2\cdot\text{ClO}_4$, well-formed, long, thin tablets, also crystallises with $2\text{H}_2\text{O}$;

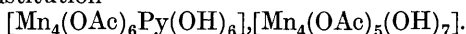
$[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_4](\text{OAc})\cdot\text{ClO}_4\cdot 2\text{H}_2\text{O}$, aggregates of thin needles; $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_3](\text{OAc})_{1.5}(\text{ClO}_4)_{1.5}$, thin needles which recrystallise unchanged from alcohol.

Nitrates. $[\text{Mn}_4(\text{OAc})_6\text{Py}_4](\text{OAc})_4(\text{NO}_3)_2$, thin, rectangular needles; $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})](\text{OAc})_{3.5}(\text{NO}_3)_{1.5}$, oblique tables; $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_2](\text{OAc})_2(\text{NO}_3)_2 +$

$2[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})](\text{OAc})_4\cdot\text{NO}_3$ very thin, long, rectangular tables, and

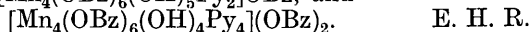
$[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_2](\text{OAc})_{2.5}(\text{NO}_3)_{1.5}$, very thin, rectangular tables.

Acetates. $[\text{Mn}_4(\text{OAc})_6\text{Py}_5\text{O}_2](\text{OAc})_2$, lustrous, octahedral crystals from a solution of manganic acetate in pyridine; recrystallised from alcohol, it gives $[\text{Mn}_4(\text{OAc})_6\text{Py}_4(\text{OH})_4](\text{OAc})_2$, of similar crystalline form; a more complex compound crystallising in brownish-black columns with a well-marked cleavage appears to have the constitution



Other more complex nitrates and perchlorates of doubtful constitution were also obtained. Red manganic acetate probably has the constitution $[\text{Mn}_3(\text{OAc})_6(\text{H}_2\text{O})_2](\text{OAc})_3\cdot 4\text{H}_2\text{O}$.

A new manganic benzoate with alcohol of crystallisation was prepared, $[\text{Mn}_3(\text{OBz})_6(\text{OH})_3\text{EtOH}]$, large, red crystals. Two pyridine compounds were isolated, both apparently containing a tetramanganation: $[\text{Mn}_4(\text{OBz})_6(\text{OH})_5\text{Py}_2]\text{OBz}$, and



The Action of Alumina, Titania, and Thoria on Ethyl and isoPropyl Acetates. HOMER ADKINS and A. C. KRAUSE (*J. Amer. Chem. Soc.*, 1922, **44**, 385—392).—Contrary to a statement of Sabatier, it is shown that alumina, titania, and thoria are not specific in so far as the mode of decomposition of ethyl acetate by them is concerned. In determining the order of efficiency of these catalysts for these reactions, the method of preparation of the catalyst is of an importance equal to, if not greater than the particular metal present in the oxide. Further, it is shown that the course of the decomposition of the ester is not determined by the relative instability of the intermediate compounds formed between the catalyst and the acid and the catalyst and the alcohol. The probability is that saponification of the ester precedes the decomposition. A sample of unignited alumina prepared from the hydroxide was found to exert a marked condensing action on acetone at 455° . W. G.

The Successive Stages in the Hydrolysis of Triacetin. E. YAMAZAKI (*J. Amer. Chem. Soc.*, 1922, **44**, 426; cf. A., 1920, i, 591).—The author acknowledges the priority of Meyer's work (A., 1907, i, 819; 1909, ii, 391, 803) on this subject. W. G.

The Formation of Salts of Sulphocarboxylic Acids. I. Cobaltous and Cupric Salts of Sulphoacetic and α -Sulphopropionic Acids. H. J. BACKER and J. V. DUBSKÝ (*Rec. trav. chim.*, 1922, **41**, 145—151).—The cobaltous and cupric salts of sulphoacetic and α -sulphopropionic acids show almost complete similarity in behaviour, the only differences observed being in respect of the quantity and stability of water content. One molecule of the water of crystallisation of the neutral and acid copper salts is very strongly bound and the suggestion is made that this is linked to the sulphonc group. The neutral salts of both metals combine with two molecules of pyridine and the additive products also retain a molecule of water, probably linked in a similar manner to the above; the water is lost more easily by the additive products than by the neutral salts. The authors consider that the metal, rendered more positive by the presence of pyridine, may show greater affinity for the sulphonc group. The following have been prepared: *Cobalt sulphoacetate*, reddish-violet crystals; with two molecules of pyridine gives a light reddish-violet crystalline powder and, with a second molecule of the acid, light orange-red crystals of the acid salt; *cobalt α -sulphopropionate* was obtained only as a syrupy solution; with two molecules of pyridine, light violet crystals of the additive product crystallised; with a second molecule of the acid hygroscopic crystals of the acid salt of a light orange-red colour were obtained. *Copper sulphoacetate* forms small bluish-green crystals; with two molecules of pyridine it yields a deep blue, crystalline precipitate; with excess of acid, light bluish-green crystals of the acid salt. *Copper α -sulphopropionate* forms light blue crystals, which give with two molecules of pyridine deep blue crystals of the additive compound and, with a second molecule of the acid, light blue, hygroscopic crystals of the acid salt.
H. J. E.

Studies of the Constitution of Soap Solutions. Solutions of Sodium Palmitate, and the Effect of Excess of Palmitic Acid or Sodium Hydroxide. JAMES WILLIAM MCBAIN, MILLICENT TAYLOR, and MARY EVELYN LAING (*T.*, 1922, **121**, 621—633).

Colophenic Acids. W. FAHRION (*Ber.*, 1922, **55**, [B], 709; cf. Fahrion, A., 1907, i, 329; 1921, i, 792; Aschan, A., 1912, i, 512; this vol., i, 221).—The different varieties of colophony contain a large but unknown number of resin acids, all of which, in so far as they have been isolated, possess the formula $C_{20}H_{30}O_2$ and are soluble in light petroleum. They are all converted by atmospheric oxygen into darker coloured, amorphous autoxidation products which are insoluble in light petroleum and are classed as oxyabietic acids.
H. W.

The Catalytic Decomposition of Oleic Acid. ALPHONSE MAILHE (*Compt. rend.*, 1922, **174**, 873—874).—When oleic acid vapours are passed over a copper-aluminium alloy at 600—650°, they are decomposed, giving gases rich in hydrocarbons of the

series C_nH_{2n+2} and C_nH_{2n} and in hydrogen, and also a liquid rich in unsaturated hydrocarbons, which when hydrogenated by passage over nickel at 180—200° give a mixture of aliphatic and aromatic hydrocarbons, among the latter of which benzene, toluene, and *m*-xylene were identified. W. G.

The Catalytic Decomposition of Shark Oil. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1922, [iv], 31, 249—252).—The method used for vegetable oils has been applied to shark oil as an example of animal oils (cf. A., 1921, i, 706, 841). The vapours of shark oil were passed over a mixture of aluminium and copper at 600—650° and gaseous and liquid products were obtained. The former consisted of some acetaldehyde together with hydrocarbons and hydrogen. The latter contained acids, after the removal of which a yellow oil was left which, on hydrogenation over nickel at 180—200°, gave a mixture of paraffins, cyclic hydrocarbons of the type of cyclohexane and methylcyclohexane, and aromatic hydrocarbons, of which benzene, toluene, and *m*-xylene were identified. The acids referred to above were unsaturated, and after hydrogenation of the mixture over nickel at 230—240° heptonic, pelargonic, and lauric acids were identified. W. G.

The Unsaturated Fatty Acids of Liver Lecithin. P. A. LEVENE and H. S. SIMMS (*J. Biol. Chem.*, 1922, 51, 285—294).—From the product of bromination of the fatty acids obtained from liver lecithin, an octobromoarachidic acid was isolated. When reconverted into a tetra-unsaturated acid, this yielded arachidonic acid, whilst the latter, on reduction, gave arachidic acid. The residue from the bromination, on similar treatment, gave first oleic and then stearic acid. On the assumption that arachidonic and oleic acids are the only unsaturated acids present in liver lecithin, it is calculated from the iodine numbers that lecithin obtained by extraction of liver with acetone contains oleic and arachidonic acids in the ratio 1.3 : 1, whilst the ratio for that extracted by ether is 4.3 : 1 (cf. A., 1921, i, 842). E. S.

Geometrical Isomerism in Unimolecular Films. N. K. ADAM (*Nature*, 1921, 107, 522; cf. A., 1921, ii, 488 and Langmuir, A., 1917, ii, 525).—In the case of certain fatty acids containing an ethylenic linking, the properties of films (considered to be one molecule in thickness) formed on the surface of water exhibit striking differences between *cis*- and *trans*-forms. It is thereby indicated that oleic and erucic acids are *cis*-forms, whilst elaidic and brassidic acids are *trans*-forms. It is considered that the molecules of saturated acids, such as palmitic acid, are attracted to the water by the carboxyl groups, whereas unsaturated acids are also attracted, although less powerfully, by their ethylenic linkings. The tendency of *cis*-forms to yield films of smaller area than those of the *trans*-forms is ascribed to the ability of the double bond in the former case to approach as closely as desired to the water, whilst in the latter case the saturated portion of the chain must be forced among the water molecules. Hence, owing

to the resistance produced by the limited flexibility of a hydrocarbon chain, the double bond of the *trans*-form will be unable to approach the water so closely as that of the *cis*-form. The area occupied by one molecule of a film of oleic acid on water under a compression of about 1.4 dynes per sq. cm. is of the order of 40×10^{-16} sq. cm., the area decreasing with time; elaidic acid occupies about 30×10^{-16} sq. cm., also diminishing with time.

A. A. E.

Preparation of Sodium Silver-thioglycollate. CHEMISCHE FABRIK FLORA (Brit. Pat. 156103).—Thioglycollic acid is treated with an equivalent quantity of a water-soluble silver salt and an excess of a solution of sodium hydroxide. Either reagent may be employed first, but if the former, the yellow precipitate of *silver-thioglycollic acid*, $\text{AgS}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, which is formed, is separated and washed, and then dissolved in the soda solution. The *sodium salt*, $\text{AgS}\cdot\text{CH}_2\cdot\text{CO}_2\text{Na}$, is exceedingly soluble in water, and is isolated by precipitation with alcohol as a heavy, yellow powder. It is of value for the therapeutic treatment of gonococci diseases.

G. F. M.

β -Halogen-substituted Fatty Acids and β -Lactones. HJALMAR JOHANSSON and SIDNEY M. HAGMAN (*Ber.*, 1922, **55**, [B], 647—658).—In continuation of the study of β -lactones (cf. Johansson, *Diss., Lund.*, 1916), α -methyl- β -butyrolactone and α -ethyl- β -butyrolactone are now described. The formation of β -lactones appears to occur much more commonly than was supposed formerly. From the preparative point of view, it is important to note that the hydrolysis of β -lactones to the hydroxy-acids is an irreversible process, whereas with γ -lactones the change is reversible; the successful production of the former from the β -halogenated acids depends, therefore, on their removal from solution before they have been converted to the hydroxy-acids. It has been observed previously (*loc. cit.*) that the hydrolysis of β -lactones (propiolactone, isobutyrolactone, and β -butyrolactone) is influenced but little if at all by the hydrogen-ion concentration. The behaviour of the present lactones is very analogous, but the action is not strictly unimolecular, and distinct evidence of hydrogen-ion catalysis is obtained. Apparently the process is complicated by simultaneous or consequent actions. In the presence of the resultant hydroxy-acid, the change appears to be uniformly unimolecular, but towards its end carbon dioxide and a gas resembling coal gas in odour are evolved; the full description of the experiments is reserved for a subsequent communication.

The preparation of β -bromo- α -methylbutyric acid, m. p. 63—64°, from tiglic acid and hydrogen bromide is described in detail. The hydrolysis of its sodium salt by water has been studied by arresting the reaction at definite intervals by pouring an aliquot portion of the solution on pure ice and titrating rapidly, first with sodium hydroxide and phenolphthalein and subsequently with silver nitrate and potassium chromate. The results show that no acid, with the exception of carbonic, is produced. Direct estimation of

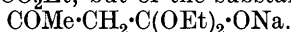
q*

the latter shows that two-thirds of the acid is transformed into carbon dioxide and Δ^8 -butene, whereas one-third is available for the production of the lactone. The *latter* is conveniently isolated by violently agitating a concentrated aqueous solution of sodium β -bromo- α -methylbutyrate with chloroform at about 30° , the organic medium being renewed from time to time and the neutrality of the solution being maintained by the addition of small crystals of sodium carbonate. It is a colourless, highly-refractive liquid, b. p. $67-67.5^\circ/21$ mm., d^{20} 0.9862; it solidifies at about -30° and melts at about -24° .

β -Bromo- α -ethylbutyric acid, m. p. 25° , is hydrolysed in neutral solution in much the same manner as the lower homologue, about 63% of it being converted into amylene and carbon dioxide, leaving about 37% available for the formation of the corresponding

lactone. α -Ethyl- β -butyrolactone, $\text{CHEt} \begin{smallmatrix} \text{CHMe} \\ \text{CO} \end{smallmatrix} \text{O}$, is a colourless, mobile liquid, b. p. $79-81^\circ/18$ mm., d^{20} 0.9700. It does not solidify completely at -50° , but is not completely re-melted below -25° . 2.46 Grams of it are soluble in 100 c.c. of water at the atmospheric temperature. H. W.

Metallic Compounds of the Enolic Forms of Carbonyl Compounds and their Application to Syntheses. II. Synthesis of Vinylideneglycol Diethyl Ether [Keten-acetal]; Explanation of the Course of the Reaction in the Acetoacetic Ester Synthesis. HELMUT SCHEIBLER and HEINRICH ZIEGNER (*Ber.*, 1922, 55, [B], 789-803; cf. Scheibler and Voss, A., 1920, i, 366).—The product obtained by the condensation of ethyl acetate with metallic sodium or sodamide does not appear to be composed mainly of ethyl sodioacetoacetate or of the compound $\text{OEt} \cdot \text{CMe}(\text{ONa}) \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, but of the substance



When decomposed by dilute acids, it yields ethyl acetoacetate and alcohol, $\text{COMe} \cdot \text{CH}_2 \cdot \text{C}(\text{OEt})_2 \cdot \text{ONa} \rightarrow \text{COMe} \cdot \text{CH}_2 \cdot \text{C}(\text{OEt})_2 \cdot \text{OH} \rightarrow \text{COMe} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et} + \text{EtOH}$; by spontaneous decomposition of its ethereal suspension or by the action of water, it is converted into sodium acetate and ketenacetal: $\text{COMe} \cdot \text{CH}_2 \cdot \text{C}(\text{OEt})_2 \cdot \text{ONa} \rightarrow \text{CH}_2 \cdot \text{C}(\text{OEt})_2 + \text{CH}_3 \cdot \text{CO}_2\text{Na}$.

The gradual addition of ethyl benzoate to a suspension of ethyl potassioacetate in anhydrous ether causes the slow separation of considerable quantities of potassium benzoate. The ethereal filtrate is treated with water and the aqueous portion yields ethyl benzoylacetate, whereas the ethereal portion contains unchanged ethyl benzoate, unsaturated ethers, a hydrocarbon of high boiling point which will be described subsequently, and the ketenacetal which could not be isolated as such from this mixture. The change may be represented by the scheme: $\text{CH}_2 \cdot \text{C}(\text{OK}) \cdot \text{OEt} + \text{Ph} \cdot \text{CO}_2\text{Et} \rightarrow \text{CH}_2 \cdot \text{Bz} \cdot \text{C}(\text{OEt})_2 \cdot \text{OK} \rightarrow \text{CH}_2 \cdot \text{C}(\text{OEt})_2 + \text{Ph} \cdot \text{CO}_2\text{K}$. The course of the reaction is here somewhat disturbed by the occurrence of hydrogenation, but this drawback is not experienced when the potassium is replaced by sodamide. A reaction does not occur

when ethyl benzoate is added to finely divided sodamide covered with ether, but the gradual introduction of ethyl acetate causes vigorous evolution of ammonia; the precipitate contains sodium benzoate, sodium acetate, and benzamide, but the isolation of ketenacetal from the filtrate is difficult. The accomplishment of the latter depends on the observation that the decomposition of the sodium salt can be effected more conveniently by means of water than by spontaneous fission in ethereal suspension; the use of ethyl benzoate and ether is thereby rendered unnecessary, and it is more practical to operate with ethyl acetate alone, the excess of which plays the part of solvent. Powdered sodamide is therefore added in small portions to freshly distilled ethyl acetate cooled in a powerful freezing mixture; after some hours, the temperature is allowed to rise to 20°. The product is diluted with ether and gently warmed on the water-bath, after which the solvent and unchanged ethyl acetate are removed in a vacuum. The residual salt is gradually added to a small quantity of water at 20°, whereupon sodium acetate separates gradually. The *ketenacetal* is extracted from the filtrate with ether. It is a volatile liquid with a faint ethereal odour, b. p. 77.5—78°/760 mm., d^{22}_4 0.7938, $[R_L]^{21}_D$ 32.54, $[R_L]^{21}_D$ 32.65, $[R_L]^{21}_D$ 33.05. It is readily oxidised by alkaline permanganate and rapidly decolorises bromine dissolved in carbon tetrachloride. It is comparatively stable towards alkali hydroxide, but is decomposed by mineral acids into ethyl acetate and ethyl alcohol. It reacts very readily in ethereal solution with the alkali metals or their amides. Its relationship to the ketenacetals appears to be purely formal, since it differs widely in its properties from substances such as acroleinacetal and behaves rather as unsaturated ether.

H. W.

Trihalogenmethyl Reactions. IV. Reaction of Trichloroacetic Acid with Copper. HOWARD WATERS DOUGHTY and BENJAMIN FREEMAN (*J. Amer. Chem. Soc.*, 1922, 44, 636—645; cf. A., 1918, i, 57; 1919, i, 513; 1921, ii, 414).—When ethyl trichloroacetate is warmed on a water-bath with copper powder, it gives *diethyl tetrachlorosuccinate*, b. p. 156°/13 mm. Attempts to hydrolyse the ester were not successful. Trichloroacetic acid reacts very vigorously with copper powder, but tetrachlorosuccinic acid could not be isolated in the pure state, only its *aniline* salt, m. p. 149—150° (corr.) being prepared. In benzene or water as solvent, trichloroacetic acid reacts with copper, giving a good yield of dichloroacetic acid and this method is recommended as a means of preparing dichloroacetic acid in any desired quantity.

There is some indication that these reactions involve the formation of a relatively unstable intermediate compound in which copper is directly linked to carbon, and that the course of the reaction is determined by the manner in which the copper is eliminated from this intermediate compound.

W. G.

The α -Alkyl-levulic Acids. H. GAULT and T. SALOMON (*Compt. rend.*, 1922, 174, 754—756).— α -Alkyl-levulic acids may readily be prepared by the following series of reactions. The sodium

derivative of diethyl malonate reacts with bromoacetone in ether to give *diethyl acetonylmalonate*, $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2$, b. p. $150^\circ/20$ mm., giving a *phenylhydrazone*, m. p. $108\text{--}109^\circ$, and a *semicarbazone*, m. p. $125\text{--}127^\circ$. At the same time, a certain amount of ethyl ethanetetra-carboxylate is also formed. The sodium derivative of the acetonylmalonic ester readily condenses with alkyl iodides to give alkylacetonylmalonic esters, of which the following are described: *Ethyl ethylacetonylmalonate*, giving a *phenylhydrazone*, m. p. $99\text{--}100^\circ$; and *ethyl isobutylacetonylmalonate*, giving a *phenylhydrazone*, m. p. $72\text{--}73^\circ$. These esters saponify more or less readily, giving the free acids. *Ethylacetonylmalonic acid*, m. p. $122\text{--}123^\circ$, gives a *phenylhydrazone*, m. p. $136\text{--}137^\circ$, but the *isobutyl* acid was not obtained pure owing to the difficulty of removing the second ester group. The free acids, when heated, readily lose a molecule of carbon dioxide, giving the corresponding α -alkyl-levulic acid, and the ester acids also lose carbon dioxide, giving ethyl α -alkyl-levulates.

W. G.

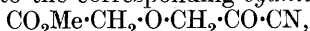
Diglycollic Acid or Anhydroglycollic Acid. RICHARD ANSCHÜTZ and SIEGFRIED JAEGER (*Ber.*, 1922, **55**, [B], 670—679).—In connexion with the recent publication by Sido (*A.*, 1921, i, 447) on cyclic imide ethers of diglycollic acid as sweetening agents, the authors describe a series of similar products.

The following diglycollarylamic acids are prepared by treating a solution of diglycollic anhydride in chloroform with an equivalent quantity of the requisite amine dissolved in the same solvent. Diglycollanilic acid, m. p. 118° ; *diglycoll-o-, -m-, and -p-toluidic acids*, slender needles, m. p. 120° , needles, m. p. $131\text{--}132^\circ$, and leaflets or long needles, m. p. 148° , respectively; *diglycoll-p-xylidic acid*, flat plates, m. p. 106° ; *diglycoll-as-m-xylidic acid*, slender needles, m. p. $116\text{--}117^\circ$; *diglycoll-1:2:4:5- ψ -cumidic acid*, slender needles, m. p. $133\text{--}135^\circ$; *diglycoll- α -naphthalidic acid*, needles, m. p. 165° ; *diglycoll- β -naphthalidic acid*, microscopic needles, m. p. 153° . Treatment of the arylamidic acids with boiling acetyl chloride results in the formation of the corresponding *arylimides*, of which the following are described: diglycollanil, m. p. 195° ; *o-tolil*, m. p. 126° ; *m-tolil*, m. p. 114° ; *p-tolil*, m. p. 180° ; *diglycoll-p-xylil*, flat, hexagonal plates, m. p. 127° ; *diglycoll-as-m-xylil*, needles, m. p. 102° ; *diglycoll- α -naphthil*, m. p. 176° ; *diglycoll- β -naphthil*, four-sided rods, m. p. $172\cdot5^\circ$.

Diglycollic anhydride is converted by hydrazine into the *hydrazidic acid*, $\text{NH}_2\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, slender needles, m. p. $113\text{--}114^\circ$; the corresponding *hydrazine* and *silver* salts have been prepared.

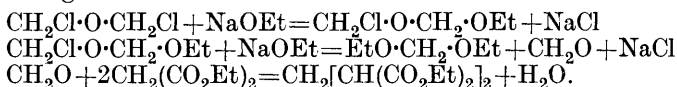
Methyl diglycollate, b. p. $130^\circ/13$ mm., m. p. 36° , is prepared by dissolving diglycollic anhydride in an excess of methyl alcohol and subsequently saturating the mixture with hydrogen chloride. *Methyl hydrogen diglycollate*, a colourless, viscous liquid which solidifies in a freezing mixture, b. p. $173\text{--}174^\circ/12$ mm., is prepared from the anhydride and methyl alcohol and is converted by thionyl chloride into the corresponding *chloride*, a mobile liquid,

b. p. 107—108°/12 mm., 114—115°/15 mm., from which the following derivatives are prepared: *anilide*, a pale yellow oil, b. p. 175—180°; *o-toluidide*, a yellow liquid, b. p. 185°/13 mm.; *p-toluidide*, slender, colourless needles, m. p. 41°. The chloride is transformed by silver cyanide into the corresponding *cyanide*,



a colourless, heavy liquid, b. p. 165—170°/16 mm., which is hydrolysed by fuming hydrochloric acid at the atmospheric temperature to the *acid*, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, m. p. 129—130°, b. p. 160°/13 mm.; the *silver* salt of the latter is described. H. W.

The Reaction between s-Dichlorodimethyl Ether and Ethyl Malonate. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1922, **44**, 649—650).—Dichlorodimethyl ether reacts with the sodium salt of ethyl malonate to give ethyl propan- $\alpha\gamma\gamma$ -tetracarboxylate together with some methylene dimethyl ether (cf. Kamm and Waldo, this vol., i, 105). It is probable that in this reaction the sodium functions as sodium ethoxide and not as the sodium salt of ethyl malonate, the reaction occurring in three stages.



W. G.

Sulphur in Proteins. I. The Effect of Acid Hydrolysis on Cystine. WALTER FRED HOFFMAN and ROSS AIKEN GORTNER (*J. Amer. Chem. Soc.*, 1922, **44**, 341—360).—Pure cystine, crystallising in hexagonal plates, was boiled for varying lengths of time up to one hundred and ninety-two hours with 20% hydrochloric acid. The analytical data indicate that cystine is only slowly decomposed or destroyed during prolonged boiling with 20% hydrochloric acid and there would not be any appreciable decomposition during an ordinary protein hydrolysis. During the one hundred and ninety-two hours' boiling there was but little decarboxylation. Similarly, the sulphur of the cystine was not eliminated to any appreciable extent. A small amount of hydrogen sulphide was evolved, some elementary sulphur separated, but no sulphates were formed, and about 90% of the original sulphur was still unchanged and unoxidised at the end of the period of boiling. The amount of cystine precipitable by phosphotungstic acid decreased rapidly during the first forty-eight hours of boiling, after which it remained practically constant. The nitrogen of the cystine was not appreciably changed during the boiling. The amount of total nitrogen remained constant, the amount of amino-nitrogen slowly decreased and there was a corresponding slowly progressive increase in the amount of ammonia nitrogen. The optical rotation of the cystine solution rapidly fell during the boiling to complete inactivity at the end of ninety-six hours. From the residual hydrolysate an isomeric cystine was isolated. It crystallised in small, microscopic prisms and differed in its

physical and chemical properties from the original cystine. It was approximately 2.5 times as soluble in water, and its phosphotungstate was four times as soluble. It was optically inactive. A number of derivatives of the two forms of cystine were prepared, and in every instance the isomeric derivatives possessed different properties from those prepared from the natural "plate" cystine. The authors suggest that this isomeric cystine which they have isolated is identical with that synthesised by Fischer and Raske (A., 1908, i, 325) and by Erlenmeyer and Stoop (A., 1905, i, 119), and that the "plate" cystine obtained by protein hydrolysis has never been synthesised.

W. G.

Resolution of Hydroxyaspartic Acids [Aminohydroxysuccinic Acids] into Optically Active Forms. H. D. DAKIN (*J. Biol. Chem.*, 1922, 50, 403—411).—Resolution of the anti-acid (cf. this vol., i, 143) was effected by fractional crystallisation of its strychnine and quinine salts, which yielded *strychnine* d-anti-aminohydroxysuccinate ($4\text{H}_2\text{O}$, $[\alpha]_D^{20} -19.1^\circ$) and *quinine* l-anti-aminohydroxysuccinate ($4\text{H}_2\text{O}$, $[\alpha]_D^{20} -95.5^\circ$), respectively. By regeneration of the acids from these salts, d-anti-aminohydroxysuccinic acid, wedge-shaped prisms, $[\alpha]_D^{20} +12.1^\circ$, and l-anti-aminohydroxysuccinic acid, wedge-shaped prisms, $[\alpha]_D^{20} -11.9^\circ$, were obtained. Both active forms gave mesotartaric acid on treatment with nitrous acid, whilst heating with water at 125° produced a partial conversion into the inactive para-acid. Attempts to resolve the para-acid were unsuccessful. Fractional crystallisation of the following alkaloid salts: *strychnine* ($3\text{H}_2\text{O}$, prisms, $[\alpha]_D^{20} -23.2^\circ$), *cinchonine* (aq., hexagonal prisms, $[\alpha]_D^{20} +122.5^\circ$), *brucine* ($4\text{H}_2\text{O}$, thin plates, $[\alpha]_D^{20} -23.4^\circ$), *quinine* ($2\text{H}_2\text{O}$, felted needles, $[\alpha]_D^{20} -116^\circ$), and the action of *Penicillium glaucum* on the sodium salt, were tried but without result. A partial resolution appeared to be effected by fermenting yeast, the lævo-acid being preferentially consumed. The amount of resolution, however, was too small to render possible the isolation of the active acid.

From an investigation of the products obtained by the tryptic digestion of casein it is concluded that aminohydroxysuccinic acid does not occur in this protein (cf. Skraup, A., 1904, i, 539):

E. S.

Preparation of Acetaldehyde and Acetic Acid. A. WOHL (*Brit. Pat.* 154579).—In the catalytic hydration of acetylene to acetaldehyde, mercury salts may be replaced by salts of heavy metals which are not appreciably volatile and are not transformed into oxides at temperatures below a red heat. The best results are obtained with basic zinc salts deposited on pumice and maintained at about 360° , the basic vanadate being preferably employed, but the molybdate or chromate may be used, as also may the corresponding salts of copper, cobalt, nickel, or cadmium, but not with such good results. The acetylene is mixed with a considerable excess of air and steam, and under favourable conditions 75—80% of the theoretical yield of acetaldehyde together with 5% of acetic acid are obtained.

G. F. M.

Synthesis and Properties of a δ -Hydroxyaldehyde. BURCKHARDT HELFERICH and THEODOR MALKOMES (*Ber.*, 1922, **55**, [B], 702—708).— δ -Hydroxyhexaldehyde has been synthesised in a manner similar to that used previously for γ -hydroxyvaleraldehyde (Helferich, A., 1920, i, 11). Like the γ -hydroxyaldehydes described previously, the new aldehyde appears to be stable in the cyclic form, $\text{CH}_2 < \begin{smallmatrix} \text{CH}_2 - \text{CHMe} \\ \text{CH}_2 \cdot \text{CH(OH)} \end{smallmatrix} > \text{O}$, but to pass readily in the course of various reactions into the true aldehyde form, $\text{OH} \cdot \text{CHMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CHO}$. The observations appear to be of considerable importance for the chemistry of the sugars, since the possibility of the formation of 1:5-rings (in place of the generally assumed 1:4-structures) must be taken into account.

Δ^6 -Hexenoic acid is prepared from *cyclohexanone oxime* by Wallach's method (a *lactone*, $\text{C}_6\text{H}_{10}\text{O}_2$, b. p. $96.5\text{--}97.5^\circ/15\text{ mm.}$, is obtained as by-product) and is converted by thionyl chloride into Δ^6 -*hexenoyl chloride*, a colourless, mobile liquid, b. p. $49^\circ/17\text{ mm.}$, d_4^{18} 1.0113, n_D^{18} 1.4471. The latter is transformed by magnesium methyl iodide into *methyl Δ^6 -amylenyl ketone*, $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COMe}$, a colourless liquid of unpleasant odour, b. p. $41\text{--}43^\circ/10\text{ mm.}$, d_4^{18} 0.8673, n_D^{18} 1.4350 (*semicarbazone*, aggregates of needles, m. p. 108°), which is reduced to *methyl- Δ^6 -amylenyl-carbinol*, a colourless liquid, b. p. $64\text{--}65^\circ/13\text{ mm.}$, d_4^{18} 0.8484, n_D^{18} 1.4387. Ozonisation of the latter and subsequent reduction of the ozonide in ethereal solution with zinc dust and glacial acetic acid give δ -*hydroxy-n-hexaldehyde* (or *6-hydroxy-2-methyltetrahydropyran*, b. p. $71\text{--}78^\circ/11\text{ mm.}$, d_4^{18} 1.0065, n_D^{18} 1.4452. The cyclic structure of the aldehyde is established by its physical constants and the observation that it reduces ammoniacal silver solution and colours magenta-sulphurous acid solution gradually. It gives a *p-bromophenylhydrazone*, small, pale yellow needles, m. p. 85° (slight decomp.), and is oxidised by silver oxide in the presence of water to δ -hydroxy-n-hexoic acid. It is converted by methyl alcoholic hydrogen chloride (1%) into *6-methoxy-2-methyltetrahydropyran*, a colourless, mobile liquid with an odour of peppermint, b. p. $71.5\text{--}76^\circ/110\text{ mm.}$, d_4^{18} 0.9232, n_D^{18} 1.4211. The latter does not reduce Fehling's or ammoniacal silver solutions, and does not appear to be hydrolysed by emulsin or α -glucosidase from yeast.

H. W.

Preparation of Aldehydes from Acid Chlorides. V. (Dialdehydes. II.) Synthesis of Decanedial. KARL W. ROSENMUND, FRITZ ZETSCHE, and FL. ENDERLIN (*Ber.*, 1922, **55**, [B], 609—612; cf. A., 1921, ii, 320; this vol., i, 39). *Decanedial* (*sebacic dialdehyde*), $\text{C}_8\text{H}_{16}(\text{CHO})_2$, is prepared in at least 80% yield by the action of hydrogen on a solution of sebacyl chloride in xylene at 150° in the presence of palladised kieselguhr and "sulphured" quinoline; it is a colourless, oily liquid with a pleasant odour, b. p. $142^\circ/15\text{ mm.}$, which polymerises rapidly to a vitreous form. Both varieties give the usual aldehydic reactions with Fehling's solution, magenta-sulphurous acid and ammoniacal

silver solution. The sodium hydrogen sulphite *compound* and the *barium* salt, $C_8H_{16}(CH:N \cdot C_{10}H_6 \cdot SO_3)_2Ba$, formed from the aldehyde and barium naphthionate, are described. The aldehyde yields a *di-p-nitrophenylhydrazone*, tile-red crystals, m. p. 104—107° (decomp. after softening at about 95°), and a *dioxime*, slender, colourless needles, m. p. 124—127° (corr.) after previous softening; the latter does not appear to be identical with the similar compound described by von Braun and Sobceki (A., 1911, i, 830). H. W.

Spontaneous Condensation of Ethoxyacetone; Formation of the Corresponding Aldol, $\alpha\epsilon$ -Diethoxy- β -methylpentan- β -ol- δ -one. VICTOR DAUDEL (*Bull. Soc. chim.*, 1922, [iv], 31, 265—268).—Ethoxyacetone, as prepared by the action of magnesium methyl bromide on ethoxyacetoneitrile, slowly undergoes condensation on keeping, probably due to traces of ammonia present. The principal product is $\alpha\epsilon$ -diethoxy- β -methylpentan- β -ol- δ -one, $OEt \cdot CH_2 \cdot CO \cdot CH_2 \cdot CMe(OH) \cdot CH_2 \cdot OEt$, b. p. 126—128°/21 mm.; d^{20} 1.011. The condensation is, however, more complex and resinous products are formed which could not be identified. A *compound*, b. p. 170—180°/16 mm.; d^{20} 1.0164, was isolated.

W. G.

Influence of Sodium Chloride on the Mutarotation of Dextrose in Alkaline Solution. I and II. HANS MURSCHAUSER (*Biochem. Z.*, 1922, 128, 215—228, 229—244).—I. In $N/2000$ -sodium carbonate solution the velocity of mutarotation of dextrose solutions is retarded by the presence of sodium chloride. The retardation is proportional to the square root of the concentration of the sodium chloride.

II. The velocity constants of the mutarotation of dextrose at 20.4° have been determined in aqueous solution, in 2*N*- and 4*N*-sodium chloride solution, in increasing concentrations of hydrochloric acid from 0.046 to 0.54% and in 2*N*- and 4*N*-sodium chloride solutions containing increasing amounts of hydrochloric acid from 0.046 to 0.54%. All follow the unimolecular law, and although at concentrations of acid below 0.089%, 2*N*- and 4*N*-sodium chloride lower the velocity of mutarotation compared with hydrochloric acid solutions below 0.089%, yet in all cases the velocity constants of the mutarotation, whether in hydrochloric acid solution alone or in 2*N*- or 4*N*-sodium chloride, increase proportionally to the concentration of hydrochloric acid.

H. K.

The Law Governing the Constants of Mutarotation of Dextrose and the Concentration of Acid. HANS MURSCHAUSER (*Biochem. Z.*, 1922, 128, 245—250).—It has been shown (preceding abstract) that at constant temperature the increase in the velocity constant of the mutarotation of dextrose in the presence of increasing amounts of hydrochloric acid is proportional to the concentration of the acid, $K_{HCl} - K_{H_2O} = 48.5 C_{HCl}$ at 20.4°. If, however, the velocity constant in the presence of hydrochloric acid, K_{HCl} , be divided by the square root of the concentration of the hydrochloric acid (or the hydrogen-ion concentration), another

constant is obtained. The first equation given enables either the strength of a hydrochloric acid solution from the velocity constant or the reverse to be determined.

H. K.

The Formation of Formic Acid during the Decomposition of Dextrose in Alkaline Solution. H. I. WATERMAN and M. J. VAN TUSSEN BROEK (*Chem. Weekblad*, 1922, **19**, 135—136).—Solutions of dextrose in *N*-sodium hydroxide solution containing barium hydroxide were treated with ordinary air and with air containing ozone. In all cases formic acid was formed; 10 grams of dextrose after one hundred and forty-two and a half hours yielded 1.66 grams of the acid. No carbon dioxide was formed except when the temperature was kept below normal. S. I. L.

The Function of Phosphates in the Oxidation of Dextrose by Hydrogen Peroxide. ARTHUR HARDEN and FRANCIS ROBERT HENLEY (*Biochem. J.*, 1922, **16**, 143—147).—The chief function of phosphates in the oxidation of dextrose by hydrogen peroxide appears to be the regulation of the hydrogen-ion concentration as other buffer mixtures ($\text{NaHCO}_3 + \text{CO}_2$; $\text{Na}_2\text{HAsO}_4 + \text{NaH}_2\text{AsO}_4$; $\text{NaC}_2\text{H}_3\text{O}_2$; $\text{K}_2\text{HPO}_4 + \text{KH}_2\text{PO}_4$) can replace the phosphates. Hydrogen peroxide is more stable in presence of phosphates than at the same P_{H} in their absence. W. O. K.

Preparation of Mannose. E. P. CLARK (*J. Biol. Chem.*, 1922, **51**, 1—2).—The method described is simpler and gives better yields than those of Hudson and Sawyer (*A.*, 1917, **i**, 321) and of Horton (*J. Ind. Eng. Chem.*, 1921, **13**, 1040). Sifted ivory-nut shavings are added to ten times their weight of boiling 1% sodium hydroxide and left for half an hour with occasional stirring. They are then thoroughly washed with water and dried. The material (500 grams) so obtained is mixed with an equal weight of 75% sulphuric acid and left for a day, after which the resulting mass is dissolved in water, diluted to $5\frac{1}{2}$ litres, and boiled for two and a half hours. The solution is then neutralised with barium carbonate paste and filtered through a thin layer of active carbon, the last traces of barium being removed by adding a few c.c. of dilute sulphuric acid and again filtering. The filtrate is concentrated until it contains 87—88% of total solids, mixed with an equal volume of glacial acetic acid, seeded, and frozen. Finally, it is allowed to thaw slowly in a refrigerator, when crystallisation of the mannose takes place. E. S.

Crystalline Chlorotetra-acetylmannose. D. H. BRAUNS (*J. Amer. Chem. Soc.*, 1922, **44**, 401—406; cf. Fischer and Hirschberger, *A.*, 1889, 480, 687).—Chlorotetra-acetylmannose was obtained in a crystalline form by applying the method of von Arlt (cf. *A.*, 1901, **i**, 369). Phosphorus pentachloride was allowed to act on β -penta-acetylmannose in the presence of aluminium chloride in chloroform. The product was obtained in crystals, m. p. 81° ; $[\alpha]_{\text{D}}^{20} + 89.50^\circ$. With methyl alcohol and silver carbonate, chlorotetra-acetylmannose gives a mixture of methyltetra-acetylmannoses, thus

resembling in this respect bromotriacetylrrhamnose, but differing from the corresponding derivatives of dextrose and galactose.

W. G.

The Constitution of Polysaccharides. J. J. LIJNST ZWIKKER (*Rec. trav. chim.*, 1922, **41**, 152).—A correction is made in the formulæ given in the author's paper (this vol., i, 230); it is maintained that it necessitates no change in the suggested molecular structure.

H. J. E.

New Observations on the Constitution of the Carbohydrates. L. DE HOOP (*Chem. Weekblad*, 1922, **19**, 106—107).—The conclusions of Karrer, based on methylation and acetylation, that the starch molecule is really simpler than the earlier molecular-weight determinations (5,000 to 20,000) indicate, are criticised as being based on insufficient evidence.

S. I. L.

Preparation of Inulin, with Special Reference to Artichoke Tubers as a Source. J. J. WILLAMAN (*J. Biol. Chem.*, 1922, **51**, 275—283).—The ground and washed tubers are boiled for fifteen to twenty minutes with water containing calcium carbonate (1,300 c.c. of water and 30 grams of calcium carbonate to each kilo.) and the juice is then expressed in a press. After repeating the process on the residue, the combined extracts are clarified by means of lead acetate, any excess of the latter being removed by addition of ammonium oxalate. The clear liquid is then evaporated until it contains 40—60% of solids, cooled slowly, and maintained at 0—5° for crystallisation. Recrystallisation from water is repeated until the specific rotation reaches -38° or -39° . A study of the optical rotation during successive recrystallisations confirms the view that inulin is a mixture of substances. Artichoke tubers are not a good source of true inulin.

E. S.

Alleged Adsorption of Alumina from Aluminium Sulphate Solutions by Cellulose. ALFRED TINGLE (*J. Ind. Eng. Chem.*, 1922, **14**, 198—199).—Neither acid-washed filter-paper nor well-washed bleached sulphite pulp removes any analytically appreciable amounts of alumina from a basic solution of aluminium sulphate, and the observed withdrawal of alumina from solutions of the sulphate in presence of cellulose is due to chemical precipitation by non-cellulose material present as an impurity. In no case could adsorption of alumina by cellulose of reasonable purity be observed. Methods of investigation which depend on attempts to separate aluminium salts from cellulose by repeated washing can only be employed when great caution is used as to the nature of the materials, and when basic solutions are in question they can never be trusted, as mere dilution of a basic aluminium sulphate solution will cause precipitation.

G. F. M.

Action of Iodine on Celluloses, Silk, and Wool. J. HUEBNER and J. N. SINHA (*J. Soc. Chem. Ind.*, 1922, **41**, 93—94T).—Celluloses, natural and artificial silk, wool, and other like substances give varying but appreciable yields of iodoform when treated with dilute aqueous solutions of iodine and potassium iodide. The

reaction was most marked with poplar wood cellulose, and by distilling with steam poplar cellulose pulp to which iodine and sodium hydroxide had been added pure iodoform was readily obtained. The operation could be repeated and even after twenty successive treatments appreciable yields of iodoform were obtained. The results seem to indicate that the amount of iodoform produced has some definite relation to the solubility of the different celluloses in alkali hydroxide solutions.

G. F. M.

Effect of Water and certain Organic Salts on Celluloses.

J. HUEBNER and F. KAYE (*J. Soc. Chem. Ind.*, 1922, **41**, 94T).—Distilled water in which purified cotton or cellulose has been soaked at 35° for twenty-four hours readily gives a silver mirror and the characteristic aldehyde reaction with rosaniline, whilst if it is steeped in sodium acetate solution under similar conditions the amount of aldehyde produced is so considerable that it can be separated by distillation. If the cotton is merely placed over distilled water in a closed vessel for several days, the water, without having come into contact with the cellulose, contains traces of aldehydic substances. If cellulose or starch remains for several days in contact with distilled water at 35° to which sodium acetate and resorcinol have been added, the solution becomes fluorescent and aldehydic substances can be separated by distillation, whilst the addition of lead acetate to the residue after distillation causes a greyish-brown precipitate. When cellulose is steeped in water there is a rise of temperature accompanied by a contraction of the total volume.

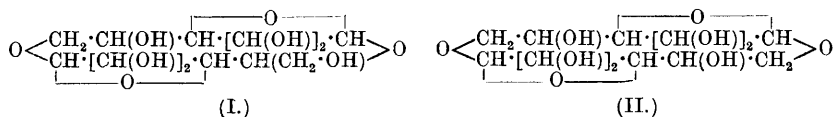
G. F. M.

Polysaccharides. XIV. The Amyloses. P. KARRER and ELISABETH BÜRKLIN (*Helv. Chim. Acta*, 1922, **5**, 181—187; cf. this vol., i, 229).—The behaviour of Pringsheim's "triamylose" towards acetyl bromide at 0—5° is similar to that of α -diamylose and β -hexamylose, since it furnishes the same quantities of aceto-bromomaltose and heptacetylmaltose as the corresponding amount of maltose. No glucose could be detected among the products. "Triamylose" is therefore either a simple or a polymeric form of maltose anhydride. Its identity with β -hexamylose is established by a comparison of their solubilities, specific rotatory powers, crystalline form, contents of water of crystallisation, indifference to pancreatic juice, and compounds with sodium hydroxide. So far, therefore, all methods of degrading starch have furnished either maltose or simple or polymeric forms of its anhydride. Also the fact that the acetylation of β -hexamylose with acetic anhydride and zinc chloride proceeds without depolymerisation opens up the possibility of avoiding such degradation in the cases of starch, cellulose, etc., in which more or less complete breaking down has hitherto been accepted.

J. K.

Polysaccharides. XV. Constitution of Diamylose and of the Anhydro-sugar (Cellosan) of Cellulose. P. KARRER and ALEX. P. SMIRNOV (*Helv. Chim. Acta*, 1921, **5**, 187—201; cf. preceding abstract).—Treatment of penta-acetyl-glucose with

phosphorus pentabromide (5 parts) for twelve minutes at 100° yields considerable amounts of tetraceto-1-bromoglucose, but no 1:6-dibromo-derivative. In agreement with this, the same product is obtained from octa-acetylcellobiose, whilst from octa-acetyl-maltose aceto-1:6-dibromo- and aceto-1-bromo-glucose are obtained. From acetylated diamylose, on the other hand, aceto-1:6-dibromoglucose, unaccompanied by any monobromo-derivative, is produced. Hence, in diamylose, the anhydro-oxygen atom connects the 1- with one of the 8-, 9-, 11-, or 12-carbon atoms of the maltose molecule. Since starch is a polymeric diamylose, its acetyl derivative also furnishes aceto-1:6-dibromoglucose as sole product. "Triacetyl-cellulose" (Ost, *Z. angew. Chem.*, 1919, 67) behaves similarly, a result irreconcilable with the view that the cellulose molecule consists of a chain or cyclic structure of cellobiose molecules, but in accordance with its conception as a polymeric anhydrocellobiose (*Cellulosechemie*, 1921, 2, 125). This anhydride, now termed cellosan, must therefore have the constitution (I). This formula at once explains the formation of 2:3:6-trimethyl-glucose, instead of tetramethylglucose, from methylated cellulose. Further, it also represents cellosan as an anhydride of maltose (or isomaltose), so that its degradation may occur in two ways—to cellobiose or to maltose. Hence it is that only 40—43% (or, allowing for that portion which suffers further degradation, at most 50—60%) of acetocellobiose is obtainable by acetolysis of cellulose (Karrer and Widmer, A., 1921, i, 310; Freudenberg, A., 1921, i, 400). The easy hydrolysis of maltose by acids explains the failure to detect its formation either in this reaction or among the products of the action of acetyl bromide on cellulose (A., 1921, i, 771). Of the three remaining possible formulæ for diamylose, that of the 1—12 anhydride (II) is alone acceptable. It explains



the complete conversion of starch and diamylose into maltose, since the same result must follow from the rupture of either of the two glucosidic linkings. Steric influences may possibly influence the stabilities of diamylose and cellulose, but the easier hydrolysis of the former is adequately explained by the fact that in it the alcoholic groups concerned in the glucosidic linkings are both primary. It now only remains to determine what degrees of polymerisation of cellosan and diamylose are respectively represented by cellulose and starch.

The aceto-mono- and -dibromo-glucoses obtained in the above reaction are always accompanied by oily products, consisting probably of the isomeric acetodibromoglucoses, the formation of which is to be anticipated, other bromination (cf. Brigl, this vol., i, 225) and decomposition products, and also undecomposed disaccharide complexes.

J. K.

Structure and Formation of the Humic Acids and Coal.

J. MARCUSSEN (*Z. angew. Chem.*, 1922, **35**, 165—166; cf. this vol., i, 326).—Polemical. The author maintains that humic acids contain condensed furan and benzene rings and stand in close relationship to, if they are not identical with, the synthetic acids prepared from sugars. Contrary to Eller's views (*loc. cit.*), these acids are carboxylic acids, as are also most probably the acids synthesised by Eller from phenols, and both probably contain a dibenzofuran nucleus. Eller's acids are, however, in no way identical with the natural humic acids, as evidenced by their hydrogen content and their behaviour towards soda. In the conversion of humic acids into brown coal, anhydride formation accompanied by loss of carbon dioxide occurs, and this so-called pyrohumic acid was isolated from brown coal after the extraction of the humic acids with ammonia by boiling the insoluble residue with 10% sodium hydroxide, and the lesser number of carboxyl groups found expression in the lower saponification value, 253, compared with 300 for humic acid. In coal formation, the author considers that cellulose as well as lignin plays a part, and although a portion is undoubtedly destroyed by bacterial action, this cannot apply to the whole of the cellulose associated with the lignin in wood.

G. F. M.

Amides and Anilides of some Saturated Fatty Acids.

MITIZÔ ASANO (*J. Pharm. Soc. Japan*, 1922, 97—105).—As the amides and anilides of fatty acids are of use in the detection and identification of these acids, whilst the melting points given in the literature are discordant, the author has prepared some of them together with the isobutylamides from the pure acids (from heptioic acid to lauric acid) and determined their melting points, the result being as follows: Heptioic acid: amide, m. p. 94—95°; anilide, m. p. 64°. Octoic acid: amide, m. p. 104°; anilide, m. p. 51·5°; isobutylamide, b. p. 154—155°/7 mm. Pelargonic acid: amide, m. p. 99°; anilide, m. p. 57·5°; isobutylamide, b. p. 162°/6 mm., m. p. 37—38°. Decoic acid: amide, m. p. 98°; anilide, 67—68°; isobutylamide, b. p. 171°/6 mm.; m. p. 37—38°. Undecoic acid: amide, m. p. 96—97°; anilide, m. p. 68°; isobutylamide, m. p. 51°. Lauric acid: amide, m. p. 98—99°; anilide, 75°; isobutylamide, m. p. 51°.

K. K.

Syntheses from Cyanamide. Preparation of Thiocarbamine Cyanides, Carbamine Cyanides, and Biurets.

EMIL FROMM [with HERMANN WENZL] (*Ber.*, 1922, **55**, [B], 804—813).—The product of the action of sodium cyanamide on phenylthiocarbimide has the constitution $\text{NPh}\cdot\text{C}(\text{SNa})\cdot\text{NH}\cdot\text{C}\cdot\text{N}$, since it is converted by benzyl chloride into the compound $\text{NPh}\cdot\text{C}(\text{S}\cdot\text{C}_6\text{H}_5)\cdot\text{NH}\cdot\text{CN}$, which has been obtained from phenyldithiobiuret, benzyl chloride, and sodium hydroxide. The benzyl haloid has, in addition, a desulphurising action which is due to the disturbance of the equilibrium, $\text{X}\cdot\text{C}(\text{NH})\cdot\text{SNa} \rightleftharpoons \text{X}\cdot\text{C}\cdot\text{N} + \text{NaSH}$, by the removal of the sulphide. This desulphurising effect is considerably more marked with ethylene chlorohydrin, which, with phenyldithio-

biuret or the product of the action of sodium cyanamide and phenylthiocarbimide, gives phenylcarbamine cyanide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$, *s*-diphenylcarbamide, and triphenylisomelamine, $(\text{NHPh}\cdot\text{CN})_3$. The initial change is doubtless expressible by the equations $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CS}\cdot\text{NH}_2 + 2\text{NaOH} \rightleftharpoons \text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CN} + \text{Na}_2\text{S} + 2\text{H}_2\text{O}$ and $2\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl} + \text{Na}_2\text{S} = (\text{OH}\cdot\text{CH}_2\cdot\text{CH}_2)_2\text{S} + 2\text{NaCl}$. The sulphur-free compounds are therefore derived from phenylthiocarbamine cyanide, but the obvious hypothesis that the next stage of the reaction occurs by a further elimination of hydrogen sulphide is negatived by the observation of a similar reaction with phenylethylthiobiuret, with which this loss is impossible. It is much more probable that phenylcarbamine cyanide is produced from its thio-analogue by simple hydrolysis, $\text{NHPh}\cdot\text{CS}\cdot\text{NH}\cdot\text{CN} + \text{H}_2\text{O} = \text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CN} + \text{H}_2\text{S}$. The phenylcarbamine cyanide is hydrolysed in boiling alkaline solution to phenylcarbamide, $\text{NHPh}\cdot\text{CO}\cdot\text{NH}\cdot\text{CN} + 2\text{H}_2\text{O} = \text{NHPh}\cdot\text{CO}\cdot\text{NH}_2 + \text{CO}_2 + \text{NH}_3$, and the latter is converted into the diphenyl derivative by protracted boiling of its solution. Triphenylisomelamine is derived from phenylcyanamide resulting from the desulphurisation of phenylthiocarbamide produced by the hydrolysis of phenylthiocarbamine cyanide.

The sodium salt of phenyl- ψ -thiocarbamine cyanide, $\text{C}_8\text{H}_6\text{N}_3\text{SNa}$, leaflets, is formed by the addition of phenylthiocarbimide to a cold aqueous solution of sodium cyanamide, and is converted by cautious acidification with acetic acid into *phenylthiocarbamine cyanide*, a colourless, unstable substance, m. p. (indefinite) 105° after becoming discoloured at 90° (the *silver*, *copper*, and *mercury* derivatives are described). The sodium salt is transformed by benzyl chloride into *N*-phenyl-*S*-benzyl- ψ -thiocarbamine cyanide, m. p. 189 – 190° . Under varying conditions which are described in detail in the original, the sodium salt of phenyl- ψ -thiocarbamine cyanide is converted by ethylene chlorohydrin and sodium hydroxide into *phenylcarbamine cyanide*, m. p. 123 – 124° , diphenylcarbamide, and triphenylisomelamine, the precise course of the reaction being governed largely by the amount and concentration of the alkali hydroxide. The isolation of these products from phenylthiobiuret is also described in detail. Phenylcarbamine cyanide is converted by hot, very dilute sulphuric acid into *as*-phenylbiuret, m. p. 167° . The following compounds have also been prepared: *p*-tolylcarbamine cyanide, m. p. 142° ; *p*-tolylbiuret, m. p. 199 – 200° (decomp.); *p*-phenethylcarbamine cyanide, m. p. 131° ; *o*-anisylcarbamine cyanide, decomp. 115° ; phenylethylcarbamine cyanide, $\text{NPhEt}\cdot\text{CO}\cdot\text{NH}\cdot\text{CN}$, large, colourless leaflets, m. p. 142° . H. W.

Dicyanamide. W. MADELUNG and E. KERN (*Annalen*, 1922, 427, 1–34).—The analogies suggested by cyanoforn and thio-cyanic acid indicate that dicyanamide should be a strong acid and although, possibly, rather unstable in the free state, quite stable in the form of its salts: $\text{HC}(\text{CN})_3$, $\text{NH}(\text{CN})_2$, $\text{HS}(\text{CN})$. The paper is devoted to a description of the preparation and properties of dicyanamide.

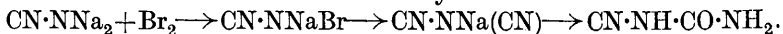
Sodium dicyanamide, $\text{NNa}(\text{CN})_2$, is obtained in good yield by treating an aqueous solution of disodium cyanamide ($\text{CN}\cdot\text{NNa}_2$) with cyanogen bromide. It is easily soluble in water, but less easily soluble in alcohol, from which it can conveniently be crystallised. Its aqueous solution is neutral to litmus. The decomposition may also be carried out by adding first cyanamide and then cyanogen bromide to an ethyl alcoholic solution of sodium ethoxide, but in these circumstances the *sodium* salt of *O*-ethylcyanoisocarbamide (below) is formed as a by-product, probably in the following way :



Free *dicyanamide* cannot be isolated owing to the speed with which it is converted into an insoluble amorphous polymericide of high molecular weight. However, it exists in solution long enough for it to be possible to show by conductivity measurements that it is a strong acid, nearly as strong as hydrochloric acid.

The *silver*, *cuprous*, and *mercurous* salts are colourless, the *lead*, *mercuric*, and *cupric* salts are sparingly soluble, and the *ferric* salt is soluble and red, but not so intensely coloured as ferric thiocyanate. The *ammonium* salt forms needles which melt at 116° without decomposition. The silver salt does not react with methylene iodide, but with methyl iodide it gives *dicyanomethylamide*, quadratic crystals, m. p. 221° .

Dicyanamide undergoes additive reactions with water, ammonia, and ethyl alcohol. With water in the presence of hydrochloric acid, it gives biuret, two molecules of water being taken up. The addition of one molecule of water was effected accidentally during an attempt to prepare dicyanamide from disodium cyanamide by reaction with bromine and sodium cyanide :



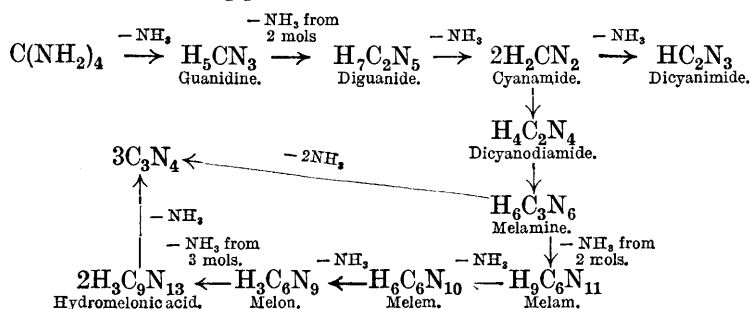
The product was cyanocarbamide. Addition of one molecule of ammonia is effected by heating the copper salt with concentrated aqueous ammonia. The product is a mixture of copper diguanide and cyanoguanidine, $\text{CN}\cdot\text{NH}\cdot\text{C}(\text{NH})\cdot\text{NH}_2$. The compound formed by the addition of one molecule of ethyl alcohol, *O*-ethylcyanoisocarbamide, needles or prisms, m. p. 119° , is obtained either from cyanamide and cyanogen bromide as described above, or by heating sodium dicyanamide with an equivalent amount of ethyl alcoholic hydrogen chloride. If an excess of hydrogen chloride is used *O*-ethylisobiuret, m. p. 129° , is also obtained : $\text{NH}\cdot\text{C}(\text{NH})\cdot\text{OEt}$. The hydrochloride of this base readily loses ethyl chloride, giving biuret.

When sodium dicyanamide is heated to dull redness it is converted into the sodium salt of tricyanomelamine, the probable formula of which is annexed. The same compound may be obtained by heating the sodium salt of cyanoguanidine, ammonia being eliminated. Bannow obtained the potassium salt (this Journal, 1871, 391, A., 1881, 144), which he thought to be potassium dicyanamide, by heating mercuric cyanide or paracyanogen with potassium cyanide.



Tricyanomelamine cannot be isolated in the free state as it passes into amorphous products of high molecular weight. It is a weak acid, as is shown by conductivity measurements, and forms salts with metals. The *trisodium* salt crystallises with $3\text{H}_2\text{O}$, which is lost on heating in a vacuum over phosphorus pentoxide. The *monosodium* salt also crystallises with $3\text{H}_2\text{O}$ and is distinctly acid to litmus. The *ammonium* salt, $\text{C}_6\text{H}_2\text{N}_9\cdot\text{NH}_4$, the *silver* salt, $\text{C}_6\text{N}_9\text{Ag}_3$, the *copper* salt, $(\text{C}_6\text{H}_2\text{N}_9)_2\text{Cu}$, and the *lead* and *mercuric* salts are also described. *Tricyanotrimethylmelamine*, m. p. 268° , is obtained by methylation of the silver salt with methyl iodide. C. K. I.

Ammono-carbonic Acids. EDWARD C. FRANKLIN (*J. Amer. Chem. Soc.*, 1922, **44**, 486—509).—The compounds guanidine, diguanide, cyanamide, dicyanimide, dicyanodiamide, melamine, melam, melem, melon, and hydromelonic acid constitute a series of compounds which may be regarded as ammono-carbonic acids, formed by the elimination of successive molecules of ammonia from one or more molecules of the hypothetical compound orthoammono-carbonic acid, $\text{C}(\text{NH}_2)_4$. The scheme of derivation is as follows:



It is pointed out that not only formally may these substances be looked on as constituting a series of products resulting from the successive de-ammonation of $\text{C}(\text{NH}_2)_4$, but that also by processes of de-ammonation it is possible to pass from guanidine to melon and inversely by processes of ammonation return to the first member of the group. In face of the facts that guanidine and melamine are alkaline and dicyanodiamide is neutral in aqueous solution, it has been shown that these substances behave as acids when in solution in liquid ammonia. Guanidine, for example, has been found to react with potassamide, the analogue of potassium hydroxide of the ammonia system, in accordance with the equation $\text{H}_5\text{CN}_3 + 2\text{KNH}_2 = \text{K}_2\text{H}_3\text{CN}_3 + 2\text{NH}_3$, to form a dipotassium salt. It has been shown that the reaction whereby atmospheric nitrogen is fixed in the cyanamide process is to be looked on as the nitridation of calcium carbide to a calcium ammono-carbonate and that the production of ammonia by the action of steam on calcium cyanamide consists in the hydrolysis of calcium ammono-carbonate to calcium aquo-carbonate. *Dicyanimide*, $(\text{CN})_2\text{NH}$, a hitherto unknown member of this series, is obtained in an impure condition by decomposing the silver salt with hydrogen sulphide in water.

The sodium salt, NaC_2N_3 and $\text{NaC}_2\text{N}_3 \cdot \text{H}_2\text{O}$, is prepared by the action of fused sodamide on melon, and by heating a mixture of sodium cyanide and mercuric cyanide. The silver, magnesium, barium, cupric, and nickel salts are prepared by double decomposition of the sodium salt with a soluble salt of the metals named. A number of attempts to prepare the final de-ammonation product of this series, carbonic nitride, have only yielded very impure specimens of this compound.

J. F. S.

Crystal Structure of Potassium Cyanide. RICHARD M. BOZWORTH (*J. Amer. Chem. Soc.*, 1922, **44**, 317—323).—The crystal structure of potassium cyanide has been investigated with X-rays, making use of the Laue photographic method, the spectrometric method, and the powder method. The X-ray data show conclusively that the structure of this substance approximates closely to the sodium chloride structure. Consequently the potassium atoms were placed in the positions of the sodium atoms and the carbon and nitrogen atoms near the positions of the chlorine atoms. The positions of the carbon and nitrogen atoms which give the best agreement with the data place these atoms 1.15×10^{-8} cm. apart, equidistant from the position of the chlorine atom. The distance between the potassium and carbon atoms and the potassium and nitrogen atoms is the same, namely, 3.0×10^{-8} cm.

J. F. S.

Decomposition of Potassium Ferricyanide by the Action of Heat. V. CUTTICA (*Gazzetta*, 1922, **52**, i, 20—25).—Protracted heating of potassium ferricyanide at 230° results in complete decomposition of the salt according to the equation $2\text{K}_3\text{Fe}(\text{CN})_6 = 2\text{FeC}_2 + 2\text{N}_2 + \text{C}_2\text{N}_2 + 6\text{KCN}$. The intermediate green substance formed during the heating (cf. Locke and Edwards, A., 1899, i, 407, 557; Cuttica and Canneri, A., 1921, i, 322) exhibits the oxidising properties of the original salt, but differs from it in certain of its reactions, and contains complex iron cyanides with less than six cyanogen groups in the molecule.

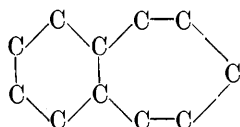
T. H. P.

Transformations during the Fission of Racemic Substances. RUDOLF WEGSCHEIDER (*Ber.*, 1922, **55**, [B], 764—766).—Pope and Peachey (P., 1900, **16**, 42, 116) have shown that in the fission of the methylethyl-*n*-propylstannic base as *d*-camphor-sulphonate the salt of the *d*-base only separates so that ultimately the *l*-form is converted completely into the *d*-variety. The phenomenon has been explained by the supposition of the racemisation of the excess of *l*-salt remaining in the solution. This and similar observations are now considered from a somewhat more general theoretical point of view, and the conditions are deduced on which the transformation depends when it is due (1) to the compounds of the optical antipodes with the active reagent, and (2) to the free optical antipodes formed by dissociation. The original must be consulted for details.

H. W.

Two cycloHeptane Models Free from Strain. ERNST MOHR (*J. pr. Chem.*, 1921, [ii], **103**, 316—328).—The geometry is worked

out of two three-dimensional *cycloheptane* models which are absolutely free from strain, that is to say, two figures each with seven equal rectilinear sides are constructed so that the angle between any two sides meeting in a corner is $\alpha = \tan^{-1}\sqrt{2} =$



$109^{\circ} 28' 16''$. It is likewise possible to construct models which are free from strain for the formula annexed. These results are of interest as the heat of combustion of *cycloheptane* shows that the strains in it are practically the same as in *cyclopentane* or *cyclohexane*.

W. O. K.

Dimethylcyclohexanes. G. CHAVANNE and P. BECKER (*Bull. Soc. chim. Belg.*, 1922, **31**, 95—98).—Reduction of xylenes in presence of platinum and of nickel as catalysts yields products of differing physical constants. The authors state that the substances obtained from *m*-xylene and from *p*-xylene in presence of platinum are mixtures, and that it is doubtful whether the *o*-xylene derivative is a pure substance. *o*-Xylene, in presence of nickel is transformed into a substance which is clearly distinct from that produced when platinum is used. In the case of *m*-xylene and *p*-xylene, the nature of the catalyst used affects the physical constants of the mixture obtained. The explanation put forward by the authors is based on the formation of *cis*- and *trans*-forms of stereoisomerides (cf. Skita, A., 1921, i, 503).

H. J. E.

The Preparation of Phenylacetylene. JOHN C. HESSLER (*J. Amer. Chem. Soc.*, 1922, **44**, 425—426).—By using molten potassium hydroxide in place of alcoholic potassium hydroxide in Nef's method (A., 1900, i, 20), the yield of phenylacetylene from ω -bromostyrene is increased from 60% to 80%. The ω -bromostyrene is dropped on to the molten potassium hydroxide heated at 200—215°.

W. G.

The Monochlorotoluenes. A. WAHL, G. NORMAND, and G. VERMEYLEN (*Compt. rend.*, 1922, **174**, 946—949).—The authors have constructed the melting-point curve for mixtures of *o*- and *p*-chlorotoluenes and use this method for the determination of the relative amounts of these two isomerides formed in the chlorination of toluene under different conditions. They find that, whilst in the absence of a catalyst benzyl chloride is almost the sole product of the action of chlorine on toluene at 100°, in the presence of lead chloride the product is a mixture of the two isomeric chlorotoluenes containing about 62% of the ortho-isomeride.

W. G.

The Wurtz-Fittig Synthesis. WALTER FUCHS and HEINRICH METZL (*Ber.*, 1922, **55**, [B], 738—747).—The behaviour of 1 : 3 : 5- and 1 : 2 : 4-tribromobenzenes and of 3 : 5-dibromotoluene towards alkali metals in ethereal solution has been investigated. The two substances first named are not attacked by metallic sodium under these conditions, but react slowly with potassium or an alloy of sodium and potassium. 1 : 3 : 5-Tribromobenzene gives a mixture of substances, some of which are soluble in alkali hydroxide solution

with the formation of salts. The portion which remains undissolved is amorphous and insoluble in all media, so that its uniformity cannot be guaranteed; analysis shows the presence of oxygen in it in addition to carbon, hydrogen, and bromine, and this surprising result is confirmed by the observation that resorcinol can be obtained from it by treatment with hydriodic acid. The substances which are soluble in alkali hydroxide are precipitated in the amorphous form by the addition of acid and can be separated by sodium hydrogen carbonate into phenols and carboxylic acids. The behaviour of 1 : 2 : 4-tribromobenzene resembles that of the symmetrical isomeride, but the yields are greater; halogenated and traces of halogen-free hydrocarbons are obtained in addition to oxygen compounds.

3 : 5-Dibromotoluene reacts with sodium, giving 3 : 3'-ditolyl; the main product of the change is composed of amorphous, yellow substances to which, according to the results of analysis, the formulæ, $C_{28}H_{24}Br_2$, $C_{35}H_{30}Br_2$, $C_{42}H_{36}Br_2$, $C_{56}H_{48}Br_2$ are assigned and are regarded as formed by the linear union of 4, 5, 6, or 8 toluene nuclei in such a manner that the terminal groups each contain a bromine atom, thus, $Br \cdot C_6H_3Me \cdot C_6H_3Me \cdot C_6H_3Me \cdot Br$. The formation of 3 : 3'-ditolyl is not to be explained by the reduction of the bromo-compound by hydrogen formed from adventitious moisture, since this is impossible under the experimental conditions, and, further, it is found that the yield of ditolyl is very noticeably increased when the duration of the experiment is curtailed. The most probable hypothesis is that metallic substitution products of the hydrocarbons are formed initially which contain the alkali metal in place of the bromine, for example, $Na \cdot C_6H_3Me \cdot C_6H_3Me \cdot Na$. These reactive compounds can either behave in the normal manner or combine with the atmospheric oxygen to give alkali phenoxides (as with the tribromobenzenes); alternatively, as in the case of 3 : 5-dibromotoluene, they may undergo only partial intermediate decomposition and then give the corresponding hydrogen compounds after being treated with water. The formation of carboxylic acids is difficult to explain; it does not appear to be due to access of atmospheric carbon dioxide, since the relative quantities of acid and phenol remain unchanged when the gas is excluded carefully. It is possible, however, that their formation is a secondary process, since they are identified as phenol-carboxylic acids by the Schotten-Baumann reaction in alkaline solutions, which are obtained only after tedious filtrations and have thus possibly become oxidised.

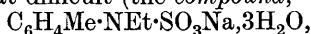
H. W.

The Influence of Nitro-groups on the Reactivity of Substituents in the Benzene Nucleus. VI. The Elimination of Halogen during the Reduction of Halogenated Nitro-compounds. HAROLD BURTON and JAMES KENNER (T., 1922, 121, 675—682).

The Action of Sodium Hydrogen Sulphite on Nitro-compounds of the Benzene Series. HUGO WEIL and E. MOSER (Ber., 1922, 55, [B], 732—737; cf. D.R.-P. 151134).—In a large

number of cases, possibly invariably, sulphamic acids are the primary products of the reduction of benzenoid nitro-compounds with sodium hydrogen sulphite. As by-products, sulphonic acids can be obtained, which, however, are not present as such in the primary mixtures, but are formed, probably from sulphasulphamic acids which are freely soluble in water, when the latter are boiled with mineral acids. Three molecules of sodium hydrogen sulphite are theoretically required for the reduction of a nitro-group, and this is found to be in practice sufficient for the purpose. Under these conditions, however, sodium hydrogen sulphate or a mixture of sulphuric acid and sodium sulphate is produced which causes the hydrolysis of the sulphamic acid; this can be avoided by the use of two additional molecular proportions of sodium hydrogen sulphite or one of normal sodium sulphite.

The following salts are prepared by boiling a mixture of the nitro-compound and an aqueous solution of sodium hydrogen sulphite under a reflux condenser: *sodium phenylsulphamate*, $\text{NHPh}\cdot\text{SO}_3\text{Na}\cdot 2\text{H}_2\text{O}$; *sodium p-tolylsulphamate*; *sodium o-chlorophenylsulphamate*, colourless needles ($+\text{H}_2\text{O}$); *sodium p-chlorophenylsulphamate*, colourless needles; *sodium p-phenetylsulphamate*, flattened prisms; *sodium o-anisylsulphamate* ($+1.5\text{H}_2\text{O}$); *sodium p-sulphaminobenzoate*, needles. The substances are very sensitive to acids, but remarkably resistant towards boiling solutions of alkali hydroxides. They are readily methylated by means of methyl sulphate (the substance, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NMe}\cdot\text{SO}_3\text{Na}\cdot 1.5\text{H}_2\text{O}$, is described); on the other hand, complete ethylation with ethyl sulphate is somewhat difficult (the compound,



has been prepared).

H. W.

The Diphensuccindene Series. IV. 9:12-Dichloro- $\Delta^{9,11}$ -diphensuccindadiene and Diphensuccind-10-ene. K. BRAND and KARL OTTO MÜLLER (*Ber.*, 1922, 55, [B], 601—608; cf. A., 1912, i, 960; 1920, i, 486, 487).—The colour of solutions of diphensuccindandione in sodium hydroxide has been attributed to the presence of the sodium salt of 9:12-dihydroxy- $\Delta^{9,11}$ -diphensuccindadiene,

$\text{OH}\cdot\text{C}=\text{C}\cdot\text{C}(\text{OH})\cdot\text{C}(\text{OH})\cdot\text{C}_6\text{H}_4$; if this is the case, the parent hydrocarbon should also be coloured as a consequence of the presence of the two conjugated double bonds and of the condensed atomic grouping. Attempts to obtain the hydrocarbon are now described.

9:9:12:12-Tetrachlorodiphensuccindane, $\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CCl}_2$, $\text{CCl}_2\cdot\text{CH}\cdot\text{C}_6\text{H}_4$, unstable, colourless needles, m. p. 135° (decomp.), is obtained by the action of phosphorus pentachloride on diphensuccindan-9:12-dione, and is rapidly converted by a solution of sodium acetate in alcohol into 9:12-dichloro- $\Delta^{9,11}$ -diphensuccindadiene, $\text{C}_6\text{H}_4\cdot\text{C}(\text{Cl})\cdot\text{C}(\text{Cl})\cdot\text{C}_6\text{H}_4$, long, slender, reddish-brown needles, m. p. 191° , which is obtained more conveniently by preserving a solution of the tetrachloro-compound in benzene at the atmospheric temperature. A boiling solution of

the dichloro-substance in alcohol is reduced by zinc dust in the presence of a little mercuric chloride solution to Δ^{10} -diphensuccindene, $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CH}_2$, very pale yellow leaflets, m. p. 210° , which is transformed by hydrogen in the presence of palladised charcoal into diphensuccindane, $\text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH}_2$, m. p. 102° (cf. Roser, A., 1888, 1301). Δ^{10} -Diphensuccindene is converted by benzaldehyde in the presence of alcoholic sodium ethoxide solution into a mixture of a substance, brownish-red needles or leaflets, m. p. 155° , and 9 : 12-dibenzylidene- Δ^{10} -diphensuccindene, $\text{C}_6\text{H}_4 \cdot \text{C} \cdot \text{CHPh}$, $\text{CHPh} \cdot \text{C} \cdot \text{C}_6\text{H}_4$, small, cinnabar-red leaflets, m. p. 244° . The latter is reduced by hydrogen in the presence of palladised charcoal to 9 : 12-dibenzylidiphensuccindane, $\text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2\text{Ph}$, colourless crystals, m. p. 141° , and by zinc dust and boiling glacial acetic acid to 9 : 12-dibenzylidenediphensuccindane, $\text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{C} \cdot \text{CHPh}$, $\text{CHPh} \cdot \text{C} \cdot \text{CH} \cdot \text{C}_6\text{H}_4$, slender, colourless needles, m. p. 255° .
H. W.

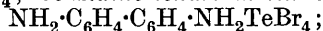
Constitution of Carbonium Dyes. HANS EDUARD FIERZ (*Ber.*, 1922, 55, [B], 429).—A reply to Hantzsch (this vol., i, 24).
H. W.

Catalytic Preparation of Aniline. O. W. BROWN and C. O. HENKE (*J. Physical Chem.*, 1922, 26, 161—191).—The conditions under which aniline may be prepared by the reduction of nitrobenzene with hydrogen in the presence of nickel or copper as catalyst have been investigated. In the preparation of the nickel catalyst it is shown that the best temperature for the ignition of the nitrate is 450° . The oxide thus prepared is reduced to metal in the reaction furnace at about 380° by hydrogen. It is shown that merely heating the reduced nickel in hydrogen is sufficient to decrease its catalytic activity, but if it is heated to temperatures below 380° it is too active and carries the reduction too far. After heating the reduced nickel catalyst in hydrogen to a high temperature, it did not lose its activity immediately, but lost it with use, the activity decreasing almost linearly. The best temperature for the reduction of nitrobenzene to aniline with nickel as the catalyst is about 192° . The rate of flow of the hydrogen and nitrobenzene vapour through the reaction tube is of more importance than the percentage excess of hydrogen present. The best temperature for the ignition of copper nitrate for the preparation of the copper catalyst is 415° ; at lower temperatures the copper loses its activity with use and does not give as high yields as when ignited at about 415° . Heating the copper catalyst in hydrogen reduces its activity but little until the temperature exceeds 475° . Its activity is 60% lower when heated at 535° than when heated at 475° . A new copper catalyst, or one that has been oxidised

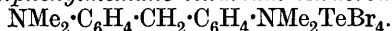
and again reduced, gains in activity with use for four to six experiments before it gives constant results. Long reduction in hydrogen increases the length of time required for it to attain its maximum activity. The best temperature for carrying out the reduction of nitrobenzene with copper as catalyst is 260° . The activity of the copper catalyst decreases when used at too high a temperature (377°). The decrease is more rapid with a more rapid rate of flow of nitrobenzene. It is further shown that with a constant rate of flow of hydrogen the lower the rate of flow of nitrobenzene the greater the yield of aniline, and with a constant rate of flow of nitrobenzene an increase in the rate of flow of the hydrogen first increases the yield of aniline and then decreases it, the increase and decrease being much more marked with copper than with nickel. The time of contact of the gaseous mixture with the catalyst is of more importance than the percentage excess of hydrogen present. It has been found that an ordinary wrought-iron pipe has considerable catalytic activity on this reaction. The activity decreases with use, and is greater when the tube has been cleaned with nitric acid before use. The activity of nickel and copper catalysts for the reduction of nitrobenzene to aniline is restored by oxidation and reduction, although not to so great an extent with copper as with nickel. As examples of the efficiency of the process, the following are quoted. (1) Nickel catalyst at 192° , 3.9 grams of nitrobenzene per hour with a 710% excess of hydrogen gives a 95.2% yield. (2) Copper catalyst at 253° , with the same quantities of hydrogen and nitrobenzene, gives a 96.2% yield of aniline.

J. F. S.

Compounds of Tellurium Tetrabromide with Organic Bases. ALEXANDER LOWY and RAYMOND F. DUNBROOK (*J. Amer. Chem. Soc.*, 1922, **44**, 614—617).—When primary, secondary, or tertiary amines or substituted amines are added to a solution of pure tellurium tetrabromide in absolute ether or glacial acetic acid, yellow or orange-coloured additive products are obtained, the following of which are described. *Dianiline tellurium tetrabromide*, $(\text{C}_6\text{H}_5\cdot\text{NH}_2)_2\text{TeBr}_4$; *di-p-bromoaniline tellurium tetrabromide*, $(\text{BrC}_6\text{H}_4\cdot\text{NH}_2)_2\text{TeBr}_4$; *di-diphenylamine tellurium tetrabromide*, $(\text{NHPh}_2)_2\text{TeBr}_4$; *di-dimethylaniline tellurium tetrabromide*, $(\text{NPhMe}_2)_2\text{TeBr}_4$; *di-β-naphthylamine tellurium tetrabromide*, $(\text{C}_{10}\text{H}_7\cdot\text{NH}_2)_2\text{TeBr}_4$; *p-phenylenediamine tellurium tetrabromide*, $\text{C}_6\text{H}_4(\text{NH}_2)_2\text{TeBr}_4$; *m-tolylenediamine tellurium tetrabromide*, $\text{C}_6\text{H}_3\text{Me}(\text{NH}_2)_2\text{TeBr}_4$; *benzidine tellurium tetrabromide*,



tetramethyldiaminodiphenylmethane tellurium tetrabromide,



They are all stable in air and decompose when heated at above 100° . When di-aniline tellurium tetrabromide is dissolved in dilute hydrobromic acid and recrystallised twice from the same solvent it gives a new compound, consisting of four molecules of aniline hydrobromide and one molecule of tellurium tetrabromide. The other bases form analogous products. Alkaloids such as

brucine or quinine also give yellow, amorphous precipitates with tellurium tetrabromide.

Selenium and tellurium dyes could not be obtained by substituting selenium or tellurium for sulphur in the usual method for preparing sulphur dyes. W. G.

Electrochemical Oxidation of Dimethylaniline. FR. FICHTER and EMIL ROTHENBERGER (*Helv. Chim. Acta*, 1922, **5**, 166—181).—Chromic acid is unnecessary for the electrochemical oxidation of dimethylaniline to tetramethylbenzidine (cf. Löb, *Z. Elektrochem.*, 1901, **7**, 608). The same result is obtained with anodes of lead dioxide, using a current density of 0.007—0.009 amp./cm.² and a solution of the base in $1\frac{1}{2}$ equivalents of 2*N*-sulphuric acid. The yield is not good, since for the best results 2—3 farads per mol. base must be used instead of 1 theoretically necessary, and carbon dioxide, nitrogen, and some carbon monoxide are evolved. Also, owing to production of formaldehyde and its condensation with unoxidised base, tetramethyldiaminodiphenylmethane is obtained. The benzidine formation is not due to a specific action of lead peroxide, since it also occurs when platinum electrodes are employed. In this case, by precipitation of the benzidine from the acid solution with barium hydroxide, an aqueous solution of a subsidiary basic product is obtained, which rapidly turns blue on exposure to air, and therefore must be concentrated in a stream of carbon dioxide under reduced pressure. The residue on distillation decomposes, sometimes explosively, into tarry products and *phenyltrimethylphenylene diamine*, $\text{Me}_2\text{N} \langle \text{C}_6\text{H}_4 \rangle \text{NMePh}$, needles or plates, m. p.

57°. Its alcoholic or dilute mineral acid solution is easily turned blue by ferric chloride, bromine, or even atmospheric oxygen, and the base is further characterised by its *perchlorate*, $\text{C}_{15}\text{H}_{18}\text{N}_2\cdot\text{HClO}_4$, blue leaflets, m. p. 186—187°; *methiodide*, $\text{C}_{15}\text{H}_{18}\text{N}_2\cdot\text{MeI}$, silky leaflets, m. p. 202°, which do not give a blue colour with ferric chloride; and a *nitroso*-derivative, green needles, m. p. 147—149°. Attempts to synthesise this base by methylation of phenyldimethyl-*p*-phenylenediamine gave indefinite results. A small amount of this base is also formed when lead peroxide anodes are used, whilst, conversely, traces of tetramethyldiaminodiphenylmethane are formed when platinum anodes are employed. The latter are known to favour the formation of peroxides, and in the present case a small amount of the picrate of dimethylaniline oxide was obtained on treating the electrolysed solution with picric acid, after neutralisation and removal of dimethylaniline and tetramethylbenzidine. An amorphous picrate, m. p. 56—60°, obtained in much larger quantity at the same time, probably corresponds with the product which furnishes phenyltrimethyl-*p*-phenylene-diamine, and is probably the oxide of *p*-dimethylaminophenol. The decomposition of this compound on distillation is probably represented by the equation $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2\text{O} + \text{NMe}_2\text{Ph} = \text{CH}_2\text{O} + \text{H}_2\text{O} + \text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{NMePh}$. In support of this, it is pointed out that formaldehyde and monomethylaniline are also among the

products of electrolysis. It is improbable that dimethylaniline oxide is the primary oxidation product in these reactions, since this view offers no explanation of the different results following the use of platinum and lead peroxide electrodes. When the latter are used for the oxidation of diethylaniline, tetraethylbenzidine is almost the sole product. J. K.

Preparation of *o*-Sulphonic Acids of Aromatic Amines.

BRITISH DYESTUFFS CORPORATION, LTD., JAMES BADDILEY, JOSEPH BARON PAYMAN, and HARRY WIGNALL (Brit. Pat. 175019).—Primary aromatic amines are treated with chlorosulphonic acid in presence of a suitable solvent, preferably tetrachloroethane, and the sulphonation is completed by heating. In certain cases, a chlorosulphonate separates as an intermediate product, and can, if desired, be collected by filtration and further treated in the absence of the solvent, when it is converted, with evolution of hydrogen chloride, into the sulphonic acid. G. F. M.

The Action of Sulphuryl Chloride on Aromatic Amines.

W. ELLER and L. KLEMM (*Ber.*, 1922, 55, 217—224).—By the action of sulphuryl chloride on aniline in ethereal solution in the cold, a mixture of about equal parts of 2:4:6-trichloroaniline, 2:4-dichloroaniline, and *p*-chloroaniline is obtained, the last two as hydrochlorides. The hydrochlorides are not further acted on in the cold, but at a higher temperature, for example, in boiling benzene, they are completely chlorinated to 2:4:6-trichloroaniline. Anthranilic acid in ether is chlorinated by sulphuryl chloride to a mixture of 3:5-dichloro-2-aminobenzoic acid and a monochloroanthranilic acid of m. p. 204°. This was identified as 5-chloro-2-aminobenzoic acid and corresponds with the *m*-chloro-2-aminobenzoic acid of the literature. The isomeride of m. p. 148° described in the literature as the 5-chloro-compound is actually 3-chloro-2-aminobenzoic acid. In benzene solution at 65—70°, anthranilic acid gives an 80—85% yield of 3:5-dichloro-2-aminobenzoic acid. *p*-Aminophenol reacts with sulphuryl chloride at 70° to give, besides a little chloranil, 2:3:5:6-tetrachloro-4-dichloro-amino-1-hydroxybenzene, white crystals, m. p. 71.5°, readily soluble in all organic solvents, insoluble in water and dilute hydrochloric acid, slightly soluble with a violet colour in sodium hydroxide solution, by which it is slowly decomposed. E. H. R.

Condensation Products of Phenylhydroxylamine with Hydroxymethylene Compounds and Carbinols. II. Hydroxymethylenedeoxybenzoin and Phenylhydroxylamine. H. RUPE and R. WITWER (*Helv. Chim. Acta*, 1922, 5, 205—216; cf. A., 1921, i, 425).—Interaction of hydroxymethylenedeoxybenzoin and β -phenylhydroxylamine in presence of glacial acetic acid yields *acetyl trans- β -phenyl- β -(α -benzoyl)-phenylvinylhydroxylamine*, CPhBz:CH·NPh·OAc, needles, m. p. 157—158°, from which *trans- β -phenyl- β -(α -benzoyl)-phenylvinylhydroxylamine*, CPhBz:CH·NPh·OH, needles, m. p. 166°, is obtained by careful acid hydrolysis. If sodium hydroxide be employed, *β -phenyl-*

β -phenylvinylhydroxylamine, $C_6H_5 \cdot CH : NPhOH$, plates, m. p. 119—120°, is obtained; its synthesis from phenylhydroxylamine and ethyl hydroxymethylenepherylacetate is to be described later; its unstable dibromide easily passes into β -phenyl-bromo- β -phenylvinylhydroxylamine, $C_{14}H_{12}ONBr$, needles, m. p. 180°. *cis*- β -Phenyl- β -(α -benzoyl)-phenylvinylhydroxylamine, $C_{21}H_{17}O_2N$, needles, m. p. 158° (methyl ether, $C_{22}H_{19}O_2N$, needles, m. p. 134—135°), results if the above condensation is carried out in alcoholic solution. It is converted into its *trans*-isomeride by dilute alcoholic sulphuric acid, whilst on treatment with sodium hydroxide it furnishes benzoic acid and β -phenyl- β -1 : 3 : 4-(or -1 : 3 : 5)-triphenyl- Δ^2 -5-(or -4)-pyrrolinylhydroxylamine, $C_{28}H_{24}ON_2$, m. p. 180° (picrate, $C_{28}H_{24}ON_2 \cdot C_6H_2(NO_2)_3 \cdot OH$, m. p. 215—216°), of which the orientation is one of the two alternatives indicated. This compound, which also results from the fusion of hydroxymethylenedeoxybenzoin with β -phenylhydroxylamine, is converted by thionyl chloride into the *chloro*-derivative, $C_{28}H_{23}N_2Cl$, m. p. 216°, which is also formed when the same reagent acts on the above *cis*-derivative. None of the products now described are soluble in alkali hydroxides or possess reducing properties. *N*- α -Benzoylstyryl-*p*-aminophenol, $C_6H_5 \cdot CBz : CH \cdot NH \cdot C_6H_4 \cdot OH$, lemon-yellow needles, m. p. 199—200°, is obtained by condensation of hydroxymethylenedeoxybenzoin with *p*-aminophenol in presence of acetic acid. J. K.

Condensation Products of Phenylhydroxylamine with Hydroxymethylene Compounds and Carbinols. III. Diphenylbromomethane and Phenylhydroxylamine. H. RUPE and R. WITTEW (Helv. Chim. Acta, 1922, 5, 217—220; cf. preceding abstract).—Diphenylcarbinol, in contrast with Michler's hydrol (A., 1921, i, 425), is unaffected by β -phenylhydroxylamine, but the reaction of the latter with diphenylbromomethane is so vigorous that decomposition ensues unless it be carried out in presence of crystallised sodium acetate. In this way, β -phenyl- β -diphenylmethylhydroxylamine (Angeli, Alessandri, and Aiazzi-Mancini, A., 1911, i, 544) is readily obtained. Its oxidation to diphenylnitron (Angeli, *loc. cit.*) is conveniently carried out in methyl alcoholic solution by means of cupric acetate. Its unimolecular formula (cf. Staudinger and Miescher, A., 1919, i, 584) is confirmed by freezing-point measurements. J. K.

Introduction of the Chloroethyl Group into Phenols, Alcohols, and Amino-compounds. GEORGE ROGER CLEMO and WILLIAM HENRY PERKIN, jun. (T., 1922, 121, 642—649).

β -Naphthol. CLARENCE E. MAY (J. Amer. Chem. Soc., 1922, 44, 650—651).—In the conversion of calcium naphthalenesulphonate into the sodium salt, it is essential to use pure anhydrous sodium carbonate, free from the hydrogen carbonate. In the conversion of the sulphonate into the naphthol, the fusion must be carried out under conditions such that no oxidation can take place. For this reason iron crucibles should be avoided and commercial hydrochloric acid should not be used in the recovery of the product of the fusion. W. G.

Influence of Substituents on Reactions. VII. The Preferential Points of Substitution in the Naphthols and in α -Naphthylamine. HARTWIG FRANZEN and GUSTAV STÄUBLE (*J. pr. Chem.*, 1921, [ii], **103**, 352—390; cf. A., 1920, i, 730).—It has been previously shown (*loc. cit.*) that on brominating β -naphthylamine, 1-bromo-, 1 : 6-dibromo-, and 1 : 6 : 3-tribromo- β -naphthylamine are successively formed. In the case of β -naphthol, the corresponding series of bromine derivatives is obtained, only here a tetrabromo- β -naphthol can also be prepared, in which the 4-position is occupied, as well as positions 1, 6, and 3. On reduction of these brominated β -naphthols with tin, or stannous chloride and hydrochloric acid, only the bromine in the position 1 is replaced by hydrogen, whilst with sodium amalgam in alkaline solution, bromine in the 3- and 4-positions is removed, that in the 6-position resisting reduction. This stability must be due to the hydroxyl group in the β -position, as both α - and β -bromonaphthalenes are reduced to naphthalene by sodium amalgam in alkaline solution.

In the cases of α -naphthol and α -naphthylamine, the hydrogen atoms in the 2- and the 4-positions appear to be equally readily replaced by bromine, forming 2 : 4-dibromo-compounds, and these, on reduction with tin, or stannous chloride, and hydrochloric acid appear to lose both atoms of bromine with equal ease. 5-Bromo- α -naphthylamine is unchanged by tin and hydrochloric acid, showing that, in this respect, the effect of the α -amino-group on the 5-position is much less than on the 2- and 4-positions.

In general, the corresponding chlorine compounds are reduced with much greater difficulty, if at all. 1-Chloro- β -naphthol, 2-chloro- α -naphthol, and 2 : 4-dichloro- α -naphthol require the action of hydrogen iodide to eliminate the chlorine atoms, whilst even this reagent leaves 3-chloro- α -naphthol unchanged. This new compound, thin needles, m. p. 134—135°, is obtained by the reduction of 2 : 3 : 4-trichloro- α -naphthol by hydrogen iodide. If instead it is reduced by tin and hydrochloric acid, a substance which is apparently a mixture of mono- and di-chloro- α -naphthol is obtained. α - and β -Chloronaphthalenes are not changed by the action of sodium amalgam.

Alcoholic potash is without action in 1 : 6-dibromo- β -naphthol, whilst it removes bromine from 2 : 4-dibromo- α -naphthol, although no definite product has been isolated.

The following new compounds are described in the paper. 1-Bromo-2-methoxynaphthalene, colourless plates with a nacreous lustre, m. p. 85°; 1 : 6-dibromo-2-methoxynaphthalene, lustrous, colourless leaflets, m. p. 102°; 6-bromo-2-methoxynaphthalene, small, colourless needles, m. p. 108°; 3 : 6-dibromo-2-methoxynaphthalene, fine, colourless needles, m. p. 103°; 3 : 6-dibromo-2-acetoxynaphthalene, brown, compact crystals, m. p. 128°; 3 : 6-dibromo-2-benzoxynaphthalene, fine, colourless needles, m. p. 128—129°; 1-chloro-2-methoxynaphthalene, pale yellow prisms, m. p. 70—71°; 3 : 6-dibromo-1-nitro- β -naphthol, fine, yellow needles, m. p. 147° (decomp.), obtained by the action of sodium nitrite and acetic acid on 1 : 3 : 6-tribromo- β -naphthol (and also by nitrating 3 : 6-dibromo- β -naphthol, fine, colourless needles, m. p. 134—135°);

1 : 3 : 4 : 6-tetrabromo-2-methoxynaphthalene, fine, colourless, felted needles, m. p. 149°; 3 : 4 : 6-tribromo-β-naphthol, colourless needles, m. p. 127—128°; 6-bromo-β-naphthol, small, colourless needles, m. p. 128°.

2 : 6-Dichloronaphthalene, when pure, melts at 140—141°, not 135° as given in the literature. W. O. K.

Tautomerism of Phenols. V. 1 : 5- and 2 : 7-Dihydroxynaphthalenes. WALTER FUCHS and WALTER STIX (*Ber.*, 1922, 55, [B], 658—670; cf. A., 1921, i, 241).—The occurrence of tautomerism with the two dihydroxynaphthalenes has been demonstrated.

1 : 5-Dihydroxynaphthalene is heated on the water-bath for about thirty days with a freshly prepared, concentrated solution of sodium hydrogen sulphite which contains rather more than two equivalents of the latter, whereby the sodium salt, $C_{10}H_{10}O_8S_2Na_2$, is obtained as a yellow, crystalline powder. It readily loses one molecular proportion of sodium hydrogen sulphite when treated with alkali hydroxide or when boiled with water, giving sodium 5-hydroxy-1-ketotetrahydronaphthalene-3-sulphonate, $OH \cdot C_6H_3 < \begin{matrix} CO \cdot CH_2 \\ CH_2 \cdot CH \cdot SO_3Na \end{matrix}$,

from which sulphur dioxide is not removed by protracted treatment with boiling acids or alkalis, and only to a small extent by hot barium chloride and hydrogen peroxide. It is not affected by a solution of bromine in anhydrous chloroform. The constitution of the substance is deduced from the observation that it is convertible into a phenylhydrazone, $C_{16}H_{16}O_4N_2S$, colourless crystals, m. p. 203° (decomp.) (the alkali, barium, calcium, copper, and lead salts were examined), from which the original ketone can be regenerated by treatment with benzaldehyde; the methyl ether of the phenylhydrazone was also prepared. Further, it is converted by diazomethane into sodium 5-methoxy-1-ketotetrahydronaphthalene-3-sulphonate, $C_{11}H_{11}O_5SNa$, an almost colourless, crystalline substance. Oxidation of either methyl ether with permanganate appears to yield 3-methoxyphthalic acid. It thus appears to be established that the product of the action of sodium hydrogen sulphite on 1 : 5-dihydroxynaphthalene

must have the constitution $OH \cdot C_6H_3 < \begin{matrix} C(OH)(O \cdot SO_2Na) \cdot CH_2 \\ CH(SO_3Na) \end{matrix} \text{---} CH_2$ or

$OH \cdot C_6H_3 < \begin{matrix} C(OH)(O \cdot SO_2Na) \cdot CH_2 \\ CH_2 \end{matrix} \text{---} CH \cdot SO_3Na$. The latter conception is preferred, mainly because the substance does not exhibit any tendency to involve the hydroxyl group in position 5 in the formation of a sulphone.

Under analogous conditions, 2 : 7-dihydroxynaphthalene behaves in a very different manner towards sodium hydrogen sulphite solution, giving a crystalline product, $C_{10}H_9O_5SNa$, in only 20% yield. The new substance is somewhat unstable and is noticeably decomposed by solution in water. It appears to have the consti-

tution $OH \cdot C_6H_3 < \begin{matrix} CH_2 \cdot C(OH) \cdot O \cdot SO_2Na \\ CH=CH \end{matrix}$. This conception is sup-

ported by the observation that it readily decolorises the solution of a molecular proportion of bromine in dry chloroform without liberation of any considerable quantity of hydrogen bromide, but it was not possible to isolate a bromodihydroxynaphthalene from the product. The ketone-bisulphite likewise reacts with phenylhydrazine, but this reaction will be fully described subsequently. It is converted by dry, gaseous ammonia at 100° into the product,

$$\text{OH} \cdot \text{C}_6\text{H}_3 < \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{NH}_2) \cdot \text{O} \cdot \text{SO}_2\text{Na} \\ \text{CH} = \text{CH} \end{array}, \text{ which is decomposed by water}$$

with the formation of 7-amino- β -naphthol (acetyl derivative, m. p. 232°).

The mechanism of Bucherer's reaction is probably as follows. The naphthol, functioning in its tautomeric form, unites with the hydrogen sulphite to give a carbonyl-bisulphite compound; the hydroxyl group of this can be replaced by the amino-group, giving an intermediate product containing nitrogen and sulphur (see above), which is ultimately transformed into the amino-compound.

H. W.

Pyrogallol 1 : 3-Dimethyl Ether. I. K. BRAND and H. COLLISCHONN (*J. pr. Chem.*, 1921, [ii], **103**, 329—351).—On attempting to acetylate pyrogallol 1 : 3-dimethyl ether with acetic anhydride in presence of a few drops of concentrated sulphuric acid, 3-acetoxy-2 : 4-dimethoxyacetophenone, colourless leaflets, m. p. 110—111°, is obtained. This forms a *phenylhydrazone*, $\text{C}_{18}\text{H}_{20}\text{O}_4\text{N}_2$, yellow crystals, which are unstable in the air, m. p. 107—108°, and with hydroxylamine it loses an acetyl group to form 3-hydroxy-2 : 4-dimethoxyacetophenone oxime, colourless crystals, m. p. 112°. Similarly, with benzaldehyde and alkali 3-hydroxy-2 : 4-dimethoxyphenyl styryl ketone, m. p. 78°, is formed which with a solution of bromine in ether yields a *dibromide*, m. p. 147—150° (decomp.). The ketone, on methylation, gives 2 : 3 : 4-trimethoxyphenyl styryl ketone, yellow crystals, m. p. 71—72°, and this on oxidation yields 2 : 3 : 4-trimethoxybenzoic acid, m. p. 99°, which proves the position of the ketonic group. 3-Acetoxy-2 : 4-dimethoxyacetophenone on hydrolysis yields 3-hydroxy-2 : 4-dimethoxyacetophenone, colourless crystals, m. p. 79—80°, which forms a *phenylhydrazone*, m. p. 108—110°, and on methylation gives 2 : 3 : 4-trimethoxyacetophenone, m. p. 15—17°.

On boiling pyrogallol 1 : 3-dimethyl ether with acetic anhydride, the simple acetyl derivative is obtained, m. p. 53·5°, which when nitrated gives 4-nitro-2-acetylpyrogallol 1 : 3-dimethyl ether, yellowish-red crystals, m. p. 92—93°. On hydrolysis, this yields 4-nitropyrogallol 1 : 3-dimethyl ether, $\text{C}_8\text{H}_9\text{O}_5\text{N} \cdot \text{H}_2\text{O}$, long, thin, yellow needles, m. p. 67—68°, and this on methylation gives 4-nitropyrogallol trimethyl ether, m. p. 44°, described by Einhorn, Cobliner, and Pfeiffer (*A.*, 1904, i, 238), which proves the position of the nitro-group. 4-Nitro-2-acetylpyrogallol 1 : 3-dimethyl ether, on electrochemical reduction, yields 4-amino-2-acetylpyrogallol 1 : 3-dimethyl ether, which is unstable; its *hydrochloride* is pure white, m. p. 210° (decomp.). On diazotisation and coupling with β -naphthol, a red

azo-compound is produced, forming metallic, lustrous needles, m. p. 165—166°. The amino-compound forms an *acetyl* derivative, colourless leaflets, m. p. 131—132°, and a *benzoyl* derivative, m. p. 150—151°. On further nitration, 4 : 6-dinitro-2-acetylpyrogallol 1 : 3-dimethyl ether, yellow crystals, m. p. 127—128°, is formed, and this on hydrolysis yields 4 : 6-dinitropyrogallol 1 : 3-dimethyl ether, yellow needles, m. p. 162—163°, which on methylation gives 4 : 6-dinitropyrogallol trimethyl ether, m. p. 87—88°, described by Thoms and Siebeling (A., 1911, i, 724). W. O. K.

The Action of Benzoyl Peroxide on Cholesterol. A. WINDAUS and H. LÜDERS (*Z. physiol. Chem.*, 1921, **115**, 257—269).—The authors have previously directed attention to the fact that the so-called metacholesterol described by Lifschütz (A., 1919, i, 591; 1920, i, 547) is only an impure cholesterol as prepared from cholesterol dibromide (A., 1920, i, 675). They now show further that the action of benzoyl peroxide on cholesterol does not, as claimed by Lifschütz (*loc. cit.*), produce metacholesterol but a mixture of unchanged cholesterol and cholestan-4 : 7-diol monobenzoate.

By the prolonged action of benzoyl peroxide on cholesterol in ethyl alcohol, a product is obtained which has m. p. 106—110°. With acetic anhydride, it gives a more than 50% yield of cholesteryl acetate. Similarly, a 60% yield of cholesterol dibromide can be obtained from the product. Finally, after precipitating the cholesterol from the mixture as its digitonide they have isolated from the residue cholestan-4 : 7-diol 7-monobenzoate, m. p. 186°, which was identified by preparing its acetyl derivative, m. p. 154°, and the dibenzoate, m. p. 212°. Further identification was obtained by saponifying the benzoate and oxidising the diol.

The product, therefore, of the action of benzoyl peroxide on cholesterol is either an isomorphous mixture of cholesterol and cholestan-4 : 7-diol monobenzoate or a loose compound of these two substances. W. G.

New Hydroxamic Acids derived from cycloPropanecarboxylic Acid, isoButyric Acid, and Dibenzylacetic Acid. A Comparative Study of the Beckmann Rearrangement of their Derivatives. LAUDER WILLIAM JONES and ALFRED W. SCOTT (*J. Amer. Chem. Soc.*, 1922, **44**, 407—423; cf. this vol., i, 248).—The hydroxamic acids described were prepared with the view of studying the influence of certain hydrocarbon radicles on the ease of rearrangement of the related hydroxamic acids. The sodium, potassium, and silver salts of the acetyl and benzoyl esters of the parent hydroxamic acids were used for comparison. The ease of rearrangement of these salts is given by the order $K > Na > Ag$. Similarly, the comparative influence of the various hydrocarbon radicles studied is given by the order dibenzylmethyl > isopropyl > benzylmethyl > cyclopropyl.

cycloPropanecarboxylhydroxamic acid, $\begin{matrix} H_2C \\ H_2C \end{matrix} > CH \cdot CO \cdot NH \cdot OH$,

m. p. 124° (decomp.), is obtained by the action of hydroxylamine hydrochloride on ethyl cyclopropanecarboxylate in the presence of

sodium methoxide. It yields a *benzoyl* ester, m. p. 150°, with its *potassium*, *sodium*, and *silver* salts. The *acetyl* ester, m. p. 108°, gives a *potassium* salt. Both these potassium salts decompose spontaneously when kept in a vacuum desiccator over sulphuric acid.

Dibenzylacetic acid reacts with thionyl chloride to give *dibenzylacetyl chloride*, b. p. 203—205°/17 mm., which with hydroxylamine hydrochloride and sodium methoxide yields *dibenzylacethydroxamic acid*, m. p. 146°. A better yield is obtained by the action of hydroxylamine itself on the acid chloride in dry benzene. From the hydroxamic acid can be prepared its *benzoyl* ester, m. p. 147°, giving a *silver* salt; and its *acetyl* ester, m. p. 126°, giving a *silver* salt. In neither case can the potassium and sodium salts be isolated owing to the ease with which they undergo rearrangement. The product of rearrangement in the presence of water is *s-bisdibenzylmethylcarbamide*, $\text{CO}[\text{NH}\cdot\text{CH}(\text{CH}_2\text{Ph})_2]_2$, m. p. 159°.

Attempts were made to prepare tribenzylacethydroxamic acid, but they were not successful. *Tribenzylmethyl chloride*, m. p. 173° (decomp.), was obtained by the action of acetyl chloride on tribenzylcarbinol. Attempts to prepare a Grignard reagent from it by the action of magnesium even in the presence of starters were not successful.

isoButyrylhydroxamic acid (*dimethylacethydroxamic acid*), m. p. 116°, was prepared either by the action of hydroxylamine hydrochloride on ethyl *isobutyrate* in the presence of sodium methoxide or by the interaction of *isobutyryl chloride* and hydroxylamine in dry benzene. It yields a *benzoyl* ester, m. p. 148°, giving *potassium*, *sodium*, and *silver* salts, and an *acetyl* ester, m. p. 87°, giving a *potassium* salt. W. G.

The Constitution of the Secondary Product in the Sulphonation of Cinnamic Acid. F. J. MOORE and RUTH THOMAS (*J. Amer. Chem. Soc.*, 1922, **44**, 367—369).—Contrary to the statement of Beilstein (*Handbuch org. Chem.*, 3 ed., **2**, 1422), it is shown that the second product obtained by Rudnew (cf A., 1875, 76) in the sulphonation of cinnamic acid is *m*-sulphocinnamic acid, and that it is identical with that obtained by Kafka (cf. A., 1891, 720) from *m*-sulphobenzaldehyde by the Perkin synthesis. It may readily be characterised by its *aniline hydrogen* salt, m. p. 238°.

W. G.

Ring-chain Tautomerism. I. The Occurrence and Effect of Keto-enol Tautomerism between a Ring Compound and its Open-chain Isomeride. GEORGE ARMAND ROBERT KON, ARNOLD STEVENSON, and JOCELYN FIELD THORPE (*T.*, 1922, **121**, 650—665).

Preparation of Phthalic Anhydride by the Catalysis of the Vapour Phase Reaction between Naphthalene and Atmospheric Air. COURTNEY CONOVER and H. D. GIBBS (*J. Ind. Eng. Chem.*, 1922, **14**, 120—125).—Naphthalene is oxidised to phthalic anhydride when a mixture of naphthalene vapour and air is passed through a heated tube containing certain catalysts. Vanadium pentoxide is the best catalyst for the purpose; at

about 400°, 55% of the naphthalene is oxidised, 27% may be recovered and 18% is lost, the yield of phthalic anhydride being 87% of the naphthalene attacked. Molybdenum trioxide is also a fairly efficient catalyst, but other metallic oxides tried and even finely divided platinum mixed with magnesia are poor or worthless. Fused and powdered vanadium pentoxide is more effective than is the light powder prepared by decomposing ammonium vanadate at low temperatures. Arsenic trioxide and sulphur dioxide do not interfere with the catalyst, but the presence of sodium compounds is injurious. Phthalic anhydride is the main solid product of the reaction; benzoic acid has been found, and naphthols are probably present in small quantity. The gaseous products consist chiefly of carbon dioxide; the presence of carbon monoxide has not been detected.

W. P. S.

Friedel and Crafts' Reaction. Diphenyl and Ditolyl Tetrahalogen Phthalides. WALTER A. LAWRENCE and HAROLD G. ODDY (*J. Amer. Chem. Soc.*, 1922, **44**, 329—330).—The method used by Rubidge and Qua for the preparation of diphenylphthalide (cf. A., 1914, i, 539) gives good results for the preparation of diphenyl- and ditolyl-tetrahalogenophthalides if tetrahalogenated phthalic anhydrides are used. New compounds prepared by this method are: *diphenyltetrabromophthalide*, m. p. 202°; *ditolyltetrabromophthalide*, m. p. 196—197°; *diphenyltetraiodophthalide*, m. p. 206°, and *ditolyltetraiodophthalide*, m. p. 213—214°.

W. G.

Mechanism of the Colour Change of some Phthaleins. A. THIEL (*Z. physikal. Chem.*, 1922, **100**, 479—488).—The author has investigated the colour changes of various chloro- and bromo-substituted phenolphthaleins and from the relative intensity of the colour discusses the mechanism of the colour change. Taking the intensity of the colour of phenolphthalein itself as unity, the following intensity values have been obtained: Phenoltetrachlorophthalein, 5; chlorophenolphthalein, 0.65; dichlorophenolphthalein, 0.25; trichlorophenolphthalein, 0.13; tetrachlorophenolphthalein, 0.01; bromophenolphthalein, 0.60; dibromophenolphthalein, 0.20; tribromophenolphthalein, 0.04, and tetrabromophenolphthalein, 0.01. The results show that the nuclear ring has no chromophoric function and that this must be sought outside the nucleus. The sensitiveness towards large excess of strong bases is practically zero in the case of phenoltetrachlorophthalein; it is noticeable with phenolphthalein and increases with increasing number of chlorine or bromine atoms in the side rings, so that under similar conditions the tetra-derivatives show the strongest decoloration by alkali hydroxides. The decolorising action of alcohol is parallel with that of alkali hydroxides; cooling reduces the colour intensity and heating increases it.

J. F. S.

The Molecular Configurations of Polynuclear Aromatic Compounds. I. The Resolution of γ -6:6'-Dinitro- and 4:6:4':6'-Tetranitro-diphenic Acids into Optically Active Components. GEORGE HALLATT CHRISTIE and JAMES KENNER (*T.*, 1922, **121**, 614—620).

Disalicylic or Anhydrosalicylic Acid and its Transformation into Xanthone-4-carboxylic Acid. RICHARD ANSCHÜTZ and WALTER CLAASEN (*Ber.*, 1922, **55**, [B], 680—689; cf. A., 1920, i, 48).—*o*-Tolylsalicylic acid, $C_6H_4Me \cdot O \cdot C_6H_4 \cdot CO_2H$, m. p. 133.5° , is prepared according to the directions of Ullmann and Zlokasoff (A., 1905, i, 597) and is oxidised by potassium permanganate to *disalicylic acid* [*anhydrosalicylic acid*], $O(C_6H_4 \cdot CO_2H)_2$, colourless needles, m. p. 230° (decomp.); the *silver*, *calcium* ($+H_2O$), and *copper* salts are described. The acid is converted by phosphorus pentachloride in the presence of *s*-tetrachloroethane into the corresponding *chloride*, $O(C_6H_4 \cdot COCl)_2$, small, colourless needles, m. p. 161° , from which the following compounds are obtained in the usual manner: *ethyl* ester, b. p. $220^\circ/12$ mm.; *di-amide*, small, colourless needles, m. p. 265° ; *di-anilide*, four-sided, lustrous leaflets, m. p. 194 — 195° . *Methyl disalicylate*, prepared by the action of methyl sulphate and potassium hydroxide on the acid, crystallises in small, colourless needles, m. p. 65.5° .

Disalicylic acid shows a somewhat unexpected behaviour towards acetyl chloride at 170° , since, in place of the expected anhydride, it gives *xanthone-4-carboxylic acid*, $C_6H_4 \langle \begin{smallmatrix} CO \\ O \end{smallmatrix} \rangle C_6H_3 \cdot CO_2H$ (the same compound is produced by means of sulphuric acid); it crystallises in almost colourless, matted needles, m. p. 289° , and is characterised by unusual stability, since it can be distilled unchanged under the atmospheric pressure. The *silver*, *calcium*, and *copper* ($+H_2O$) salts are described. The acid is characterised further by conversion into the following derivatives; *chloride* (by phosphorus pentachloride or thionyl chloride), m. p. 165° ; *methyl* ester (by means of methyl sulphate), long, yellow needles, m. p. 146.5° ; *ethyl* ester (from the silver salt and ethyl iodide), microscopic yellow needles, m. p. 123° ; *amide* (from the chloride and ammonia in *s*-tetrachloroethane solution), m. p. above 320° (decomp.); *anilide*, colourless, lustrous leaflets, m. p. 252° .

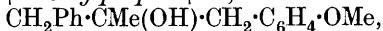
H. W.

Some Derivatives of Anisylacetone (Methoxyphenylpropanone) [*p*-Methoxybenzyl Methyl Ketone]. EMILIEN LE BRAZIDEC (*Bull. Soc. chim.*, 1922, [iv], **31**, 255—265).—*p*-Methoxybenzyl methyl ketone is converted by the action of hydrobromic acid in solution in glacial acetic acid into *p-hydroxybenzyl methyl ketone*, $COMe \cdot CH_2 \cdot C_6H_4 \cdot OH$, m. p. 35.5° , d^{20}_D 1.1159, giving a *semi-carbazone*, m. p. 213° . With potassium cyanide, the bisulphite compound of anisylacetone yields α -hydroxy- β -anisyl- α -methylpropionitrile, $OMe \cdot C_6H_4 \cdot CH_2 \cdot CMe(OH) \cdot CN$, which on hydrolysis gives first the *amide*, m. p. 179° , and then α -hydroxy- β -anisyl- α -methylpropionic acid, m. p. 84° . By the action of magnesium methyl iodide on anisylacetone, α -anisyl- β -methyl- Δ^a -propene, $CH \cdot CMe \cdot CH \cdot C_6H_4 \cdot OMe$,

b. p. $118^\circ/15$ mm., d 1.0089, is obtained, but its properties do not entirely correspond with those given by Klages (cf. A., 1904, i, 567) for a compound thus named and prepared from anisaldehyde and

sodium isobutyrate. Its constitution is shown by the fact that on oxidation it yields anisic acid. On reduction by sodium in absolute alcohol, it gives α -anisyl- β -methylpropane, b. p. 123—125°/15 mm., d_4^{20} 0.9887.

By the action of magnesium benzyl chloride on anisylacetone, γ -phenyl- α -anisyl- β -methylpropan- β -ol,



b. p. 225—230°/15 mm., is obtained, and on dehydration by acetic anhydride it yields γ -phenyl- α -anisyl- β -methyl- Δ^a -propene,

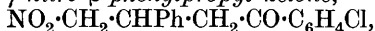


b. p. 206°/12 mm., d_4^{20} 1.0551, and this on oxidation gives anisic acid. W. G.

The Synthesis of Aromatic Ketones by means of Mixed Zinc Organic Compounds. F. MAUTHNER (*J. pr. Chem.*, 1921, [ii], **103**, 391—396).—Following Blaise (A., 1911, i, 415), the author has prepared various aromatic ketones by the action of mixed zinc organic compounds on the corresponding acid chlorides. From *o*-toluoyl chloride is obtained *o*-tolyl ethyl ketone, an oil, b. p. 219—220°. The following compounds are also described: *m*-tolyl methyl ketone, an oil, b. p. 220°; *p*-tolyl ethyl ketone, an oil, b. p. 238—239°; 2-methoxy-*m*-toluoyl chloride, b. p. 121—122°/17 mm.; 2-methoxy-*m*-tolyl ethyl ketone, b. p. 122°/12 mm.; 2-methoxy-*p*-toluoyl chloride, b. p. 153—154°/18 mm.; 2-methoxy-*p*-tolyl ethyl ketone, b. p. 147°/14 mm.; 4-methoxy-*m*-toluoyl chloride, b. p. 146—147°/14 mm.; 4-methoxy-*m*-tolyl ethyl ketone, b. p. 142—143°/13 mm.; *p*-anisyl methyl ketone, and 3:5-dimethoxyphenyl ethyl ketone, b. p. 168—170°/17 mm. The last compound, when reduced with zinc and hydrochloric acid, yields 3:5-dimethoxy-1-*n*-propylbenzene. If the formula proposed by Hesse (A., 1911, i, 208) for divarinol is correct, this compound ought to be identical with divarinol dimethyl ether. W. O. K.

The Reaction between Alkalis and certain Nitrocyclopropane Derivatives. E. P. KOHLER and L. I. SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 624—634).—It has previously been shown (A., 1919, i, 582) that 3-nitro-2-benzoyl-1-phenylcyclopropane is decomposed by potassium hydroxide, giving potassium nitrite and an open-chain β -diketone. It is suggested that the first step in this reaction is the elimination of nitrous acid and then the resulting cyclopropene derivative immediately undergoes rearrangement to an acetylenic compound which in the presence of the alkali hydroxide combines with water to give the β -diketone. Certain experimental evidence in support of this view is given. Proof of the intermediate formation of an acetylenic ketone was obtained by carrying out the reaction in the presence of diethyl malonate, when α -pyrone esters were obtained (cf., this vol., i, 461).

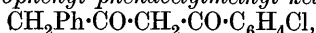
p-Chlorophenyl γ -nitro- β -phenylpropyl ketone,



m. p. 80°, is obtained by the action of sodium nitromethane on *p*-chlorophenyl styryl ketone. When brominated, it yields *p*-chlorophenyl α -bromo- γ -nitro- β -phenylpropyl ketone, m. p. 88—89°, which

γ^*

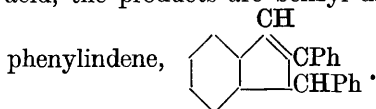
by the elimination of hydrogen bromide with potassium acetate gives 3-nitro-1-p-chlorobenzoyl-2-phenylcyclopropane, m. p. 121°. This compound is converted into an isomeride, m. p. 144°, by the action of ammonia in methyl alcohol. Further, it combines with hydrogen bromide, giving p-chlorophenyl γ -bromo- β -nitro- γ -phenylpropyl ketone, $\text{CHPhBr}\cdot\text{CH}(\text{NO}_2)\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_4\text{Cl}$, m. p. 128°, which readily loses nitrous acid and hydrogen bromide, giving 1-phenyl-4-p-chlorophenylfuran, m. p. 123°. The nitrocyclopropane described above is decomposed by sodium methoxide, giving as its sole product p-chlorophenyl phenacetylmethyl ketone,



m. p. 78°, giving a copper derivative, m. p. 218—220° (decomp.). If the nitrocyclopropane is warmed with the sodium derivative of diethyl malonate in methyl alcohol, then the product is methyl 5-p-chlorophenyl-3-benzylpyrone-2-carboxylate, m. p. 171°, giving the free acid, m. p. 155—157° (decomp.), and some γ -p-chlorobenzoyl- β -benzylcrotonic acid, $\text{C}_6\text{H}_4\text{Cl}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{C}(\text{CH}_2\text{Ph})\cdot\text{CH}\cdot\text{CO}_2\text{H}$, m. p. 147° (decomp.). The pyrone acid, when heated at 165—170°, gives 6-p-chlorophenyl-4-benzylpyrone, m. p. 167—168°. The pyrone ester when shaken with a saturated solution of ammonia in methyl alcohol gives ethyl 2-hydroxy-6-p-chlorophenyl-4-benzylpyridine-3-carboxylate, m. p. 210°.

Starting from phenyl p-chlorostyryl ketone, a similar series of compounds can be prepared as follows. Phenyl γ -nitro- β -p-chlorophenylpropyl ketone, m. p. 96°; phenyl α -bromo- γ -nitro- β -p-chlorophenylpropyl ketone, m. p. 116°; 3-nitro-1-benzoyl-2-p-chlorophenylcyclopropane, m. p. 66—67°, and its isomeride, m. p. 157—159°; phenyl γ -bromo- β -nitro- γ -p-chlorophenylpropyl ketone, m. p. 112—114°; phenyl β -nitro- γ -hydroxy- γ -p-chlorophenylpropyl ketone, m. p. 142°; phenyl p-chlorophenylacetylmethyl ketone, m. p. 52—54°, and its copper derivative, m. p. 229—230° (decomp.); methyl 3-p-chlorobenzyl-5-phenylpyrone-2-carboxylate; phenyl $\alpha\gamma$ -dibromo- β -nitro- γ -p-chlorophenylpropyl ketone, m. p. 143°. W. G.

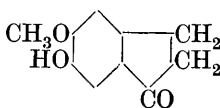
The Dehydration of Benzylhydrobenzoin ($\alpha\beta\gamma$ -Triphenylpropane- $\alpha\beta$ -diol). Formation of Benzyl Diphenylmethyl Ketone (Semipinacolic Transposition) and of Diphenylindene (Cyclisation). A. ORÉKHOFF and M. TIFFENEAU (*Bull. Soc. chim.*, 1922, [iv], 31, 253—255).—It has previously been shown that $\alpha\beta\gamma$ -triphenylpropane- $\alpha\beta$ -diol is dehydrated by concentrated sulphuric acid, giving benzyl diphenylmethyl ketone (A., 1919, i, 205). It is now shown that if phosphoric oxide is used in place of sulphuric acid, the products are benzyl diphenylmethyl ketone and 1:2-di-



ating agent, the product is exclusively diphenylindene. W. G.

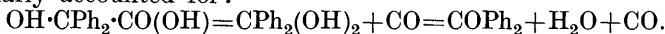
Hydrindones. I. The Hydrindone of the Vanillin Series. FRITZ VON KONEK and NIKOLAUS SZAMÁK (*Ber.*, 1922, 55, 102—109).—The object of the research was to determine the influence

of a third ring substituent on the condensation to hydroxyhydrindones of suitable phenolic acids. Hydroferulic acid (β -*m*-methoxy-*p*-hydroxyphenylpropionic acid), was prepared by reducing ferulic acid with sodium amalgam, the ferulic acid being obtained from vanillin by Perkin's synthesis. The hydroferulic acid was condensed by heating with concentrated sulphuric acid at 140° . The resulting hydrindone, which was obtained in poor yield, crystallises from hot water in long needles, m. p. $193\text{--}194^\circ$. It forms a *phenylhydrazone*, m. p. $205\text{--}210^\circ$ (decomp.), crystallising in yellow needles. By methylation and oxidation with nitric acid, it is converted into *m*-hemipinic acid (4:5-dimethoxyphthalic acid), which establishes the constitution of the hydrindone as 6-hydroxy-5-methoxydihydrindone (annexed formula). Condensation therefore takes place in the position para to the methoxyl group.



E. H. R.

The Rearrangement of Benzil to Benzilic Acid. ARTHUR LACHMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 330—340).—By prolonged boiling with water, benzil is converted into benzilic acid. The addition of small amounts of alkali accelerates the change, but the acceleration is by no means proportional to the increase in hydroxyl-ion concentration. There is some slight experimental evidence that the reversal of the benzil rearrangement is not unlikely, but so far it has not definitely been accomplished. When boiled with water, benzilic acid yields benzophenone and carbon monoxide. The author is of the opinion that the new experimental evidence is not in accord with the hypotheses of Nef (cf. A., 1898, i, 102), Tiffeneau (cf. A., 1907, i, 304, 404, 922), or Michael (cf. A., 1920, i, 417, 536) as to this rearrangement. He propounds a new hypothesis similar to that suggested for the rearrangement of dihydroxytartaric acid (cf. this vol., i, 109), that is to say, on the basis of intramolecular oxidation and reduction. The rearrangement is indicated as follows, $\text{COPh}\cdot\text{COPh} \rightarrow \text{CPh}(\text{OH})_2\cdot\text{CPh}(\text{OH})_2 \rightarrow \text{OH}\cdot\text{CPh}_2\cdot\text{C}(\text{OH})_3 \rightarrow \text{OH}\cdot\text{CPh}_2\cdot\text{CO}_2\text{H}$. The decomposition of benzilic acid to benzophenone and carbon monoxide may be similarly accounted for:



From a study of this and other rearrangements, it is stated that if two carbon atoms in a compound are in a symmetrical or a similar state of oxidation, such a structure is unstable; one of the carbon atoms tends to a greater degree of oxidation, the other becoming reduced. This tendency is enhanced by rise in temperature or by different catalysts.

W. G.

Piperitone. II. Benzylidene-*dl*-piperitone. JOHN READ and HENRY GEORGE SMITH (*T.*, 1922, **121**, 574—582).

Piperitone. III. The Oximes of *dl*-Piperitone. JOHN READ, HENRY GEORGE SMITH, and MARIE BENTIVOGLIO (*T.*, 1922, **121**, 582—593).

New Halogen Derivatives of Camphor. II. α' -Bromocamphor. THOMAS MARTIN LOWRY, VICTOR STEELE, and HENRY BURGESS (T., 1922, 121, 633—641).

New Distinctive Characteristics of the Three Propan- β -olcamphorcarboxylolides Melting Respectively at 141°, 117—118°, and 89—90°. A. HALLER and (MME) RAMART-LUCAS (*Compt. rend.*, 1922, 174, 785—789; cf. A., 1921, i, 673).—With sodium ethoxide the camphorcarboxylolide, m. p. 141°, gives
propan- β -olcamphorcarboxylic acid, $C_8H_{14} < \begin{matrix} C(CO_2H) \cdot CH_2 \cdot CHMe \cdot OH, \\ CO \end{matrix}$

m. p. 160—170° (decomp.), $[\alpha]_D + 33^\circ 5'$, which when heated loses carbon dioxide, giving camphopropan- β -ol. The acid is the *cis-trans*-acid. The camphorcarboxylolide, m. p. 117—118°, under the same conditions gives the *sodium* salt of an isomeric *cis-cis-propan- β -olcamphorcarboxylic acid*. Attempts to isolate the free acid were not successful as the addition of acid to a solution of the sodium salt always regenerated the olide. The third camphor carboxylolide, m. p. 89—90°, can be obtained in small amounts by treating the isomeride, m. p. 141°, with concentrated sulphuric acid. When treated with sodium ethoxide as described above, it gives an isomeric *propan- β -olcamphorcarboxylic acid*, m. p. 115—120° (decomp.), $[\alpha]_D + 25^\circ 3'$, which when heated loses carbon dioxide, giving a *camphopropan- β -ol*, m. p. 100—101°, $[\alpha]_D + 62^\circ 4'$, which yields a *phenylurethane*, m. p. 120—120·5°, $[\alpha]_D + 5^\circ 47'$. W. G.

Various Oils of *Origanum vulgare* from Different Parts of Italy. E. ANGELESCU (*Gazzetta*, 1922, 52, i, 157—166).—Three samples of *Origanum vulgare*, (1) one purchased in Rome, and the others gathered (2) at Valle d'Inferno and (3) in Sicily, respectively, have been distilled in a current of steam, the whole plant being employed. The yields of oil obtained were 0·204, 0·072, and 1·106%, respectively, and the compositions as follows: (1) 6·7% of thymol, 15·4% of unidentified free alcohols, 2·63% of esters, a small proportion of free acid, and 12·5% of a sesquiterpene, b. p. 245—250°, the density and refraction of which indicate it to be bicyclic; (2) 2·2% of thymol, 12·86% of unidentified free alcohols, 2·56% of esters, and probably a sesquiterpene; (3) 50% of thymol, 4% of unidentified free alcohols, 0·85% of esters, traces of free acid, 17·5% of cymene, and 10·5% of dipentene. [Cf. *J. Soc. Chem. Ind.*, 1922, 346A.] T. H. P.

Italian Oil of *Thymus striatus*. P. LEONE and E. ANGELESCU (*Gazzetta*, 1922, 52, i, 152—157).—The dried complete plant yields 0·342% of a lemon-yellow oil of aromatic odour and burning taste and containing 30% of thymol, 9·5% of unidentified free alcohols, 2·83% of esters, little free acid, 29% of cymene, and 4·5% of a sesquiterpene, b. p. 250—260°, which is apparently monocyclic. [Cf. *J. Soc. Chem. Ind.*, 1922, 346A.] T. H. P.

The Dithiocarbamate Accelerators of Vulcanisation. D. F. TWISS, S. A. BRAZIER, and F. THOMAS (*J. Soc. Chem. Ind.*, 1922, 41, 83—88r).—The dithiocarbamate accelerators of vulcanisation

include the alkylthiocarbamates, the corresponding thiouram disulphides, and the xanthates. Unlike aldehyde-ammonia and the simple amines, the effectiveness of these compounds as vulcanisation catalysts is influenced to a remarkable extent by the presence of zinc oxide. Their use with zinc oxide gives rise to vulcanised products of exceptionally high tensile strength and resistance to extension, and accelerates the physical alteration of the rubber in a greater degree than the chemical alteration, as indicated by the combination of caoutchouc with sulphur. The alkylammonium alkylthiocarbamates and thiouram disulphides derived from secondary amines are much more powerful catalysts than the corresponding derivatives of primary amines. It is remarkable that in the absence of zinc oxide even the zinc dialkylthiocarbamates and zinc ethylxanthate are relatively feeble in their action, and that with the last-named substance a high vulcanisation temperature is unfavourable. When applied in the presence of a limited proportion of zinc oxide, thiocarbanilide causes the development of a discontinuous progress of vulcanisation similar to that described earlier for thiocarbo-*p*-toluidide. (See also Twiss and Brazier, A., 1920, i, 751; Twiss and Howson, A., 1920, i, 751; Twiss, A., 1921, i, 876.)

D. F. T.

The Constitution of Catechin. IV. MAXIMILIAN NIERENSTEIN (T., 1922, 121, 604—613).

The Addition of Malonic Esters to Benzoylphenylacetylene.

E. P. KOHLER (*J. Amer. Chem. Soc.*, 1922, 44, 379—385).—Malonic esters combine with benzoylphenylacetylene in the presence of sodium ethoxide to give compounds of the type $\text{COPh}\cdot\text{CH}:\text{CPh}\cdot\text{CH}(\text{CO}_2\text{Me})_2$, which, however, immediately lose alcohol and pass into α -pyrone derivatives, having the ester group in the position 3. These pyrone derivatives are characterised by the fact that on treatment with alkalis they can be hydrolysed without breaking the pyrone ring, the product being either the pyrone acid or the corresponding pyrone. In this way, the author has prepared 2:4-diphenyl-6-pyrone-5-carboxylic acid, in the form of its *methyl* ester, m. p. 129° , its *ethyl* ester, m. p. 119° , and its *sodium* salt. The free acid when heated for two hours at 210 — 212° gives 2:4-diphenyl-6-pyrone, m. p. 142° , which by solution in alcoholic potassium hydroxide and subsequent addition of acid gives γ -benzoyl- β -phenyl-crotonic acid, m. p. 130° , giving a *methyl* ester, m. p. 36° . A second acid, apparently isomeric with the crotonic acid, was also obtained during this opening of the pyrone ring, but it could not be isolated in the pure state.

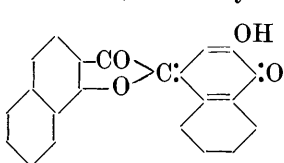
The pyrone esters when heated with aqueous ammonia give ammonium salts of amino-compounds, but with concentrated alcoholic ammonia at the ordinary temperature they are slowly converted into a mixture of hydroxypyridine esters and the corresponding hydroxypyridines. Of these 6-hydroxy-2:4-diphenylpyridine, m. p. 210° , and *ethyl* 6-hydroxy-2:4-diphenylpyridine-5-carboxylate, m. p. 197° , have been prepared.

W. G.

The Oxidation of α -Dinaphthaxanthenes. HEMENDRA KUMAR SEN-GUPTA and STANLEY HORWOOD TUCKER (T., 1922, **121**, 557—568).

Autoxidation of 2-Acetyl- α -naphthol in Alkaline Solution.

K. FRIES and H. LEUE (*Ber.*, 1922, **55**, [B], 753—763).—Solutions of 2-acetyl- α -naphthol in sodium or potassium hydroxide which contain more than one molecular proportion of the hydroxide to one of the acetyl derivative are completely stable towards air, even when heated; on the other hand, when an excess of base is avoided, the acetyl compound is readily oxidised to acetic acid



and a substance, $C_{22}H_{12}O_4$, to which, on account of its synthesis and reactions, the annexed constitution is assigned. The course of the reaction has not yet been elucidated fully, and it has not been found possible to isolate any intermediate product. The completely inhibitive effect

of even a slight excess of alkali hydroxide is attributed to the existence of two types of salts of 2-acetyl- α -naphthol, of which only that which predominates in solutions of smaller hydroxyl-ion concentration is autoxidisable.

If oxygen is passed through a boiling solution of 2-acetyl- α -naphthol in alcohol which has been treated with an amount of sodium hydroxide solution insufficient for complete combination, ethyl acetate is produced and a dense precipitate of the *sodium salt*, $C_{22}H_{11}O_4Na$, black crystals, separates. The parent *compound*, $C_{22}H_{12}O_4$ (see above), crystallises in dark red needles, m. p. 306° ; the *acetate*, lustrous, orange-yellow needles, m. p. 284° , *carboxy-derivative*, orange-coloured, silky needles, m. p. 239° , and *methyl ether*, slender red needles, m. p. 264° , are described. The compound, $C_{22}H_{12}O_4$, is reduced by a saturated solution of stannous chloride in glacial acetic acid to the corresponding trihydroxy-*derivative*, $C_{10}H_6<\text{CH(OH)}>\text{CH}\cdot C_{10}H_5(\text{OH})_2$, yellow leaf-

lets, m. p. 195° , which is oxidised slowly to the parent substance on exposure to air, rapidly in alkaline solution. It gives a *triacetate*, colourless leaflets, m. p. 212° . The methyl ether, m. p. 264° , undergoes a peculiar transformation under the influence of alkali hydroxide, being converted by loss and subsequent addition of a molecule of water into the *diketone*, $\text{OH}\cdot C_{10}H_6\cdot \text{CO}\cdot \text{CO}\cdot C_{10}H_5(\text{OH})\cdot \text{OMe}$, yellow needles, m. p. 186° , which is reconverted into the red methyl ether when heated above its melting point or treated with concentrated acid; it gives a well-defined *calcium salt*, $C_{23}H_{14}O_5Ca$, small, pale yellow needles, and is converted by *o*-phenylenediamine into the *quinoxaline derivative*, small, red, prismatic crystals, m. p. above 300° (decomp.) after softening at 270° . The diketone and also the red methyl ether are reduced by stannous chloride in the presence of glacial acetic acid to the *dihydroxy-compound*, $C_{10}H_6<\text{CH(OH)}>\text{CH}\cdot C_{10}H_5(\text{OH})\cdot \text{OMe}$, colourless needles, m. p.

198° (*diacetate*, m. p. 185°), which is oxidised by ferric chloride to the red methyl ether.

The compound $C_{22}H_{12}O_4$ is converted by short ebullition with aniline into anilino- β -naphthaquinone, m. p. 245°. This observation has provided the key to the synthesis of the compound which is obtained by boiling a saturated solution of 6 : 7-benzocoumaranone and anilino- β -naphthaquinone (which behaves as 2-hydroxy-1 : 4-naphthaquinone-4-anil) in glacial acetic acid. H. W.

Strychnos Alkaloids. XXXI. Violet and Green Colour Reactions of Cacothelin. HERMANN LEUCHS [and, in part, KACHRN] (*Ber.*, 1922, 55, [B], 724—732).—The recognition of cacothelin as a quinone, $C_{21}H_{21}O_7N_3.HNO_3$ (this vol., i, 362), has necessitated a re-examination of its colour reactions. It is found that the violet salts are derived from the corresponding quinol. The unusual deepening of the colour, however, can only be explained by the assumption that fresh quinoid linkings are developed to replace those lost during the conversion of quinone into quinol. Information on this point is derived from a study of the esterification of the “nitroquinol” which, under regulated conditions, gives violet salts of a mono-ester and ultimately similar salts of di-esters. Since the formula of the nitroquinol in so far as it has been elucidated, $C_{16}H_{17}\{C(OH) \dots C(OH); :C(NO_2); :N; :NH; \cdot CO_2H; :CH(OH)\}$, only indicates the possibility of the production of a mono-ester, the formation of a di-ester can only be explained by the hypothesis that the nitro- passes into the isonitro-group, $:C:N \leq \begin{smallmatrix} O \\ O \end{smallmatrix} \rightarrow :C:N \leq \begin{smallmatrix} O \\ OH \end{smallmatrix}$. This rearrangement involves the production of a new quinoid arrangement. Evidence obtained during the acetylation of the “nitroquinol” points to the conclusion that the migrating hydrogen atom is supplied by the imino-group.

The free “nitroquinol” is obtained by the addition of alkali hydroxide to a solution of the violet hydrochloride in boiling water and in an atmosphere of hydrogen. The violet salts are obtained readily from it by use of the requisite acid if precautions are taken to exclude air; the sulphate, hydrochloride, nitrate, and *hydrobromide* have been examined. Methyl sulphate converts the base into the compound, $C_{23}H_{29}O_{11}N_3S$, dark violet prisms.

The hydrochloride of the nitroquinol is converted by methyl alcohol and hydrogen chloride in the presence of acetone into the *hydrochloride* of the corresponding methyl ester, long, almost black needles, and by more drastic treatment in the absence of acetone into methylnitroquinol *methyl* ester, hydrochloride, lemon-yellow plates, $C_{23}H_{27}O_7N_3.HCl.2HCl.3MeOH$, or violet prisms, $C_{23}H_{27}O_7N_3.HCl.3H_2O$. With ethyl alcohol, the compounds $C_{23}H_{27}O_7N_3.HCl$, reddish-violet, quadratic leaflets and $C_{25}H_{31}O_7N_3.HCl$, tile-red, slender needles, are produced.

The “nitroquinol” hydrochloride is converted by acetic anhydride at 100° in the absence of air into the “*diacetyl nitroquinol*” *anhydride*, dark yellow prisms, from which the corresponding *monoacetate*,

$C_{23}H_{23}O_7N_3$, red crystals which become discoloured at 230° , is derived; the *sulphate*, *hydrochloride*, and *hydrobromide* were prepared.
H. W.

Preparation of Neutral Soluble Double Compounds of the Alkyl Xanthines and their *N*-Acyl Derivatives. KNOLL & CO. (D.R.-P. 340744; from *Chem. Zentr.*, 1921, iv, 1102—1103).—Dialkyl xanthines and their *N*-acyl derivatives form soluble crystalline salts with alkali benzoates and salicylates. The following double compounds are mentioned: theophylline-sodium salicylate; theobromine-sodium salicylate; *N*-acetyltheobromine-sodium salicylate; theophylline-sodium benzoate; *N*-acetyltheobromine-lithium salicylate; *N*-acetyltheobromine-ammonium salicylate; *N*-acetyl theobromine-potassium salicylate; theophylline-sodium salicylate; theophylline-potassium benzoate.
G. W. R.

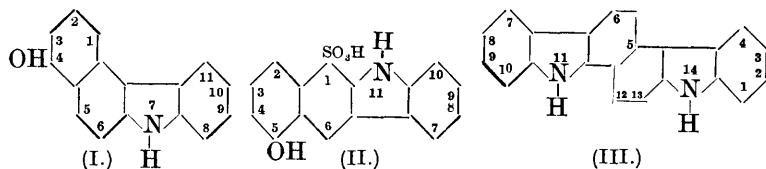
1-Phenyl-4-pyridone. ALEXANDER P. SMIRNOV (*Ber.*, 1922, 55, [B], 612—613; cf. A., 1921, i, 594).—In reply to Borsche and Bonacker (this vol., i, 50), the author considers that the evidence brought forward favours his view of the internal ammonium oxide structure of the compound and not the ketonic constitution.

Anhydrous 1-phenyl-4-pyridone has m. p. 126° when slowly heated instead of 116° as recorded by Borsche and Bonacker (*loc. cit.*).
H. W.

Synthesis of Quinic Acid. ADOLF KAUFMANN (*Ber.*, 1922, 55, [B], 614—616).—In his recent communication (this vol., i, 172, 174) on the synthetic production of quinic acid in quantity, Halberkann appears to have overlooked the work of Kaufmann and his colleagues (cf. A., 1909, i, 958; 1911, i, 749, 750; 1912, i, 651; 1918, i, 187).
H. W.

The Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. IX. 6-Amino- α -naphthol-5-sulphonic Acid (*A*-Acid) and the Sulphite Reaction. HANS TH. BUCHERER and RUDOLF WAHL (*J. pr. chem.*, 1921, [ii], 103, 253—276).—*A*-Acid, when boiled with 40% sodium hydrogen sulphite, is converted into the *disulphurous acid* ester of 1:6-dihydroxynaphthalene-5-sulphonic acid, the sodium salt of which, $C_{10}H_5S_3O_9Na_3$, separates in long, colourless needles. The dihydroxynaphthalenesulphonic acid itself could not be isolated, being exceedingly soluble. *A*-Acid, with 40% ammonium sulphite and ammonia, yields 2:5-diaminonaphthalene-1-sulphonic acid, prismatic crystals and rectangular prisms, whilst with aniline and sodium hydrogen sulphite it yields 6-anilino- α -naphthol, which was isolated as the *monobenzoyl* derivative, m. p. 128.5° . With phenylhydrazine and sodium hydrogen sulphite, the corresponding phenylhydrazino-compound, apparently to be postulated as an intermediate stage, undergoes a further series of reactions (cf. following abstract), and the final products are 4-hydroxypheno- β -naphthacarbazole, I, m. p. 215° , 5-hydroxypheno- $\beta\beta$ -naphthacarbazole-1-sulphonic acid, II,

and *diphenonaphthadiazole*, III (?), m. p. 209°, I and III involving the elimination of a sulphonic acid group.

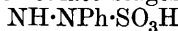


In the same way, phenylhydrazine and sodium hydrogen sulphite acts on 6-amino- α -naphthol-3 : 5-disulphonic acid to give, not only 5-hydroxypheno- $\beta\beta$ -naphthacarbazole-1 : 3-disulphonic acid, but also small quantities of 4-hydroxypheno- β -naphthacarbazole-2-sulphonic acid.

Sodium hydrogen sulphite, either alone or with aniline, appears to have no action on β -naphthylamine-1 : 5-disulphonic acid.

W. O. K.

The Action of Sulphites on Aromatic Amino- and Hydroxy-compounds. X. Action of Phenylhydrazine-Bisulphite Mixture, Particularly on Aminonaphtholsulphonic Acids, and Azo-dyes. HANS TH. BUCHERER and WALTHER ZIMMERMANN (*J. pr. Chem.*, 1921, [ii], **103**, 277—315).—Bucherer and various co-workers have shown (cf. A., 1908, i, 455; A., 1909, i, 521; A., 1910, i, 144) that the action of a mixture of phenylhydrazine and 40% sodium hydrogen sulphite on certain naphtholsulphonic acids leads to the formation of phenonaphthacarbazole derivatives, and other naphtholsulphonic acids have now been investigated. Carbazole formation takes place in the case of β -naphthol-8-sulphonic acid, α -naphthylamine-7-sulphonic acid, 7-amino- α -naphthol-3-sulphonic acid (γ -acid), 6-amino- α -naphthol-3-sulphonic acid (J -acid), 5-amino- α -naphthol-3-sulphonic acid (M -acid). Usually the N -sulphonic acid of the carbazole is first formed, and this loses its N -sulphonic group on acid hydrolysis. The following compounds have been analysed: sodium pheno- β -naphthacarbazole-1 : 7-disulphonate, white needles; sodium pheno- α -naphthacarbazole-2-sulphonate; sodium 4-hydroxypheno- α -naphthacarbazole-2-sulphonate, opalescent leaves. Sodium pheno- β -naphthacarbazole-1 : 7-disulphonate when boiled with acid loses both sulphonic acid groups, giving pheno- α -naphthacarbazole, m. p. 132° (acetyl derivative, m. p. 149°). In the cases of 5-amino- α -naphthol-3-sulphonic acid and of α -naphthylamine-7-sulphonic acid, the corresponding diaryl hydrazine- N -sulphonic acids (which are presumably intermediate stages



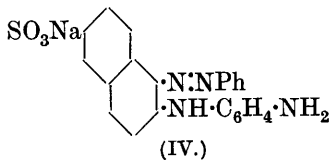
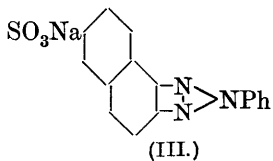
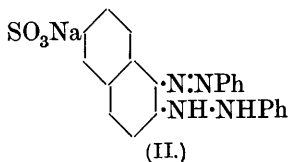
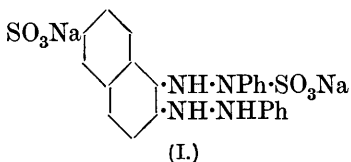
in the carbazole formation) of the type

are also formed, whilst in the cases of 8-amino- α -naphthol-5-sulphonic acid (S -acid) and 8-amino- α -naphthol-3 : 5-disulphonic

acid (*K*-acid) no carbazole formation could be detected. From these diarylhydrazine-*N*-sulphonic acids from *S*-acid, and from α -naphthylamine-7-sulphonic acid, *azo*-compounds are formed by the action of alkali hydroxide of the formulæ $C_{16}H_{11}ON_2 \cdot SO_3Na$ and $C_{16}H_{11}N_2SO_3Na$ respectively.

K-Acid and *M*-acid, when boiled with sodium hydrogen sulphite, yield "dioxy-*K*-acid," and "dioxy-*M*-acid" as greyish-white precipitates; that is, the amino-groups are replaced by hydroxyl. These give with diazotised *p*-toluidine red dyes. "Dioxy-*K*-acid" (1 : 8-dihydroxynaphthalene-3 : 5-[4 : 6]disulphonic acid), on long boiling with concentrated hydrochloric acid, loses a sulphonic acid group to give 1 : 8-dihydroxynaphthalene-3-(6)-sulphonic acid.

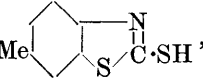
The action of phenylhydrazine and sodium hydrogen sulphite on *azo*-dyes has been reinvestigated (cf. Bucherer and Sonnenberg, A., 1910, i, 144). The yellow *product* obtained from croceine (1-benzeneazo- β -naphthol-6-sulphonic acid) has apparently the constitution I, and with alkali hydroxide forms the red *dye*, II, which crystallises in long needles; its constitution is verified by the following reactions. With nitrite it loses aniline, and forms the *triazole*, III, and on reduction it forms 1 : 2-naphthylene-diamine-6-sulphonic acid, the properties agreeing with those of this compound as described by Witt (A., 1889, i, 270). The red compound, II, with concentrated hydrochloric acid undergoes a semidine transformation to give 1-benzeneazo-2-*p*-aminophenyl-amino-6-sulphonic acid, IV, the sodium salt of which crystallises in long, fine needles.



Similar *yellow* and *red* compounds are obtained from 1-*p*-acetylaminobenzeneazo- β -naphthylamine-6-sulphonic acid, whilst the action of phenylhydrazine and sodium hydrogen sulphite on naphthol-blue-black (8-amino-2-benzeneazo-7-*p*-nitrobenzeneazo- α -naphthol-3 : 6-disulphonic acid) is due simply to the sodium hydrogen sulphite, and the dye is reduced to 7 : 8-diamino-2-benzeneazo- α -naphthol-3 : 6-disulphonic acid, a bluish-red dye. This gives a brownish-red *dye* with phenanthraquinone, which separates in small needles, and is turned yellow by mineral acids. W. O. K.

Derivatives of Benzthiazole. E. ROMANI (*Gazzetta*, 1922, 52, i, 29—32).—Thiolbenzthiazole, first prepared by Hofmann

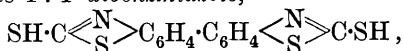
(A., 1887, 823, 1039; cf. Jacobson and Frankenbacher, A., 1891, i, 1048), may be obtained easily and cheaply by heating with sulphur at 260° in a closed space either phenylthiocarbamide or thiocarbanilide or methyleneaniline, phenylthiocarbimide being formed as an intermediate product; the yield of the pure compound amounts to 75—80%. 1-Thiolbenzthiazole is a moderately energetic acid and forms salts of the formula $[C_6H_4<\overset{N}{S}>CS]_2X$.

1-Thiol-5-methylbenzthiazole, , prepared from *p*:*p*-ditolylthiocarbamide and sulphur, forms white crystals, m. p. 177°.

1-Thiol-6-(or 4)-methylbenzthiazole, similarly obtained, has m. p. 161°.

1-Thiol-3-methylbenzthiazole, has m. p. 185°.

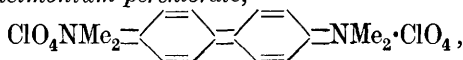
1:1'-Dithiolbis-4:4'-dibenzthiazole,



prepared from *p*:*p*-diphenylenethiocarbamide, forms dark yellow crystals, m. p. 320°, and in alkaline solution readily forms salts of the heavy metals. T. H. P.

The Blue Oxidation Product of Diphenylamine. F. KEHRMANN and G. ROY (*Ber.*, 1922, 55, 156—158).—It was shown by Kehrmann and Micewitz (A., 1912, i, 1020) that the blue product formed by oxidation of diphenylamine with nitric acid in concentrated sulphuric acid is an imonium salt of *N*-*N*'-diphenylbenzidine. In view of doubts thrown on this explanation (this vol., i, 28), further experiments have been made. By oxidation in 60% sulphuric acid with potassium nitrate, the quinhydrone salt of *N*-*N*'-diphenylbenzidine was isolated and was reduced to diphenylbenzidine, m. p. 234—235°. When oxidising in concentrated sulphuric acid, it is necessary to remove nitrous acid by means of a current of air, since this reacts with the imonium salt on diluting, forming products which cannot be reduced to diphenylbenzidine. By oxidation with manganese dioxide in 80% sulphuric acid, a yield of 62% of the theory was obtained. E. H. R.

The So-called Peroxidation Products of Leuco-triphenylmethane Dyes. F. KEHRMANN, GUSTAVE ROY, and MARIE RAMM (*Helv. Chim. Acta*, 1922, 5, 153—157).—It is well known that if excess of lead peroxide be used for the preparation of triphenylmethane dyes from their leuco-compounds, the yield and quality of the product are unsatisfactory. It is now shown that by gradual treatment at the ordinary temperature of a malachite-green solution, not too dilute and acidified with sulphuric acid, with lead peroxide until a diluted sample shows no green tinge, and addition of the filtered solution to perchloric acid, tetramethyl-diphenylquinoneimonium perchlorate,



is precipitated in the form of orange needles, benzoic acid being present in solution. The same perchlorate results from the oxidation of tetramethylbenzidine. Similarly, brilliant-green and tetraethylbenzidine furnish *tetraethyldiphenoquinoneimonium perchlorate*, $C_{20}H_{28}O_8N_2Cl_2$. The same products, with carbon dioxide, were obtained from Michler's hydrol and the corresponding tetraethyl derivative (cf. Rosenstiehl, A., 1895, i, 541). Further, the formation of dinitrotetramethylbenzidine by treatment of tetramethylbenzidine with dilute nitric acid (Bourgeois, *Bull. Soc. Ind. Rouen*, 1882, 503) or nitrous acid (Michler and Pattinson, A., 1882, 199) is preceded by that of tetramethyldiphenoquinoneimonium salts, of which quantitative yields may be obtained in the latter case. J. K.

Preparation of New Therapeutically Active Acridine Derivatives. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 176038).—Therapeutically active acridine derivatives having a bactericidal action are obtained by introducing into the 9-position of acridine, or of its substitution products, an amino-, or substituted amino-group, the substituents being any organic radicles other than aryl groups. These compounds are obtained by causing ammonia or a primary or secondary amine (other than an arylamine) to act on a 9-halogen acridine or a 9-alkoxy- or phenoxy-acridine in presence or absence of a catalyst such as a copper salt. They may also be obtained by reducing a 9-hydrazino-acridine or a 9-nitroacridine, or by decomposing the azides of 9-acridine-carboxylic acids with elimination of nitrogen, or finally by the action of a hypochlorite or hypobromite on the amide of a 9-acridinecarboxylic acid. The following briefly summarises the detailed examples given in the patent specification for the preparation of these acridine derivatives by these various methods, and of the necessary intermediate products. *2-Ethoxy-9-ethanolamino-acridine*, yellow crystals, m. p. 146° , is obtained by mixing amino-ethanol with 2-ethoxy-9-chloroacridine in alcoholic solution at 100° . *2-Ethoxy-9-p-hydroxyphenylethylaminoacridine*, m. p. 233° , is similarly obtained from *p*-hydroxyphenylethylamine. *2-Ethoxy-9-antipyreneaminoacridine*, a yellowish-red base, m. p. 257° , is prepared similarly from 4-aminoantipyrene. *9-Aminoacridine* forms yellow needles, m. p. 236° , and gives a water-soluble *hydrochloride*. It may be obtained by heating 9-chloroacridine with alcoholic ammonia at 140° in presence of copper acetate, or alternatively by heating alcoholic ammonia with 9-ethoxyacridine at 120° for several hours. The reduction of 9-phenylhydrazinoacridine hydrochloride with zinc dust and acetic acid or other reducing agents also furnishes 9-aminoacridine, as also does the decomposition of the amide of acridine-9-carboxylic acid by digestion in a ball mill with potassium hypobromite. The *9-chloroacridine* and its derivatives required for the above preparations are obtained from the corresponding acridones or directly from the arylanthranilic acids by heating them with phosphorus penta- or oxy-chloride. *9-Ethoxyacridine* is obtained by the action of sodium ethoxide on 9-chloro-

acridine; it melts at 83° , and yields acridone when heated with a mineral acid. 2:9-Diethoxyacridine forms fine needles, m. p. 83° . The hydrazinoacridine derivatives are produced by treating 9-halogenacridines with hydrazines. 9-Phenylhydrazinoacridine forms yellow needles, m. p. $173-174^{\circ}$; 2-ethoxy-9-phenylhydrazinoacridine is a light yellow powder, m. p. $232-234^{\circ}$; 9-hydrazinoacridine, $C_{13}H_8N \cdot NH \cdot NH_2$, forms orange needles from alcohol, m. p. 169° ; hydrazino-9:9-bisacridine, $C_{13}H_8N \cdot NH \cdot NH \cdot C_{13}H_8N$, forms dark red crystals, m. p. 265° . 9-Diethylamino-2-ethoxyacridine is prepared by heating 9-chloro-2-ethoxyacridine with diethylamine in alcoholic solution at $130-140^{\circ}$ for six hours in presence of cuprous chloride and copper bronze. The base itself is a thick oil, and it gives a red, crystalline hydrochloride, m. p. 177° . 9-Piperidino-2-ethoxyacridine is prepared in a similar way, using piperidine instead of diethylamine. The base melts at 122° , and gives a water-soluble hydrochloride, m. p. 252° (with decomp.). 9-Ethylaminoacridine from 9-ethoxyacridine and alcoholic ethylamine is an oil which soon solidifies, and recrystallised from dilute alcohol has m. p. 129° . The nitration of 9-aminoacridine in concentrated sulphuric acid yields a dinitro-9-aminoacridine, a dark red base, m. p. above 300° , which on reduction with stannous chloride gives a triaminoacridine hydrochloride, long, yellow needles, and the free base, dark red laminae. 3:9-Diaminoacridine is prepared from 2-chloro-4-nitrobenzoic acid and aniline by way of 5-nitrodiphenylamine-2-carboxylic acid, 3-nitroacridine by elimination of water, 9-chloro-3-nitroacridine by the action of phosphorus pentachloride, yellow needles, m. p. 213° , and 3-nitro-9-aminoacridine, m. p. above 300° (with decomp.), and reduction of this with stannous chloride, or ferrous sulphate and ammonia. 3:9-Diamino-7-ethoxyacridine is prepared by a similar series of reactions starting with *p*-phenetidine instead of aniline. Of the intermediate substances, 4-nitro-2-*p*-phenetidino-benzoic acid melts at $233-234^{\circ}$, 9-chloro-3-nitro-7-ethoxyacridine melts at $186-187^{\circ}$, 3-nitro-9-amino-7-ethoxyacridine is obtainable in two forms, red and yellow; crystallised from nitrobenzene it melts at 310° , and on reduction gives the diaminoethoxyacridine, m. p. $123-124^{\circ}$ (with decomp.). The azide of acridine-9-carboxylic acid, $C_{13}H_8N \cdot CO \cdot N_3$, a very unstable substance decomposing even at the ordinary temperature, is obtained by the action of sodium nitrite on the hydrazine, m. p. 244° , prepared by heating the ester with hydrazine in alcoholic solution. On heating the azide in aqueous suspension, 9-aminoacridine is formed with evolution of nitrogen, whilst if the same decomposition is carried out in alcoholic solution, the urethane, $C_{13}H_8N \cdot NH \cdot CO_2Et$, crystallises on cooling. It melts at $188-194^{\circ}$ and on hydrolysis with 2*N*-sulphuric acid is converted into 9-aminoacridine sulphate. In a similar way, 2-chloro-9-aminoacridine, m. p. $272-274^{\circ}$, is obtained from 2-chloroacridine-9-carboxylic acid, m. p. 264° . The latter substance is synthesised from *o*-chlorobenzaldehyde and magnesium methyl iodide, which give *o*-chlorophenylethyl alcohol and by oxidation *o*-chloroacetophenone, b. p. $98^{\circ}/6$ mm. This is condensed with *p*-chloroaniline to 2-chloro-9-methylacridine, which by Kaufmann's

process (A., 1912, i, 655) is transformed into 2-chloro-9-aldehydo-acridine, m. p. 171—172°, which on oxidation gives the acid. Its *ethyl* ester melts at 71—72°, and the *hydrazide* at 210—211°. From this the azide is obtained by the action of nitrous acid, and on heating it in alcoholic solution the *urethane*, $C_{13}H_7NCl \cdot NH \cdot CO_2Et$, m. p. 205°, is formed. The latter on hydrolysis yields 2-chloro-9-aminoacridine. G. F. M.

Dissociation of the so-called 1:1'-Dibenzyltetrahydro-4:4'-dipyridyl. ERNST WEITZ (*Ber.*, 1922, 55, [B], 599—600; cf. Weitz and Ludwig, this vol., i, 365).—A reply to Emmert (A., 1909, i, 602; 1917, i, 221; 1919, i, 455; 1920, i, 331; this vol., i, 179). The di-iodide results from the bimolecular radicle formed with the aid of oxygen; the monoiodide is derived from the colourless product. H. W.

The Acylated and Alkylated Leuco-indigotins. E. GRANDMOUGIN (*Compt. rend.*, 1922, 174, 758—760).—The author is of the opinion that the acylation or alkylation of leuco-indigotin gives oxygen-substituted derivatives. The acylated derivatives on oxidation give nitrogen acylated derivatives of indigotin owing to the migration of the acyl group. The alkylated derivatives simply undergo saponification and regenerate indigotin. In support of this, it is shown that if methyl sulphate acts on an alkaline solution of indigo white, kept alkaline throughout, a new *dimethyl* derivative, m. p. 252° (decomp.), of leuco-indigotin is obtained, which on oxidation with nitrous acid regenerates indigotin, and on oxidation with chromic acid gives isatin. Acylation under similar conditions must also give an oxygen-substituted derivative, during the oxidation of which the acyl group migrates and the stable ketonic form of the indigotin results. W. G.

Electrochemical Studies in the Pyrazole Group. FR. FICHTER and HUGUES DE MONTMOLLIN (*Helv. Chim. Acta*, 1922, 5, 256—262).—Electrochemical oxidation of a number of pyrazole derivatives results for the most part in the formation of carbon dioxide, with a small amount of subsidiary products. Thus from 1-phenyl-3-methylpyrazolone, a compound, $C_{21}H_{20}O_2N_4, 1\frac{1}{2}H_2O$, apparently methylenbisphenylmethylpyrazolone (Pellizzari, A., 1890, 646) is obtained. Oxidation apparently attacks the 4-position first, since 4-keto-1-phenyl-3-methylpyrazolone and antipyrine are completely destroyed with great rapidity. 1-Phenyl-3:4-dimethylpyrazolone is more resistant, and a small amount of bis-1-phenyl-3:4-dimethylpyrazolone is formed, identical with that prepared by oxidation with nitrous acid, or, better, dilute chromic acid solution. It is accompanied by a compound, $C_{15}H_{14}O_4N_2$, m. p. 242—243°, which is hydrolysed by warm concentrated sulphuric acid to bis-1-phenyl-3:4-dimethylpyrazolone (from oxidation of the phenyldimethylpyrazolone first produced) and fumaric acid, and is therefore probably 1-phenyl-3:4-dimethylpyrazolonyl-2-fumaric acid. Oxidation of 1-phenyl-3-methylpyrazole in acid suspension yields quinone, quinol, and oxalic acid, but no methyl-

pyrazole. From a suspension in potassium carbonate solution, however, pyrazole-3-carboxylic acid is produced. From 3:5-dimethylpyrazole, with sodium sulphate solution as electrolyte, a very small amount of pyrazole-3-carboxylic acid is formed. In these cases, therefore, the action of anodic oxygen is much more vigorous than that of alkaline permanganate (Claisen and Roosen, A., 1894, i, 346; Marchetti, A., 1893, i, 179; Rothenburg, A., 1894, i, 384), and it is noteworthy that oxidation of 1-phenyl-3-methylpyrazole by acid permanganate also destroys, not the pyrazole ring as in the above electrochemical oxidation, but the benzene nucleus (Knorr and Macdonald, A., 1894, i, 543). The electrochemical reduction of the bisulphite compound of 4-keto-1-phenyl-3-methylpyrazolone to 4-hydroxy-1-phenyl-3-methylpyrazolone (Knorr and Pschorr, D.R.-P. 75378) in satisfactory yield is described, as also is the formation of rubazonic acid by electrochemical reduction of 4-oximino-1-phenyl-3-methylpyrazolone, followed by anodic oxidation of the resulting 4-amino-1-phenyl-3-methylpyrazolone. J. K.

The Action of Diazomethane on Uracil. TREAT B. JOHNSON, ARTHUR J. HILL, and FRANCIS H. CASE (*Proc. Nat. Acad. Sci.*, 1922, 8, 44—45).—Diazomethane and uracil slowly react in dry ether to give 1:3-dimethyluracil. The reaction is applicable to pyrimidines of this type, and there is some indication that this reaction may furnish a method for the detection of replaceable hydrogens in the more complicated pyrimidine and purine glucosides. W. G.

The Hydrolysis of Antipyrine Salicylate. I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, 41, 135—144).—Antipyrine salicylate should be regarded as a salt of antipyrine and salicylic acid; it is much hydrolysed in aqueous solution. Its molecular solubility at 18° is 1.32×10^{-2} , its ionic product 6.2×10^{-6} , and its solubility product 1.2×10^{-4} . According to theory, its solubility in solutions of antipyrine should be less, whilst salicylic acid should have only a slight influence; experiment confirms these predictions.

H. J. E.

Spirans. IX. Preparation of Bishydrocarbostyryl-3:3-spiran and its By-products. HERMANN LEUCHS and HANS VON KATINSZKY [with EVA CONRAD] (*Ber.*, 1922, 55, [B], 710—723).—The reduction of ethyl di-*o*-nitrobenzylmalonate to bishydrocarbostyryl-3:3-spiran, $C_6H_4 \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ NH \quad CO \end{smallmatrix} > C \begin{smallmatrix} CH_2 \\ \diagdown \quad \diagup \\ CO \quad NH \end{smallmatrix} > C_6H_4$, has been described by Lellmann and Schleich (A., 1887, 490) and by Radulescu (A., 1911, i, 498); the analytical data quoted by these chemists are not entirely satisfactory, and re-examination of their product has disclosed the presence of a number of chlorinated and oxygenated impurities, some of which have been identified. Suitable modification of their method of preparation leads to the isolation of the pure spiran, which is also obtained by a different process.

According to Radulescu (*loc. cit.*), ethyl di-*o*-nitrobenzylmalonate

is reduced by the gradual addition of concentrated hydrochloric acid to a solution of the ester in hot alcohol in the presence of granulated zinc. The crude spiran which is thereby precipitated is purified by solution in alcoholic potassium hydroxide, filtration, and precipitation with hydrochloric acid; as thus obtained, it is free from zinc, but contains chloro-derivatives which cannot be removed and gives a violet coloration with ferric chloride. It is more conveniently purified by glacial acetic acid, but a homogeneous product cannot thus be obtained. The filtrate from the spiran yields, when concentrated, a mixture of phenolic and neutral substances from which the former are isolated by protracted digestion with concentrated ammonia and subsequent precipitation with acid. They contain *pp'*-*dihydroxybishydrocarbostyryl-3:3-spiran*, $\text{HO}\cdot\text{C}_6\text{H}_3\langle\text{CH}_2\text{---}\text{NH}\cdot\text{CO}\rangle\text{C}\langle\text{CH}_2\text{---}\text{CO}\cdot\text{NH}\rangle\text{C}_6\text{H}_3\cdot\text{OH}$, colourless needles, m. p. 265—268° (decomp.) (*acetate*, coarse, four-sided crystals, m. p. 177—179°), and *p-hydroxybishydrocarbostyryl-3:3-spiran*, thin, colourless needles or prisms, decomp. 255—285° [*acetate*, needles, m. p. 246—248° (decomp.)]. The final residues from the preparation of the spiran contain a basic substance, $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_2$, long, colourless needles, m. p. 192—194° (see later).

Bishydrocarbostyryl-3:3-spiran is prepared in 65—80% yield by dissolving ethyl di-*o*-nitrobenzylmalonate in semi-saturated alcoholic hydrogen chloride solution at -5° to +10° and gradually adding zinc dust; when hydrogen has been evolved freely for some time, the solution is filtered, the filtrate is diluted with an equal volume of water and heated on the water-bath, whereon the spiran separates. It crystallises in broad, lustrous needles, m. p. 350—360°, after darkening at 320°, and sublimes almost without decomposition at 300°/15 mm. The basic substance, $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_2$ (cf. above), is isolable from the filtrates from the spiran and its nature is established by the isolation of a well-defined *hydrochloride*, $\text{C}_{19}\text{H}_{18}\text{O}_2\text{N}_2\cdot\text{HCl}$. Since it contains the ethoxyl group, the following constitutions are possible: $\text{C}_6\text{H}_4\cdot\text{CH}_2\text{---}\text{C}\langle\text{CH}_2\cdot\text{C}_6\text{H}_4\text{---}\text{N}\cdot\text{C(OEt)}\rangle\text{CO}\cdot\text{NH}$ and

$\text{C}_6\text{H}_4\langle\text{CH}_2\cdot\text{C(CO}_2\text{Et)}\cdot\text{CH}_2\text{---}\text{N}\text{---}\text{C}\rangle\text{NH}\cdot\text{C}_6\text{H}_4$. It is converted by hydriodic and acetic acids or by hydrobromic acid into the alkyl-free base, $\text{C}_{16}\text{H}_{14}\text{N}_2$, m. p. 217—218°, which has been described by Reissert as Δ -*N*-tetrahydronaphtholine, but the reaction is of little value in elucidating its constitution. Evidence in favour of the lactim ether formula is based on the observations that it does not yield an acetyl derivative with acetic anhydride, and that it can be prepared from the hydrocarbostyrylspiran by conversion into the imide chloride (cf. Radulescu, *loc. cit.*) and treatment of the latter with sodium ethoxide.

An improved method for the preparation of ethyl di- and mono-*o*-nitrobenzylmalonates is given, but only the former of these is crystalline; the reduction of the latter to ethyl hydrocarbostyryl- β -carboxylate is described. Similar results are recorded with the methyl esters; *methyl di-o-nitrobenzylmalonate* crystallises in colour-

less plates or coarse prisms, m. p. 137—138°, whereas *methyl mono-o-nitrobenzylmalonate* is a yellow liquid which is reduced to *methyl hydrocarbostyryl-β-carboxylate*, colourless, matted needles, m. p. 163—165°. *Ethyl β-o-nitrobenzylhydrocarbostyryl-β-carboxylate*, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > C \begin{smallmatrix} \text{CH}_2 \cdot C_6H_4 \cdot NO_2 \\ CO_2Et \end{smallmatrix}$, pale yellow prisms, m. p. 143·5—144·5°, is prepared by the action of *o*-nitrobenzyl chloride and sodium ethoxide on ethyl hydrocarbostyryl-β-carboxylate, and is reduced to bishydrocarbostyryl-3 : 3-spiran. The conversion of the above ester or of ethyl di-*o*-nitrobenzylmalonate into the spiran takes place with the intermediate formation of the corresponding amino- or diamino-esters; these are too unstable to be isolated in substance, but their formation is demonstrated by diazotisation and subsequent boiling of the diluted solutions of the reduction product whereby *hydrocarbostyryldihydrocoumarin-3 : 3-spiran*, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{O} \cdot \text{CO} \end{smallmatrix} > C \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > C_6H_4$, slender, colourless needles, m. p. about 280° after previous softening, and *bishydrocoumarin-3 : 3-spiran*, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{O} \cdot \text{CO} \end{smallmatrix} > C \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \cdot \text{O} \end{smallmatrix} > C_6H_4$, colourless plates, m. p. 237°, are obtained.

H. W.

A Method for Making Methyl-violet. HENRY JERMAIN MAUDE CREIGHTON (*Proc. Nova Scotia Inst. Sci.*, 1922, **15**, [i], 57—61).—A method is described by which, by the oxidation of dimethylaniline with copper sulphate in presence of phenol and sodium chloride, methyl-violet, a mixture of the hydrochlorides of penta- and hexa-methylpararosaniline, can be obtained in 75—85% yield. [Cf. *J. Soc. Chem. Ind.*, 1922, 323A.] E. H. R.

Behaviour of Azides of Acids. E. OLIVERI-MANDALÀ (*Gazzetta*, 1922, **52**, i, 101—106).—The formation of azides of carbamic acids by the interaction of alkylcarbimides with azoimide (Schroeter, A., 1909, i, 617; Oliveri-Mandalà and Noto, A., 1913, i, 774; Oliveri-Mandalà and Calderaro, A., 1913, i, 961) is found to be a reversible reaction, $R \cdot N : CO + N_3H \rightleftharpoons NHR \cdot CO \cdot N_3$, since addition of phenylcarbylamine to a hot benzene solution of the azide results in the formation of 1-phenyltetrazole, owing to the fixation of the liberated azoimide by the carbylamine. Unlike the azides of carbamic acids, those of thiocarbamic acids, when heated in an indifferent solvent or in aqueous hydrochloric acid, yield polymerides of the corresponding alkylcyanamides (Freund and Hempel, A., 1895, i, 193; Freund and Schwarz, A., 1897, i, 125; Oliveri-Mandalà, A., 1914, i, 1144), derivatives of tetrazole thus being obtainable directly from thiocarbimides by means of the following reactions: (1) $R \cdot N : CS + N_3H \rightarrow NHR \cdot CS \cdot N_3 \rightarrow$ (2) $NHR \cdot C : N$, (3) $NHR \cdot C : N + N_3H \rightarrow NHR \cdot C(N_3) : NH \rightarrow$ (4) $N \begin{smallmatrix} \text{N} \cdot \text{NH} \\ \text{N} : \text{C} \cdot \text{NHR} \end{smallmatrix}$.

The reaction of azoimide on methylthiocarbimide yields a compound, $C_2H_5N_5$, which crystallises in small needles, m. p. 218°.

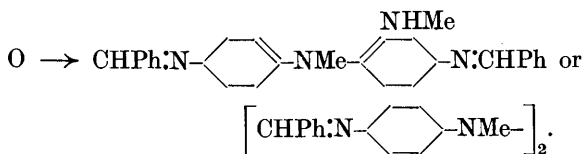
and is probably formed in accordance with the scheme $\text{NMe:C:NH} + \text{N}_3\text{H} = \text{NMe:C(N}_3\text{)·NH}_2 \rightarrow \text{N} \begin{smallmatrix} \text{N·NMe} \\ \text{N:C·NH}_2 \end{smallmatrix}$.

In view of the formation of azides by treatment of the sodium derivative of azoimide with acid chlorides (Schroeter, A., 1909, i, 773), an attempt has been made to prepare nitrosoazide, O:N:N:N or $\text{O:N·N} \begin{smallmatrix} \text{N} \\ \text{N} \end{smallmatrix}$ or $\text{O} \begin{smallmatrix} \text{N:N} \\ \text{N:N} \end{smallmatrix}$, by the action of nitrosyl chloride on sodium azoimide in ethereal solution. The readiness with which the action takes place and the liberation of nitrous oxide and nitrogen in equal volumes indicate the initial addition of azoimide to nitrous acid, thus: $\text{O:NH:O} + \text{N}_3\text{H} = \text{O:NH(N}_3\text{)·OH}$, the unstable additive compound then decomposing into $\text{H}_2\text{O} + \text{N}_2 + \text{N}_2\text{O}$. A further proof of the instability of inorganic compounds containing the triazo-group is furnished by the results of several attempts to obtain the compound $\text{N}_3\text{·OH}$ by decomposing iodoazide (Hantzsch, A., 1900, ii, 274) by means of water and potassium hydroxide at low temperatures.

T. H. P.

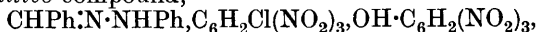
Basic Properties of the Hydrazones. II. R. CIUSA and L. VECCHIOTTI (*Gazzetta*, 1922, 52, i, 128—134; cf. A., 1921, i, 749).—In the formation of an additive compound of a phenylhydrazone with one molecule of each of two aromatic polynitro-derivatives, one and the same compound results, no matter in which order the two polynitro-derivatives are added.

In order to ascertain the influence of substitution of methyl for the methinic hydrogen of benzaldehyde phenylhydrazone on the coloration of the halochromic hydrochloride, the action of gaseous hydrogen chloride on benzaldehyde phenylmethylhydrazone in ethereal solution has been investigated. As with the phenylhydrazone, an orange-yellow hydrochloride is obtained, but on hydrolysis this yields, not the original phenylmethylhydrazone, but a compound, $\text{C}_{28}\text{H}_{26}\text{N}_4$, which corresponds with two mols. of the phenylmethylhydrazone less one mol. of hydrogen and yields benzaldehyde and a compound, $\text{C}_{14}\text{H}_{18}\text{N}_4$, when hydrolysed. The formation of the compound $\text{C}_{28}\text{H}_{26}\text{N}_4$ probably takes place according to the scheme: $2\text{C}_6\text{H}_5\text{·NMe·N:CHPh} \rightarrow 2\text{CHPh·N} \begin{smallmatrix} \text{NHMe} \\ \text{N} \end{smallmatrix} \text{N} \begin{smallmatrix} \text{NHMe} \\ \text{N} \end{smallmatrix} \text{CHPh} +$



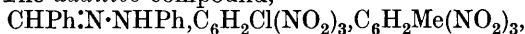
Under similar experimental conditions, anisaldehyde phenylmethylhydrazone yields a compound, $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$, which is isomeric with the phenylmethylhydrazide of anisic acid.

The additive compound,



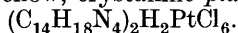
formed by benzaldehyde phenylhydrazone with picryl chloride and

picric acid, crystallises in lustrous, reddish-brown needles, m. p. 94—95°. The *additive* compound,



formed by the same hydrazone with picryl chloride and trinitrotoluene, forms reddish-brown needles, m. p. 82°.

The compound $\text{C}_{28}\text{H}_{26}\text{N}_4$ (*vide supra*) crystallises in small, white needles, m. p. 155°, and in acetic acid solution or when suspended in an acid medium rapidly turns successively green, blue, and violet. The compound $\text{C}_{14}\text{H}_{18}\text{N}_4$ rapidly reduces Fehling's solution and yields a greenish-yellow, crystalline *platinichloride*,



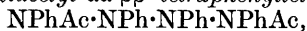
The compound $\text{C}_{15}\text{H}_{16}\text{O}_2\text{N}_2$ (*vide supra*) crystallises in colourless needles, m. p. 233°.

Benzophenonediphenylhydrazone, $\text{C}_{25}\text{H}_{20}\text{N}_2$, forms long, yellow needles, m. p. 145°, and, like tetraphenylhydrazine, yields coloured salts and xylene and formamidine solutions which become more highly coloured when heated, so that the base must be regarded as undergoing hydrolysis: $\text{CPh}_2\cdot\text{N}\cdot\text{NPh}_2 \rightleftharpoons \text{CPh}_2\cdot\text{N}\cdot + \cdot\text{NPh}_2$.

T. H. P.

Amine-oxidation. III. Bivalent Nitrogen. Diarylacylhydrazyls. STEFAN GOLDSCHMIDT and KARL EULER (*Ber.*, 1922, 55, [B], 616—628).—The previous work on triphenylhydrazyl (A., 1920, i, 257) has been extended to α -acetyl(α -benzoyl)-diphenylhydrazyl and α -acetyl(α -benzoyl)-di-*p*-tolylhydrazyl. Evidence of dissociation rests partly on the failure of the solutions to obey Beer's Law, but mainly on the behaviour towards nitric oxide and triphenylmethyl. Results of determinations of molecular weight also indicate dissociation, but these are interpreted with considerable reserve on account of the instability of the solutions. The following order of dissociability is given: $\alpha\alpha'$ -diacetyltetraphenyltetrazen $<$ $\alpha\alpha'$ -dibenzoyltetraphenyltetrazen $<$ $\alpha\alpha'$ -diacetyltetra-*p*-tolyltetrazen $<$ $\alpha\alpha'$ -dibenzoyltetra-*p*-tolyltetrazen.

A suspension of monoacetylhydrazobenzene in cold benzene is converted by lead peroxide in the presence of solid potassium carbonate into $\alpha\alpha'$ -diacetyl- $\alpha\alpha'\beta\beta'$ -tetraphenyltetrazen,



colourless, prismatic crystals, m. p. 126° (decomp.). The substance dissolves in chloroform to a very pale violet-brown solution; in cold toluene, it forms a pale yellow solution which becomes brownish-violet when heated, returning to yellow when cooled, but the operation cannot be repeated indefinitely on account of its instability. The tetrazone, when dissolved in benzene, is immediately decomposed by dry hydrogen chloride into acetanilide and *p*-chloroazobenzene. It combines with nitric oxide, but the product could not be caused to crystallise. (Acetylhydrazobenzene and nitrous fumes give *N*-nitroso-*N'*-acetylhydrazobenzene, a yellow, non-crystalline substance.)

$\alpha\alpha'$ -Dibenzoyl- $\alpha\alpha'\beta\beta'$ -tetraphenyltetrazen, m. p. 114° (decomp.), is prepared by the oxidation of *N*-benzoylhydrazobenzene, m. p. 138°; it gives pale green solutions in benzene, toluene, or chloroform

which undergo rapid decomposition at the atmospheric temperature. It combines readily with triphenylmethyl to give the *compound* $C_{38}H_{30}ON_2$, prismatic plates, m. p. $165-166^\circ$ (decomp.) after darkening at 120° . With nitric oxide, it yields the *substance*, $C_{19}H_{15}O_2N_3$, yellow, prismatic leaflets, m. p. 104° . The action of lead peroxide on *N*-benzoylhydrazobenzene, m. p. 126° (cf. Biehringer and Busch, A., 1903, i, 296; Freundler, A., 1903, i, 663) leads to the immediate formation of azobenzene.

N-Acetylhydrazo-*p*-toluene (from *p*-hydrazotoluene and acetic anhydride at $40-50^\circ$), almost colourless, prismatic platelets, m. p. 120° , is oxidised to $\alpha\alpha'$ -diacetyl- $\alpha\alpha'\beta\beta'$ -tetra-*p*-tolyltetrazan, colourless prisms, m. p. 109° (decomp.). It dissolves in chloroform to an initially colourless solution which rapidly becomes brownish-violet. With triphenylmethyl it gives the *compound* $C_{35}H_{32}ON_2$, colourless crystals, m. p. $156-157^\circ$ (decomp.).

Benzoyl-*p*-hydrazotoluene (cf. Biehringer and Busch, *loc. cit.*) is converted by lead peroxide into $\alpha\alpha'$ -dibenzoyl- $\alpha\alpha'\beta\beta'$ -tetra-*p*-tolyltetrazan, aggregates of needles, m. p. 115° (decomp.), which dissolves in organic media to solutions which are colourless initially, but very rapidly become green and are very unstable. It unites with triphenylmethyl to give the *substance* $C_{40}H_{34}ON_2$, colourless, prismatic crystals, m. p. $146-147^\circ$ (decomp.) after becoming discoloured at 144° .
H. W.

Preparation of *p*-Nitrophenylhydrazine and other Aromatic Hydrazines. WILLIAM DAVIES (T., 1922, 121, 715-721).

Amine-oxidation. IV. Bivalent Nitrogen. $\alpha\alpha$ -Diphenyl- β -trinitrophenylhydrazyl. STEFAN GOLDSCHMIDT and KONRAD RENN (*Ber.*, 1922, 55, [B], 628-643; cf. preceding page).—The elucidation of the exact relationship between triphenylhydrazyl and hexaphenyltetrazan (A., 1920, i, 257) is rendered difficult by the instability of these substances. The present communication is devoted to a description of attempts to prepare more stable hydrazyls, a suitable example being found in $\alpha\alpha$ -diphenyl- β -trinitrophenylhydrazyl, $NPh_2 \cdot NC_6H_2(NO_2)_3$. . ., which exists entirely in the unimolecular form, and is so unusually stable that its molecular weight can be determined in solution with accuracy and certainty. The substance appears to be the nitrogen analogue of Schlenk's tri-triphenylmethyl (A., 1910, i, 236).

It is remarkable that the stability of the hydrazyls cannot be foretold from a consideration of the valency demand of the radicles and that they do not appear to conform to the regularities which have been established by Wieland for the dissociation of tetra-arylhydrazines. Signs of uniform behaviour can be detected within the group, but a general theory cannot be put forward until further members of the series have been prepared.

as-Diphenylhydrazine and *p*-benzoquinone give *benzoquinone-diphenylhydrazone*, $NPh_2 \cdot N \cdot C_6H_4 \cdot O$, m. p. 136° , which is smoothly reduced by ammonium sulphide in alcoholic solution to the corresponding leuco-*compound*, $NPh_2 \cdot NH \cdot C_6H_4 \cdot OH$; the latter is rather

unstable, particularly in the presence of alcohol or alkali hydroxide, and all attempts to methylate it were unsuccessful.

as-Diphenylhydrazine reacts readily with picryl chloride in chloroform solution with almost quantitative production of $\alpha\alpha$ -diphenyl- β -trinitrophenylhydrazine, $\text{NPh}_2\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, long prisms, m. p. $172-173^\circ$ (decomp.), which is reduced by stannous chloride and hydrogen chloride in the presence of ether to diphenylamine and tetra-aminobenzene. When dissolved in dry chloroform it is oxidised readily by lead peroxide in the presence of anhydrous sodium sulphate to $\alpha\alpha$ -diphenyl- β -trinitrophenylhydrazyl, violet-black prisms which show a remarkable resemblance to potassium permanganate. The substance dissolves in all media with the formation of violet solutions similar to those of permanganate; the colour of these shows no diminution in intensity when they are cooled in a mixture of ether and carbon dioxide, thus showing the degree of dissociation to remain unchanged at this low temperature. The solutions are, in general, remarkably stable, but decomposition occurs slowly when they are exposed to direct sunlight. The radicle converts quinol into quinone and is itself reduced to $\alpha\alpha$ -diphenyl- β -trinitrophenylhydrazine, the change in colour being so sharp that solutions of the hydrazyl can be titrated with standard quinol solutions.

The hydrazyl reacts very readily with bromine in chloroform solution, giving the substance, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, slender needles, m. p. $179-180^\circ$ (decomp.) after previous softening; the constitution of the compound follows from the observations that it can be oxidised to a radicle and that it is reduced to tetra-aminobenzene and *bromodiphenylamine*, colourless needles, m. p. 64° .

In contrast to other radicles containing bivalent nitrogen, the hydrazyl does not unite with nitric oxide. It reacts with tetraphenylhydrazine in boiling toluene (under these conditions the latter suffers incipient dissociation); the product, however, is not formed by the expected union of the radicles. The hydrazyl behaves as a dehydrogenating agent, being itself converted into the corresponding hydrazine and transforming the tetraphenylhydrazine into 5:10-diphenyldihydrophenazine, $\text{C}_6\text{H}_4\langle\text{NPh}\rangle\text{C}_6\text{H}_4$, m. p. $169-174^\circ$. It exerts a similar action towards amines and phenols, but the products have not been investigated closely.

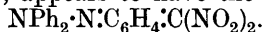
Diphenyltrinitrophenylhydrazyl and triphenylmethyl give a compound, $\text{C}_{37}\text{H}_{27}\text{O}_6\text{N}_5$, short, yellowish-red prisms, m. p. (indefinite) $182-183^\circ$ (decomp.); which cannot have the expected constitution, $\text{NPh}_2\cdot\text{N}(\text{CPh}_3)\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, since it is readily oxidised to a violet radicle. It is therefore assumed that wandering of the triphenylmethyl group has occurred (cf. Wieland, A., 1919, i, 324) with the production of the compound, $\text{CPh}_3\cdot\text{C}_6\text{H}_4\cdot\text{NPh}\cdot\text{NH}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$. Simultaneously, dehydrogenation of the triphenylmethyl must have taken place, since a considerable proportion of the hydrazyl is recovered as hydrazine; this side of the reaction has not been investigated completely.

Diphenyltrinitrophenylhydrazyl, dissolved in benzene, reacts

readily with nitrogen peroxide, yielding β -hydroxy- α -diphenyl- β -trinitrophenylhydrazine, $\text{NPh}_2 \cdot \text{N}(\text{OH}) \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$, large, red crystals with a bluish-black glance, m. p. (indefinite) 156 — 157° (decomp.), after softening and darkening at 145° . The course of the change is probably represented by the scheme $\text{NPh}_2 \cdot \text{N} \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \xrightarrow{\text{NO}_2} \text{NPh}_2 \cdot \text{N}(\cdot\text{O} \cdot \text{N} \cdot \text{O}) \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3 \xrightarrow{\text{H}_2\text{O}} \text{NPh}_2 \cdot \text{N}(\text{OH}) \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$. The constitution assigned to the compound is based on the following observations. It is an acid which dissolves in sodium carbonate to a red solution; it does not yield diphenylamine, tetra-aminobenzene, or *p*-hydroxydiphenylamine when reduced. It is oxidised by lead peroxide to a substance, $\text{C}_{18}\text{H}_{12}\text{O}_7\text{N}_5$, short, blackish-green prisms, m. p. 198° (decomp.), which gives red solutions in organic media. Since it reacts only slowly and gradually with bromine, the substance is regarded as a radicle containing quadrivalent nitrogen, $\text{NPh}_2 \cdot \text{N}(\cdot\text{O}) \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3$. The investigation of the substance is, however, not yet concluded.

H. W.

Amine-oxidation. V. Action of Tetranitromethane on Triphenylhydrazine. STEFAN GOLDSCHMIDT and KONRAD RENN (*Ber.*, 1922, 55, [B], 644—647).—In the hope of obtaining well-crystallised additive compounds of triarylhydrazines, the action of tetranitromethane on triphenylhydrazine dissolved in anhydrous ether has been investigated; the product, bluish-green, lustrous leaflets, decomp. 107° , appears to have the constitution,



It liberates two atomic proportions of iodine from acidified potassium iodide solution and thereby becomes reduced to the leuco-compound, $\text{C}_{19}\text{H}_{16}\text{O}_4\text{N}_4$, colourless crystals, m. p. 85° (decomp.), after darkening at 75° , in a capillary tube filled with carbon dioxide; the latter substance is isolated by reduction of an ethereal solution of the primary compound with zinc dust and glacial acetic acid. More drastic reduction of the quinone with stannous chloride gives diphenylamine and the compound $\text{NPh}_2 \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{N} \cdot \text{OH}$, yellow crystals, m. p. 175° . The position of the $\cdot\text{C}(\text{NO}_2)_2$ group is not established definitely.

H. W.

Action of Mercuric Acetate on certain Aminoazo-compounds. L. VECCHIOTTI (*Gazzetta*, 1922, 52, i, 137—139).—The interaction of mercuric acetate and aminoazobenzene in aqueous alcoholic solution yields the brown compound, $\text{C}_{12}\text{H}_{10}\text{N}_3 \cdot \text{Hg} \cdot \text{OAc}$, m. p. 174° , which blackens and decomposes in light.

The action of mercuric acetate on chrysoidine under similar conditions yields: (1) *Dimercuridiaminoazobenzene diacetate*, $\text{C}_{12}\text{H}_{10}\text{N}_4(\text{Hg} \cdot \text{OAc})_2$, which crystallises in violet-red scales, m. p. 186° . (2) *Monomercuridiaminoazobenzene acetate*, $\text{C}_{12}\text{H}_{11}\text{N}_4 \cdot \text{Hg} \cdot \text{OAc}$, which forms an orange-red powder, m. p. 165° . (3) The compound $(\text{C}_{12}\text{H}_{11}\text{N}_4)_2\text{Hg}$, which crystallises in dark red needles, m. p. 110° .

T. H. P.

Mobility of Protein Ions. WOLFGANG PAULI (*Biochem. Z.*, 1922, 127, 150—155).—Potentiometric experiments on the chlorides

of basic proteins at constant temperature show that the mobility of the protein kation increases to a maximum with increasing concentration of the acid added, due to an increase in the equivalence of the protein ion. This applies to horse serum-albumin, gluten, and glucose. For acidic proteins, casein, globulin, fibrin, which form neutral salts with alkali, conductivity measurements are applicable. Casein forms a trivalent and globulin a quadrivalent anion. H. K.

Are the Carbohydrate Groups which appear in the Acid Hydrolysis of Blood Globulin a Fission Product of the Protein Molecule? LEO LANGSTEIN (*Biochem. Z.*, 1922, 127, 34—37).—Carefully purified globulin on hydrolysis by dilute sulphuric or hydrobromic acid gives between 0.5 and 1% of reducing substances with a positive fermentation test. The carbohydrate is considered to be an essential constituent of the globulin molecule. H. K.

Casein from Cow's Milk. B. BLEYER and R. SEIDL (*Biochem. Z.*, 1922, 128, 48—75).—A comparison has been made of two specially purified caseins, one prepared by the action of lactic acid on milk and the other by the action of rennin. The acid-casein contained 15.5% N and rennin-casein 15.64%. The equivalent weight of both caseins was 1145 when neutralised to phenolphthalein by alkali hydroxides, ammonia, or alkaline-earth hydroxides. When excess of the two caseins was shaken with increasing amounts of calcium, strontium, or barium hydroxides at constant temperature, the ratio of the alkali taken up by the caseins to the amount left free in the solution was a constant (Henry's law). When shaken with increasing content ($N/2500$ to $N/100$) of hydrochloric, sulphuric, lactic, or acetic acid the rennin-casein absorbed more of each of the acids than the acid-casein. Henry's law was obeyed for the highest dilutions of acids, but at higher concentrations the relation is one of adsorption. H. K.

The Thermostable Active Agent of Pig's Pancreas. WALTER JONES (*J. Biol. Chem.*, 1922, 50, 323—328).—Evidence is now adduced to show that hydrolysis of yeast-nucleic acid into its nucleotides by boiled pancreas extract (A., 1920, i, 687) does not produce any increase in the titratable acidity of the solution, although addition of adenine nucleotide to the digested solution increases the titratable acidity by an amount which agrees with that calculated from the weight added. Levene's criticism (A., 1921, i, 821) of the author's formula for yeast-nucleic acid can, therefore, no longer be maintained. E. S.

Histopeptone. K. FELIX (*Z. physiol. Chem.*, 1922, 119, 66—71).—Histopeptone is a homogeneous substance. The figures obtained for the hexone bases agree with those obtained by Kossel. No new substances could be obtained by fractionating the peptone by "salting out" or by precipitation by the silver-baryta method at different hydrogen-ion concentrations. S. S. Z.

The Action of Pepsin and Trypsin on Diastase. W. BIEDERMANN (*Biochem. Z.*, 1922, **127**, 38—46).—Experiments with salivary diastase show that the enzyme is destroyed by pepsin, but not by trypsin. H. K.

Asymmetric Syntheses by means of Enzyme Action. IV. L. ROSENTHALER (*Fermentforsch.*, 1922, **5**, 334—341; cf. A., 1909, i, 74, 622; 1910, i, 603).—A dextrorotatory nitrile is obtained by the action of hydrocyanic acid in the presence of emulsin on citronellal, isovaleraldehyde, or *p*-tolualdehyde, whereas *o*-chlorobenzaldehyde gives a dextrorotatory product. The nitrile obtained from *o*-methoxysalicylaldehyde, benzoyl-*o*-methoxysalicylaldehyde, or benzoylvanillin is optically inactive.

The optical activity of the products obtained from isovaleraldehyde, heptaldehyde, benzaldehyde, anisaldehyde, cinnamaldehyde, citral, or citronellal attains a maximum value after a given interval of time and subsequently diminishes; the rates of increment and decrement vary greatly with the different aldehydes.

The possibility that emulsin not only catalytically accelerates the formation of nitrile but also causes a displacement of the equilibrium towards the nitrile side has been discussed previously; with acetaldehyde and isobutaldehyde, this displacement is not very marked, whereas with benzaldehyde the results are not uniform, although in one instance a pronounced displacement was observed.

The addition of hydrocyanic acid to acetaldehyde, isobutaldehyde, and benzaldehyde is a reaction of the second order; in the presence of emulsin this is not strictly the case, since the "constants" generally diminish regularly, thus indicating a consumption or inactivation of the catalyst (cf. Nordefeldt, this vol., i, 66). The action of hydrocyanic acid on acetaldehyde, isobutaldehyde, benzaldehyde, anisaldehyde, or *o*-nitrobenzaldehyde in the presence of sodium hydroxide is termolecular, but the mode of action of the alkali hydroxide has not yet been elucidated. H. W.

Carboligase. III. CARL NEUBERG and HEINZ OHLE (*Biochem. Z.*, 1922, **127**, 327—339; cf. A., 1921, i, 480; this vol., i, 305).—The product arising from benzaldehyde and pyruvic acid under the influence of carboligase has now been shown to have the constitution $l\text{-OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{CH}_3$. On treatment with magnesium phenyl bromide, it gives *d*- $\alpha\beta$ -dihydroxy- $\alpha\beta$ -diphenylpropane, m. p. 83—84°, $[\alpha]_D^{25} +45.1^\circ$ in alcohol, $+31.85^\circ$ in acetone (cf. McKenzie and Wren, T., 1910, **97**, 473). Further treatment with dilute sulphuric acid gave α -methyldeoxybenzoin. The racemic substances, $\text{OH}\cdot\text{CHPh}\cdot\text{CO}\cdot\text{CH}_3$ and $\text{Ph}\cdot\text{CO}\cdot\text{CH}(\text{CH}_3)\cdot\text{OH}$, stated to have been synthesised by previous workers, are now shown to be the same substance, probably an equilibrium mixture of the two. H. K.

Artificial Zymogens. II. MARTIN JACOBY (*Biochem. Z.*, 1922, **128**, 80—88; cf. A., 1920, i, 690).—More nickel is taken up by a urease solution than by water, as is indicated by Tschugaev's test. The longer a urease solution is kept in contact with nickel powder or nickel oxide, the greater is the falling off of enzymic activity

due to formation of artificial zymogen. The filtrates from such solutions are restored to their original or slightly greater activity by potassium cyanide. H. K.

Artificial Zymogens. III. MARTIN JACOBY and T. SHIMIZU (*Biochem. Z.*, 1922, **128**, 89—94).—Metallic nickel, cobalt, copper, and zinc inactivate urease, but iron is without action. Cobalt, copper, and zinc act more quickly than nickel, and in the case of cobalt and copper, the quantity of artificial zymogen which can be reactivated by potassium cyanide or glycine falls off rapidly with time. H. K.

Artificial Zymogens. IV. Inactivation and Reactivation of Takadiastase. MARTIN JACOBY and T. SHIMIZU (*Biochem. Z.*, 1922, **128**, 95—99).—Diastase solution is not inactivated by contact with metallic iron, nickel, copper, or cobalt. Inactivation by mercuric chloride is temporary, being restored by potassium cyanide. H. K.

Adsorption of Ferments and Zymogens. I and II. MARTIN JACOBY and T. SHIMIZU (*Biochem. Z.*, 1922, **128**, 100—102, 103—107).—I. Tribasic calcium phosphate partly adsorbs urease, but does so more completely in the presence of electrolytes. Urease inactivated by nickel or cobalt is completely adsorbed and is reactivated by potassium cyanide. Dibasic calcium phosphate has no action.

II.—Urease solution treated with an alcoholic solution of cholesterol and filtered loses activity, the precipitate being very slightly active and the filtrate slightly active, but having its activity restored by glycine or serum. An inactivated urease (by nickel), when treated with cholesterol and filtered, passes unchanged into the filtrate and is reactivated by glycine or potassium cyanide. H. K.

The Influence of Cobaltammines on the Action of Catalase and Amylase. EBERHARD FUNK (*Biochem. Z.*, 1922, **128**, 108—118).—Hexamminecobaltic chloride, nitropentamminecobaltic chloride, dinitrotetramminecobaltic chloride, trinitrotri-aminocobalt, potassium tetranitrodiamminecobaltate, and sodium cobaltinitrite inhibit the action of catalase, the inhibition increasing with decrease in the number of ammonia groups. In the presence of a phosphate buffer, P_H about 7, the earlier members of the series no longer inhibit. Unlike catalase, amylase (takadiastase) has its action accelerated by this series of complex salts. H. K.

Preparation of Derivatives of 3 : 3'-Diamino-4 : 4'-dihydroxyarsenobenzene. GEORG SPEYER-HAUS (Brit. Pat. 155577).—Derivatives of salvarsan which are stable in aqueous solution are obtained by dissolving together equal weights of the methylene sulphonylate of 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene and its sodium salt or the complex silver compound of the sodium salt. That new chemical compounds are thereby formed is proved by the fact that the resulting solutions no longer give precipitates with

carbon dioxide, and the silver solution gives no precipitate with sodium chloride. The solutions keep unchanged for many hours without formation of any precipitate or increase in toxicity or any loss of therapeutic activity.

G. F. M.

Aromatic Compounds of Antimony. V. Differing Behaviour of Lithium Hydroxide from that of Sodium or Potassium Hydroxide in the Hydration of Polymeric Arylstibinic Acids. HANS SCHMIDT (*Ber.*, 1922, 55, [B], 697—701; cf. A., 1920, i, 900).—It has been shown previously that a solution of trimeric phenylstibinic acid appears to be neutralised initially by one molecular proportion of sodium hydroxide (indicator, phenolphthalein) but that in course of time further quantities of alkali hydroxide are required until, finally, nearly three molecular proportions have been added. The phenomenon has been regarded as a fission of the trimeric to the monomeric form. Potassium hydroxide resembles sodium hydroxide in its behaviour, but the acid appears capable of neutralising only a markedly smaller proportion of lithium hydroxide, with which hydration seems only to proceed to the dimeric stage: $(\text{PhSbO}_2)_3 = (\text{PhSbO}_2)_2 + \text{PhSbO}_2$. *p*-Aminophenylstibinic acid resembles the parent acid closely in its behaviour. On the other hand, *p*-chloro-, *m*-nitro-, and *p*-chloro-*m*-nitro-phenylstibinic acids are hydrated by lithium hydroxide in the same manner as by sodium hydroxide. A satisfactory explanation of the differing behaviour of the various alkali hydroxides cannot at present be given.

H. W.

Physiological Chemistry.

Comparative Investigations on the Blood Sugar Content of the Arterial and Venous Vascular Systems. KARL TURBAN (*Z. physiol. Chem.*, 1922, **119**, 4—10).—The sugar content of the arterial and venous blood of starving and fed dogs was studied. Generally the arterial blood showed a higher sugar content than venous blood.
S. S. Z.

Blood Sugar. I. A Critical Survey of the Methods of Estimation of Blood Sugar and of the "Threshold" Concept. MAX ROSENBERG (*Arch. expt. Path. Pharm.*, 1922, **92**, 153—164).—The methods dealt with are those of Bang and of Bertrand. The sources of error are considered and stress is laid on the importance of making the estimations under basal physiological conditions, and on the advisability of estimating the sugar of the plasma rather than that of the whole blood.

From a consideration of the available literature the author concludes that the threshold value is not a constant in any individual, but varies with the physiological needs of the organism as a whole.

C. R. H.

Influence of Amino-acids and Fatty Acids on the Regulation of the Blood Sugar. LEO POLLAK (*Biochem. Z.*, 1922, **127**, 120—136).—Subcutaneous injection into normal rabbits of 1 gram of glycine, alanine, or asparagine produced hyperglycæmia, as also does Witte peptone, but not leucine. Hyperglycæmia is also produced by saturated fatty acids with an uneven number of carbon atoms, those with an even number being inactive. Previous or simultaneous injection of ergotamine (Sandoz) completely inhibits the hyperglycæmia. The effect is in each case attributed to mobilisation of glycogen due to stimulation of the sympathetic nerve-endings.
H. K.

The Ammonia Content of Blood. THOMAS P. NASH, jun., and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, **51**, 183—185).—Further experiments are described confirming the conclusion that ammonia is formed by the kidney (cf. this vol., i, 191).
E. S.

The Amino-acid Nitrogen Content of the Blood. SEIZABURO OKADA and TOWORU HAYASHI (*J. Biol. Chem.*, 1922, **51**, 121—133).—Estimations were made of the amino-acid nitrogen content of the blood in certain pathological cases, and in animals under experimental conditions. No increase was observed following subcutaneous injection of adrenaline or pituitrin or removal of the thyroid gland. Increases were, however, observed after injection of pilocarpine and after removal of the kidneys, whilst complete removal of the pancreas produced a transient rise. The amino-acid content of human blood varies with the number of white corpuscles, in which the amino-acids appear to be concentrated. It is suggested that the nuclei are responsible for this concentration.
E. S.

The Effect of Carbon Monoxide, Illuminating Gas, and Benzene on Blood Coagulation Time. H. S. FORBES and LOUISE HOMPE (*J. Ind. Hyg.*, 1921, **3**, 213—216).—Experiments showed no constant change of coagulation time in the blood of cats gassed with these gases. The prothrombin content of the blood was unaltered; there was no evidence of hæmolysis or of blood destruction. The condition of coma found in fatal human cases of illuminating gas poisoning could not be duplicated in cats. They died in the gas or recovered entirely.
CHEMICAL ABSTRACTS.

Separate Analyses of the Corpuscles and the Plasma. HSIEN WU (*J. Biol. Chem.*, 1922, **51**, 21—31).—The system of blood analysis developed by Folin and Wu (A., 1919, ii, 308; A., 1920, ii, 337) may be applied to the corpuscles and plasma separately. From the results of analyses of normal human blood the following approximate ratios, representing the concentration in the plasma to that in the corpuscles, are given for the various constituents: urea 1 : 1, sugar 1 : 1, uric acid 2 : 1, chloride 2 : 1, amino-acids 1 : 2. Creatine is practically absent from the plasma, whilst undetermined non-amino-nitrogen, which, it is suggested, represents peptides and peptones, is confined almost entirely to

the corpuscles. These and other results indicate the desirability of substituting plasma analysis for whole blood analysis. E. S.

Fixation of Quinine by Corpuscles and its Action on Cell Respiration. P. RONA and E. BLOCH (*Biochem. Z.*, 1922, **128**, 169—184; cf. A., 1922, i, 65).—The red blood-corpuscles of birds and of mammals are permeable to quinine and its salts, but yeast-cells are only permeable to quinine. On the respiration of corpuscles, the base alone has an inhibitory action, the first effect being to accelerate respiration, followed by inhibition of respiration until an equilibrium is reached where the respiration attains a constant value with time. At this point the inhibition is proportional to the concentration of the quinine. H. K.

The Non-hæmoglobin Nitrogen Content of Corpuscles, a Contribution to the Nitrogen-metabolism of Tissues. RUDOLF SCHOEN (*Biochem. Z.*, 1922, **128**, 293—309).—The author has estimated the nitrogen content, by Bang's micro-Kjeldahl method of analysis, of washed and defibrinated blood-corpuscles of normal and pathological cases. The hæmoglobin content, the volume, and the number of the corpuscles have been estimated simultaneously. As the nitrogen content of hæmoglobin is known, an approximate value for the non-hæmoglobin nitrogen can be obtained. For normal men, one million corpuscles contain 0.00563 mg. of nitrogen, for women 0.00527. The value is not subject to much variation. H. K.

The Glycogen Content of White Blood-corpuscles. J. DE HAAN (*Biochem. Z.*, 1922, **128**, 124—143).—By means of a micro-method for the estimation of glycogen depending on the use of Pflüger's method and Bang's method for the estimation of the dextrose produced on hydrolysis, the author has examined the glycogen content of the leucocytes with special reference to their iodophilic properties. The glycogen content of leucocytes from serous exudates from rabbits and goats is between 1 and 2%, and is uninfluenced by injections of starch or dextrose. In vitro, however, the glycogen content of leucocytes quickly falls off, due probably to lysis, unless fixed by some reagent, when it becomes resistant to diastase. The normal leucocytes of the blood of the horse and of the pig contain about 1% of glycogen, which is the sole glycogen in the blood. H. K.

Comparison of the Viscosity and Velocity of Ultra-filtration of Serum. ALEXANDER ELLINGER and S. M. NEUSCHLOSZ (*Biochem. Z.*, 1922, **127**, 241—254).—A comparison of the relative viscosities of serum-Ringer solution mixtures and their relative velocities of ultra-filtration shows a relationship to exist but no exact inverse proportionality. With increasing P_H of the solution, the velocity of ultra-filtration falls off and the viscosity increases. Anions increase the viscosity of inactivated horse-serum in the order citrate > sulphate > acetate > Cl > Br > I > SCN. The presence of small quantities of caffeine may raise or depress the viscosity, depending on the P_H of the solution. H. K.

Water and Ionic Distribution in the Organism. HEINRICH REICHEL (*Biochem. Z.*, 1922, **127**, 322—326).—The change of colour of a dialysed serum solution containing methyl-orange on addition of sodium chloride is attributed to a new distribution of the indicator between what the author regards as practically anhydrous emulsoid phase and the aqueous solution. H. K.

The Influence of Radiations on the Hydrolysis of Fats. LUDWIG PINCUSSEN and J. L. ANAGNOSTU (*Biochem. Z.*, 1922, **128**, 268—273).—Butyrin or tributyrin in aqueous solution, exposed to the light of an arc or incandescent lamp, with or without the addition of sensitising dyes (eosin or methylene-blue) are unchanged, as is shown by measurements with the viscostalagmometer. The hydrolytic action of normal rabbit's serum on butyrin or tributyrin falls off slightly on exposure to an incandescent lamp, but is unchanged under Röntgen radiation. Experiments on exposure of rabbits to various sources of radiation are interpreted in a somewhat similar manner. H. K.

Distribution of Enzymes in the Alimentary Canal of the Chicken. ROBERT HENRY ADERS PLIMMER and JOHN LEWIS ROSEDALE (*Biochem. J.*, 1922, **16**, 23—26).—In the crop of the chicken diastase, lactase, and a weak peptic enzyme are present; in the proventriculus, a peptic enzyme; in the pancreas, diastase, lipase, and proteoclastic enzymes which act in neutral, acid, and, particularly, alkaline media; in the whole intestine, invertase, diastase, and peptic and tryptic enzymes; in the duodenum, peptic and tryptic enzymes; and in the caeca, diastase.

W. O. K.

Intestinal Saccharase. E. KNAFFL-LENZ (*Z. physiol. Chem.*, 1922, **119**, 60—65).—The surviving intestine of the rabbit can invert sucrose. The inversion velocity is of the same order of magnitude as that obtained by Euler and Svanberg with minced pig's intestine. The inversion velocity is one-half the normal after the intestine is irrigated, which shows that the enzyme is secreted by the cells in the intestine. S. S. Z.

The Rôle of Acid in Carbohydrate Metabolism. V. The Action of Acid and Alkali on the Carbohydrate Metabolism of Yeast-cells. H. ELIAS and ST. WEISS (*Biochem. Z.*, 1922, **127**, 1—12).—By treatment with acid, the glycogen content of yeast-cells remains unaltered, but with alkali the glycogen increases and at higher concentrations of alkali passes into the surrounding fluid. The increase of glycogen is not at the expense of the sugar, but of protein, as is demonstrated by the increase in non-precipitable nitrogen. H. K.

Carbohydrate Metabolism. III. A Study of Urinary Sugar Excretion in Twenty-six Individuals. ISAAC NEUWIRTH (*J. Biol. Chem.*, 1922, **51**, 11—16).—An extension of work previously described (Benedict, Österberg, and Neuwirth, A., 1918, i, 322) to a larger number of individuals. E. S.

The Relations between Fats and Carbohydrates. HANS MÜLLER (*Helv. Chim. Acta*, 1922, 5, 163—166).—Whilst much light is thrown on the metabolic relationships of carbohydrates to proteins by the interconversions of alanine and lactic acid (Neuberg and Langstein, *Arch. Anat. Physiol.*, 1913, *Suppl.*, 514; Embden and others, *A.*, 1911, ii, 53; 1912, ii, 278, 279), less is known in regard to the fats, which mostly contain an even number of carbon atoms, and of which β -oxidation furnishes only compounds containing two carbon atoms. It is probable, however, that δ -oxidation may occur (Spiro, this vol., i, 489) furnishing, for example, succinic and butyric acids. The organism contains an oxydase by which succinic acid can be converted into fumaric acid (Battelli and Stern, *A.*, 1911, ii, 132); the latter has been detected in fresh meat (Einbeck, *A.*, 1914, i, 773) and is now stated rapidly to furnish carbon dioxide and lactic acid when its sodium salt is treated with fresh yeast. This observation explains the "gluconeogeny" arising from succinic and fumaric acids (Cremer, *Berl. klin. Woch.*, 1913, 50, 1457). The formation of lactic acid from succinic acid is to some extent analogous to that of acetone from butyric acid. Since acetone may also be produced from proteins (Friedmann, *A.*, 1908, ii, 719; 1913, i, 1277), and succinic acid is an oxidation product of glutamic acid (Neuberg and Ringer, *A.*, 1915, i, 1046), the question arises as to whether the above observations are not applicable to the question of protein metabolism.
J. K.

The Biological Difference of Stereoisomerides. A. JUNG and H. MÜLLER (*Helv. Chim. Acta*, 1922, 5, 239—243).—Fumaric acid, but not its stereoisomeride, maleic acid, can give rise to "gluconeogeny" (Cremer, *Berlin. klin. Woch.*, 1913, 50, 1457). Further, the formation of lactic acid (into which fumaric acid is convertible by a carboxylase in yeast), in the organism of starving dogs suffering from phosphorus poisoning is suppressed in favour of gluconeogeny by administration of phlorricin. The connexion between the conversion of fumaric acid into lactic acid and gluconeogeny is borne out by the fact that yeast has no action on maleic acid. This, rather than their relative toxicities (Cremer, *loc. cit.*), is the cause of their different gluconeogenetic properties. Further, it is shown that whilst fumaric acid facilitates fermentation, maleic acid inhibits it. Malic acid is fermented even more rapidly than fumaric acid, a fact which supports the view, arrived at from other considerations, that the latter, rather than the former, represents the primary product of the metabolism of succinic acid. The fact that β -hydroxybutyric acid is easily fermented whilst crotonic acid is unchanged points to the same conclusion. Acrylic and cinnamic acids are unaffected by yeast.
J. K.

Reductions and Oxidations and a Coupled Reaction in the Intermediary Metabolism of the Animal Body. F. KNOOP (*Biochem. Z.*, 1922, 127, 200—209).—When α -amino- γ -phenylbutyric acid was administered orally to a dog, the *N*-acetyl derivative was excreted in the urine in proportionate amount.

If there be administered simultaneously pyruvic, butyric, or acetic acid the increase of acetylated product is respectively 50%, 18%, nil. Pyruvic acid is therefore the acetylating agent of the body. The amino-acid is oxidised to an imino-acid which combines with loss of carbon dioxide to yield the acetyl derivative of the amino-acid.

H. K.

Observations on Sugar Synthesis. I. J. K. PARNAS and RICHARD WAGNER (*Biochem. Z.*, 1922, **127**, 55—65).—A nine-year-old girl with a liver tumour had an abnormal sugar metabolism as indicated by negligible content of sugar in the blood after a fast (morning) and a urine rich in acetone. After a meal rich in carbohydrate the blood sugar rose to as high as 0.4%. This lasted a considerable time with absence of ketonuria, but with pronounced glycosuria. Administration of adrenaline showed no effect on the normal sugar content, but feeding with the following, proteins, glycine, alanine, glutamic acid, calcium lactate, caused an increase of sugar in the blood to about 0.1%. Administration of fats in the aglycæmic condition failed to produce sugar in the blood.

H. K.

Metabolism of Sulphur. IV. The Oxidation of Cystine in the Animal Organism. HOWARD B. LEWIS and LUCIE E. ROOT (*J. Biol. Chem.*, 1922, **50**, 303—310).—The administration of phenylcarbamido-cystine, both orally and subcutaneously, to rabbits was found to produce an increase in the unoxidised sulphur content of the urine. Using cystine under the same conditions, no such increase was observed, the sulphur in this case being eliminated as sulphate. Protection of the amino-group thus prevents oxidation of the cystine molecule, a result which indicates that deamination precedes, or is connected with, oxidation of the sulphur. A slight increase in the sulphate content of the urine which was observed after oral administration of phenylcarbamido-cystine is attributed to bacterial action.

E. S.

The Transportation, Retention, and Excretion of Carbohydrates. OTTO FOLIN and HILDING BERGLUND (*J. Biol. Chem.*, 1922, **51**, 213—273).—A critical review of the more important literature of the subject is given. In the experiments performed, estimations were made of the sugar content of blood and urine after ingestion of various carbohydrates. Lower values than those given by other investigators were obtained for blood sugar, a result which is attributed to the absence from the subjects employed of emotional complications. With the exception of one case of renal glycosuria (subnormal renal threshold), and in the absence of emotional hyperglycæmia, no glycosuria was obtained after the ingestion of pure dextrose in amounts up to 200 grams. Following every ordinary carbohydrate meal, however, a definite glycuressis (Benedict, Osterberg, and Neuwirth, A., 1918, i, 322) was obtained, which was found to be independent of the level of blood sugar. This, apparently, is due to the absorption and excretion of sugars other than dextrose and lævulose, of unusable

materials present in food or produced from it during preparation, and to products of endogenous metabolism. The sugar of normal urine thus consists of a variety of carbohydrate products and derivatives.

A renal threshold analogous to, but independent of, that of dextrose exists for l  vulose, but not for galactose or lactose. The utilisation of galactose depends on the amount of dextrose available.

The failure of sugar to accumulate in the blood is considered to be due, in the first place, to absorption by the tissues rather than to glycogen formation. When the tissues are well supplied, the need for sugar transportation ceases. Hypoglyc  mia is probably a reflection of this, and is thus a normal consequence of carbohydrate ingestion.

The distribution of blood sugar between plasma and corpuscles is almost uniform during fasting, but varies irregularly at other times. Hydrolysis usually diminishes the sugar content of the plasma and increases that of the corpuscles. The latter, therefore, probably contain polysaccharides. E. S.

The Value of Gelatin in Relation to the Nitrogen Requirements of Man. ROBERT ROBISON (*Biochem. J.*, 1922, **16**, 111—130).—On a diet practically free from nitrogen, a certain minimum amount of nitrogen, derived from the tissues of the body, is used and excreted. If a diet otherwise equivalent but containing nitrogen in the form of gelatin be given there is a saving in the body-nitrogen so used. By feeding on diets containing, in the gelatin, 4.88 grams, 7.54 grams, and 12.00 grams of nitrogen per day, the author has found, after making certain allowances, a saving of between 11.9 and 15.9%, 0 and 5.3%, 8.1 and 14.7%, respectively, of the minimum body-nitrogen.

The ratio of the nitrogen balance (nitrogen intake minus nitrogen output in urine) to the creatinine nitrogen is found to be fairly constant, and to be equal to that ratio as determined by McCollum (A., 1912, ii, 72) for the pig. W. O. K.

Conditions of Inactivation of the Accessory Food Factors. SYLVESTER SOLOMON ZILVA (*Biochem. J.*, 1922, **16**, 42—48).—The accessory food factors in cod liver oil and in decitrated lemon juice are easily destroyed by ozone at the ordinary temperature, whereas autolysed yeast retains its activity under exposure to ozone. Passing air through decitrated lemon juice at the ordinary temperature, or through cod liver oil at 120  , destroys their active factors. Ultra-violet rays have no effect on the accessory food factors in the absence of air. The effect of boiling is apparently due to oxidation as the potency of decitrated lemon juice is not destroyed by boiling in an atmosphere of carbon dioxide. It also retains its activity to a very considerable extent after hydrolysis for five hours by 2*N*-hydrochloric acid in an atmosphere of carbon dioxide. W. O. K.

Calcium in Egg-shell Formation. G. D. BUCKNER, J. H. MARTIN, W. C. PIERCE, and A. M. PETER (*J. Biol. Chem.*, 1922, **51**, 51—54).—The experiments described indicate that hens can

utilise calcium carbonate for the production both of egg-shell and bones, whilst tricalcium phosphate can be utilised for the latter purpose only. E. S.

Chemistry of Normal and Abnormal Pregnancies. J. A. KILLIAN and CARL P. SHERWIN (*Amer. J. Obstet. Gynecol.*, 1921, 2, 6—16).—In nephritic toxemias there is an increase in the non-protein and urea nitrogen of the blood, and more than 50% of the non-protein nitrogen is in the form of urea nitrogen. In normal pregnancies the urea nitrogen amounts to about 44% of the non-protein nitrogen, and for both the values are low. Normally in pregnancy the uric acid, creatinine, chloride, and sugar concentrations of the blood are not changed as compared with non-pregnant women. The carbon dioxide-combining power of the blood plasma is slightly increased late in pregnancy. In pernicious vomiting and eclampsia the non-protein nitrogen is greatly increased but the urea nitrogen amounts to but 15 to 38% of the non-protein nitrogen. Uric acid is increased. CHEMICAL ABSTRACTS.

Blood Chemistry in Normal and Abnormal Pregnancy. WM. E. CALDWELL and WM. G. LYLE (*Amer. J. Obstet. Gynecol.*, 1921, 2, 17—34).—Comparative values are given as follows :

	Non-protein N.	Urea N.	Creatinine.	Uric acid.	Ratio : Urea N : Non-protein N.
Non-pregnant	35 mg. or less	18 mg. or less	2 mg. or less	3 mg. or less	50%
Normal pregnancy	29·69	11·51	1·05	1·73	39%
Eclampsia and toxemia...	49·7	26	2·17	6·19	52%

CHEMICAL ABSTRACTS.

Lipoids of the Crystalline Lens. M. GOLDSCHMIDT (*Biochem. Z.*, 1922, 127, 210—213).—The dried and powdered crystalline lens of the human eye at various ages was extracted successively with alcohol, light petroleum, acetone, and benzene. The light petroleum fraction consisted of cholesterol. The alcohol-soluble fraction was separable into substances no longer soluble in alcohol, cholesterol, and a phosphatide. Graphs are given showing the variations in cholesterol, phosphatide, acetone-soluble substances, and benzene-soluble substances with age. H. K.

The Cleavage Products of the Crystalline Lens. YOSHIZUMI HIRIKATA (*J. Biol. Chem.*, 1922, 51, 155—164).—The following percentages of amino-acids, calculated on the ash- and water-free substance, were isolated from the hydrolysis product of the crystalline lens of the ox : Alanine 4·7, valine 1·0, leucine 6·8, aspartic acid 1·4, glutamic acid 15·5, lysine 1·6, arginine 3·3, phenylalanine 1·9, tyrosine 4·5, proline 2·2, histidine 1·6. A positive test was obtained for tryptophan. Adenine, identified by the melting point of its picrate, was also present, but no other purine bases were isolated. E. S.

Lyotrope Series and β -Oxidation. K. SPIRO (*Biochem. Z.*, 1922, 127, 299—311).—Experiments on the isolated frog's heart
s*

show that anions affect the action of potassium. Potassium combined with thiocyan-anion is more toxic than with chloridion and the latter more so than with acetanion. Calcium chloride inhibits the toxicity of potassium chloride but not that of potassium thiocyanate. The primary toxic action of methyl and ethyl alcohols on the frog's heart is equivalent, but whereas the action of ethyl alcohol can be inhibited by washing out, that of methyl alcohol is almost unaffected. H. K.

Localisation of the Degradation of Fats in the Body. JULIUS BAER (*Biochem. Z.*, 1922, **127**, 275—285).—Injection of butyric acid into the lymph sac of frogs is followed by excretion of small quantities of acetoacetic acid. This acid and butyric acid are destroyed to a considerable extent by normal frogs and by frogs with extirpated livers. β -Hydroxybutyric acid is oxidised by both types of frogs to acetoacetic acid. H. K.

Liver Function. III. Phenol Conjugation as Influenced by Liver Injury and Insufficiency. K. F. PELKAN and G. H. WHIPPLE (*J. Biol. Chem.*, 1922, **50**, 513—526; cf. this vol., i, 86).—Experiments on dogs in which *p*-cresol was ingested before and after injury to, or exclusion of, the liver, the percentage conjugation which occurred being estimated in each case, indicate that conjugation of phenols is a function of the liver and of no other organ. E. S.

Oil from the Liver of *Acanthias vulgaris*. T. LEXOW (*Chem. Umschau*, 1922, **29**, 59—60).—The oil from the liver of *Acanthias vulgaris* is almost water-white and has a faint, not unpleasant odour. When kept at 15°, some stearin is deposited. The following numbers were obtained: d_{15}^{15} , 0.9125; acid number, nil; saponification number, 156.4; iodine number (Wijs), 110.1; unsaponifiable matter, 12.31%; fatty acids, 79.28%; glycerol, 8.18%. The fatty acids freed from unsaponifiable matter had m. p. 27.8°; acid number, 177.8; saponification number, 189.5; mean molecular weight, 296.1. The unsaponifiable matter is soft and crystalline: iodine number, 72.9; m. p. 61.3—85°. It is soluble in an equal weight of lukewarm alcohol and crystals are deposited at -5°. The cholesterol test is given, but the acetate melts under 100°. The presence of higher alcohols or of squalene is not indicated. H. C. R.

Permeability of the Glomerulus Membrane for Stereoisomeric Sugars, with Special Reference to Galactose. H. J. HAMBURGER (*Biochem. Z.*, 1922, **128**, 185—206).—Perfusion experiments on the frog's kidney with the Hamburger-Brinkman modification of Ringer's solution (increased calcium content) and containing various hexoses and pentoses in solution showed that *l*-mannose, *l*-arabinose, *l*-glucose, *d*-mannose, *d*-glucoseamine, and *d*-arabinose passed through the membrane completely, whereas *d*-galactose, *l*-xylose, *d*-ribose, and *d*-xylose were partly retained and *d*-glucose completely. Whatever the concentration of *d*-galactose, about one-half is always retained, and about 30% of *l*-xylose.

The tentative explanation adopted is that in the case of partial retention of the sugar only one form, α or β , can pass the membrane and in the case of *d*-glucose, neither modification can pass. Experiments on the α - and β -glucosides are foreshadowed. H. K.

Change of Permeability with Special Reference to Stereoisomeric Sugars. H. J. HAMBURGER (*Biochem. Z.*, 1922, **128**, 207—214).—The author discusses the importance of calcium on the permeability of membranes, with special reference to the work of Clowes (A., 1916, i, 583) on the change of a water-oil emulsion under the influence of calcium ion from a continuous water phase to a continuous oil phase. The former would be permeable to glucose, the latter impermeable. This gives a picture of the glomerulus membrane, the permeability of which may be likewise influenced by increasing or decreasing amounts of calcium and also by other substances, for instance, phloridzin. H. K.

Physiology of the Glands. LIII. Function of the Spleen under Normal and Increased Oxygen Requirements. LEON ASHER and ERNST BERNET (*Biochem. Z.*, 1922, **128**, 251—267).—A comparison has been made of the daily excretion of ammonia and total nitrogen in the urine of normal rabbits with the excretion in the case of rabbits, (1) with extirpated spleen, (2) suffering from lack of oxygen (with artificial pneumothorax), (3) with extirpated spleen and suffering from lack of oxygen. Extirpation of the spleen causes an increased excretion of nitrogen which is still greater where the respiratory surface of the lungs is diminished.

H. K.

The Function of the Thyroid Gland in the Regulation of Temperature and in the Metabolism of Fever. E. GRAFE and E. VON REDWITZ (*Z. physiol. Chem.*, 1922, **119**, 125—138).—The thyroid gland has no influence on the regulation of the body temperature of the dog or on the metabolic functions during fever in this animal. S. S. Z.

The Influence of the Thyroid Gland on Metabolism, with Special Reference to Heat-regulation. PAUL SCHENCK (*Arch. exp. Path. Pharm.*, 1922, **92**, 1—21).—A study of the respiratory quotient in starvation experiments with normal and thyroidectomised animals indicates that the effect of the thyroid hormone on metabolism is qualitative rather than quantitative. The author states that the metabolism-regulating hormone of the thyroid is free from protein and almost free from iodine. He regards the heat regulation during muscular rest as being brought about, not by direct nervous stimulation of the heat centre, but indirectly by means of the thyroid hormone, and possibly also by the hormones of the other ductless glands. C. R. H.

Tethelin—the Alleged Growth-controlling Substance of the Anterior Lobe of the Pituitary Gland. JACK CECIL DRUMMOND and ROBERT KEITH CANNAN (*Biochem. J.*, 1922, **16**, 53—59).—Tethelin, which Robertson (A., 1916, i, 350) claims to have

isolated from the anterior lobe of the pituitary gland, is apparently a mixture, chiefly of substances of the lipid class.

Robertson's deductions as to the effect of tethelin and of the anterior lobe of the pituitary on growth are not warranted.

W. O. K.

The Pharmacology of Cell Respiration. PHILIPP ELLINGER (*Z. physiol. Chem.*, 1922, **119**, 11—38).—The endocrine glands contain products of protein degradation which can support the respiratory function of the erythrocytes of the goose. The presence of specific substances could not be demonstrated in these tissues. Urea increases whilst quinine decreases the velocity of oxidation of the erythrocytes of the goose owing to the increase and decrease in the absorptive surface produced by the respective substances.

S. S. Z.

Change of Choline Content of the Frog's Musculature through Electric Stimulation. E. GEIGER and O. LOEWI (*Biochem. Z.*, 1922, **127**, 174—180).—Faradic stimulation of frog's muscle leads to an increased choline content as estimated by a slight modification of Reid Hunt's method. The source of choline is possibly hydrolysis of lecithin.

H. K.

Formation of Phosphoric Acid in the Contraction of Frog's Muscle. GUSTAV EMBDEN and HEINZ LAWACZECK (*Biochem. Z.*, 1922, **127**, 181—199; cf. A., 1921, i, 529).—A comparison of the free phosphoric acid content of the two gastrocnemius muscles of frogs, submitted to faradic stimulation for short but different lengths of time shows that the free phosphoric acid very readily disappears, re-forming lactic acid.

H. K.

The Amino-acids of Flesh. The Diamino-acid Content of Rabbit, Chicken, Ox, Horse, Sheep, and Pig Muscle. JOHN LEWIS ROSEDALE (*Biochem. J.*, 1922, **16**, 27—30).—Estimations have been made by the Van Slyke method of the diamino-acid content of the flesh of the rabbit, chicken, ox, horse, sheep, and pig. The red meats show a higher lysine content than the white meats.

W. O. K.

Swelling Processes in Subcutaneous Tissues. P. MORAWITZ and G. DENECKE (*Biochem. Z.*, 1922, **127**, 47—54).—Agar tablets which have increased in weight up to 30% by immersion in serum or Ringer's solution, when introduced into the subcutaneous tissues of normal rabbits for twenty-four hours, lose in weight, but in the tissues of animals suffering from an artificial incipient oedema there is a slight increase in weight. Attempts to explain this through change of P_H or osmotic pressure of the fluids were not successful.

H. K.

Synthesis of Amino-acids in Animal Organisms. I. Synthesis of Glycine and Glutamine in the Human Organism. GEORGE J. SHIPLE and CARL P. SHERWIN (*J. Amer. Chem. Soc.*, 1922, **44**, 618—624).—It has been shown that man will synthesise glycine at the expense of carbamide, as do the lower

animals. The synthesis of glutamine at the expense of carbamide nitrogen is now also demonstrated in the case of man. The two amino-acids may be built simultaneously as readily as either compound alone. The carbamide nitrogen dropped from about 75% of the total nitrogen to 28%, and during a portion of a certain day to 12%, whilst these amino-acids were being synthesised in the organism. After feeding a moderate dose of benzoic acid, glycine for its detoxication is built within six hours, but for the detoxication of a corresponding dose of phenylacetic acid a somewhat longer period of time is required for the synthesis of glutamine.

W. G.

The Zinc Content of the Organs of the Rabbit and of some Vertebrates. GABRIEL BERTRAND and R. VLADESCO (*Bull. Soc. chim.*, 1922, [iv], **31**, 268—272).—In continuation of previous work (A., 1921, i, 382, 907), the authors record the zinc content of numerous organs of the rabbit and of certain organs of other vertebrates, such as the calf, bullock, sheep, chicken, etc. In general, the organs of birds are richer in zinc than those of mammals or fish. In the case of mammals or fish, the large organs such as muscle, liver, heart, etc., contain, on an average, 20—40 mg. of zinc per kilo. of fresh substance, whilst in birds the figure is about double this amount. In hen's eggs the zinc is entirely in the yolk, the white and shell of the egg being devoid of this metal. W. G.

Vitamin Requirements of *Drosophila*. I. Vitamins-B and -C. ARTHUR WILLIAM BACOT and ARTHUR HARDEN (*Biochem. J.*, 1922, **16**, 148—152).—The complete development of flies of the genus *Drosophila* requires the presence of vitamin-B, but not of vitamin-C, and of, at most, very small quantities of vitamin-A. W. O. K.

Occurrence of Manganese in the Tube and Tissues of *Mesochætopterus Taylora*, Potts, and in the Tube of *Chætopterus variopedatus*, Renier. CYRIL BERKELEY (*Biochem. J.*, 1922, **16**, 70—77).—Manganese is found in considerable quantities in the tube (0.03—0.07%) and tissues (0.002—0.015%) of *Mesochætopterus Taylora*, and in the tube (0.4—0.6%) of *Chætopterus variopedatus*. It is probably to be regarded as a waste material and not of physiological importance.

W. O. K.

Hæmotoxins from Parasitic Worms. BENJAMIN SCHWARTZ (*J. Agric. Research*, 1921, **22**, 379—432).—Certain worms parasitic on animals contain substances toxic to blood. The body-fluid and extracts of *Ascaris lumbricoides* contain a hæmolytic agent which is thermostable and non-specific. It is not found in worms immediately after removal from the host, but appears in a few days after keeping them alive in vitro. A substance is found which inhibits coagulation, and also a substance causing agglutination, specific for rabbit blood-cells. Hæmolytic substances were found in other parasitic worms (*Ancylostoma caninum*, *Bufo marinus*, *Phlebotomus*, *Hæmonchus contortus*, *Trichuris depressiuscula*, and *Thysanotoma actinioides*). Normal blood-serum may inhibit hæmolysis by these agents.

G. W. R.

The Colouring Matter and Wax of the Blood Louse (*Schizoneura lanigera*). FR. N. SCHULZ (*Biochem. Z.*, 1922, **127**, 112—119).—The woolly threads of wax which surround the blood-louse (a parasite of apple trees) have been examined, as well as the red juice obtained on crushing the insects. The alcoholic extract containing wax and colouring matter shows the spectrum and some reactions of cochineal contaminated by a second colouring matter, possibly a lipochrome. The wax, when purified, crystallises readily, has m. p. 48—49°, and gives 7—10% of glycerol and 76% of fatty acid. The latter acid has m. p. 36°, solidifies very readily, has a molecular weight 327, and has probably 20—22 carbon atoms in a branched chain.

H. K.

Do the Amino-acids occur in Cow's Milk? YOSHIKUMI HIJIKATA (*J. Biol. Chem.*, 1922, **51**, 165—170).—After removal of proteins and lactose from fresh cow's milk, derivatives of the following substances were isolated from the filtrate: lysine, arginine, histidine, guanine, adenine, choline. Evidence was also obtained of the presence of monoamino-acids.

E. S.

The Effect Produced on the Composition of Milk by the Administration of certain Inorganic and Organic Substances. W. DENIS, WARREN R. SISSON, and MARTHA ALDRICH (*J. Biol. Chem.*, 1922, **50**, 315—322).—The experiments were performed on goats and the substances investigated were urea and calcium chloride. Ingestion of the former increased the urea content of both the blood and milk, whilst ingestion of the latter increased the chloride, but had no effect on the calcium content of these fluids. Intravenous injection of calcium chloride did not produce any change in the calcium content of milk.

E. S.

Fatty Acids of Butter. F. FROG and S. SCHMIDT-NIELSEN (*Biochem. Z.*, 1922, **127**, 168—173).—Fractionation of the methyl and ethyl esters of the acids of butter fat prepared from the milk of cows fed on a standard mixed diet gave the following composition: acetic acid—a trace, butyric acid 3.4%, hexoic acid 3.3%, octoic acid 1.9%, decoic acid 3.0%, lauric acid 3.7%, myristic acid 12.9%, palmitic acid 20.8%, stearic acid 6.2%, oleic acid 27.0%, and unidentified acids 9.8%. Some of the unidentified acids probably arise from the feeding materials.

H. K.

Effect of Loss of Carbon Dioxide on the Hydrogen-ion Concentration of Urine. E. K. MARSHALL, jun. (*J. Biol. Chem.*, 1922, **51**, 3—10).—The escape of carbon dioxide from acid urines produces no great change in the hydrogen-ion concentration. With neutral, alkaline, or dilute urines, however, an appreciable decrease occurs unless precautions are taken to prevent the loss of carbon dioxide.

E. S.

Carbonic Acid and Bicarbonate in Urine. JAMES L. GAMBLE (*J. Biol. Chem.*, 1922, **51**, 295—310).—The content of free carbonic acid in urine is nearly constant; that of bicarbonate, however, varies inversely as the hydrogen-ion concentration. With increasing

acidity, there is consequently a rapid diminution in total carbonic acid. From these results the inference is drawn that the elimination of carbon dioxide in urine is determined by the carbon dioxide tension of blood plasma. Further, the reaction of urines more alkaline than $P_H 7.0$ is determined by the carbonic acid : bicarbonate ratio rather than by the ratio of the phosphates. E. S.

Acetaldehyde as a Constituent of Normal Urine. W. STEPP and R. FEULGEN (*Z. physiol. Chem.*, 1922, **119**, 72—73).—The presence of acetaldehyde in normal human urine was demonstrated by the dimethyldihydroresorcinol reaction. The Stepp and Fricke "silver method" showed a content of 0.3 mg. of acetaldehyde in 1 litre of the fluid. Precautions were taken to demonstrate that the acetaldehyde was not produced by the bacterial fermentation after collection and that the persons from whom the urine was derived did not consume any alcohol. S. S. Z.

The Presence of Pyruvic Acid in Normal and Diabetic Urines. ROBERT FRICKE (*Z. physiol. Chem.*, 1922, **119**, 39—45).—Appreciable quantities of pyruvic acid cannot be demonstrated in either normal or diabetic urines. S. S. Z.

Effect of Severe Muscular Work on the Composition of the Urine. JAMES ARGYLL CAMPBELL and THOMAS ARTHUR WEBSTER (*Biochem. J.*, 1922, **16**, 106—110).—The urine of a subject accustomed to do 67,500 kilogrammetres of work in five hours showed an increase in creatinine, undetermined nitrogen, neutral sulphur, and lactic acid when an attempt was made to do 100,000 kilogrammetres of work in five hours. Acetone substances were present during part of the experiment.

During such severe muscular work, the acidity and the ammonia and phosphate content are higher during the night than during the day; the sulphur is evenly distributed, and the total nitrogen is higher during the day than during the night, as found in a previous research (cf. Campbell and Webster, this vol., i, 197). W. O. K.

Distribution of the Nitrogenous Constituents of the Urine on Low Nitrogen Diets. ROBERT ROBISON (*Biochem. J.*, 1922, **16**, 131—133).—Estimations have been made of the urinary nitrogen (total, urea, ammonia, creatinine, uric acid) in the human being on a diet containing only about 0.3 gram of nitrogen per day. The results show agreement with those of Folin (A., 1905, ii, 183 and 268) and others. W. O. K.

Influence of Putrefaction Products on Cellular Metabolism.
II. The Influence of Phenylacetic and Phenylpropionic Acids on the Distribution of Nitrogen in the Urine. YOSHIZUMI HIJIKATA (*J. Biol. Chem.*, 1922, **51**, 141—154).—Phenylacetic and phenylpropionic acids, administered either orally or subcutaneously to rabbits, have the same effect on the excretion of nitrogen in the urine. With small doses, there is an increase in amino-acid and a slight decrease in urea whilst total nitrogen and ammonia remain unchanged. Larger doses produce an increase

in all four types of nitrogen both with fasting animals and with those maintained in nitrogen equilibrium. E. S.

Lævulosuria. HERMANN K. BARRENSCHEEN (*Biochem. Z.*, 1922, **127**, 222—230).—Examination of the metabolism of a case of lævulosuria (female aged twenty-two) showed that dextrose and galactose were utilised completely, as was white bread. When lævulose was given in a single dose, 10% passed into the urine independently of the dose; but where the administration was spread over a period, the excretion of lævulose was much greater. The blood sugar increased from 0.1 to 0.2% on oral administration of 50 grams of lævulose within forty-five minutes, falling off to normal in six and a half hours. H. K.

Acetonuria Produced by Diets containing Large Amounts of Fat. ROGER S. HUBBARD and FLOYD R. WRIGHT (*J. Biol. Chem.*, 1922, **50**, 361—402).—Experiments were made on a number of normal subjects to determine the effect of diets rich in fat on the excretion of acetone compounds. Using as a basis for calculation the conclusion reached by Shaffer (*A.*, 1921, i, 754) that the minimum molecular ratio of ketogenic to antiketogenic substance for the avoidance of ketonuria is unity, the authors conclude from their results that proteins and the glycerol portion of the fat molecule function as antiketogenic substances only to the extent that they produce dextrose in the organism. E. S.

A Case of Unusual Acetonuria. OTTO PORGES (*Biochem. Z.*, 1922, **127**, 293—298).—An account of a female patient who developed an acetonuria very rapidly after withdrawal of carbohydrate diet. H. K.

Reduction Reactions in the Urine of Patients treated with Arsenobenzenes. A. GAVIATI and T. PAVOLINI (*Arch. Farm. sperim. Sci. aff.*, 1921, **32**, 1—10, 17—26).—Aqueous solutions of arsenobenzene derivatives readily reduce alkaline bismuth and copper solutions. Solutions of these derivatives in urine reduce the bismuth solutions appreciably and the copper but slightly, respond to Abelin's test for amino-groups in all cases, and exhibit the presence of formaldehyde when the derivatives contain the aldehyde group. The reactions given by the urines of patients to whom arsenobenzene preparations have been administered by injection are, excepting in cases of glycosuria, mostly the expression of physico-chemical modifications produced in the urine and only occasionally due to the direct action of the preparations on the reagents. The administration of silver-salvarsan may be followed by transitory symptoms of albuminuria, glycosuria, and urobilinuria. T. H. P.

Bladder Calculus of Silicic Acid. A. SCHLICHT (*Pharm. Zeit.*, 1922, **29**, 316).—Stones found in the bladder of a wether were approximately spherical, of 1—6 mm. diameter, and very hard. The amount of organic matter was very small, the major portion of the mass consisting of silica. H. K.

Chemistry of Amyloid Degeneration. HANS EPPINGER (*Biochem. Z.*, 1922, **127**, 107—111).—An amyloid tumour of the liver proved to be protein in nature, but free from sulphur and phosphorus. It was rich in diamino-acids and in tyrosine, but cystine and histidine were absent as also were carbohydrates. H. K.

Zinc and Cancer. PAUL CRISTOL (*Compt. rend.*, 1922, **174**, 887—889).—An examination of the zinc content of benignant conjunctive tumours and malignant epithelial tumours show that the latter contain a much higher percentage of zinc than the former. W. G.

Cancerous Anæmia. A. ROBIN and A. BOURNIGAULT (*Bull. acad. med.*, 1921, **85**, 198—203).—Estimations of the iron content of the blood and tissues of normal and cancerous individuals indicate that in the latter there is a considerable decrease in iron. Normal blood averages 0·439 gram; that of cancerous persons 0·257 gram, or a loss of 41%. In the tissues at the cancerous foci the difference in iron content amounts to 60%. Urinary elimination of iron in the non-cancerous averages 2·15 mg. as compared with 5·85 mg. for cancerous individuals.

CHEMICAL ABSTRACTS.

The Kidney Factor in Phloridzin Diabetes. THOMAS P. NASH, jun. (*J. Biol. Chem.*, 1922, **51**, 171—181).—In phloridzinised dogs there is a lower concentration of sugar in renal venous blood than in general arterial blood. These and other results indicate that phloridzin diabetes is not accompanied by an active production of sugar in the kidneys, and confirm an increased permeability of the renal epithelium. E. S.

Composition of a Rhinolith. L. DEBUCQUET (*J. Pharm. Chim.*, 1922, **25**, 305—306).—A rhinolith, taken from the nasal chambers of a young soldier, contained 79·5% of calcium phosphate and 10·7% of calcium carbonate, the remainder being material insoluble in hydrochloric acid. It is of interest to note that the ratio of phosphate to carbonate is 7·43, a value which is very close to that for human bones. W. G.

The Protein Requirement in Tuberculosis. WM. S. McCANN (*Arch. Int. Med.*, 1922, **29**, 33—58; cf. *ibid.*, 1921, **28**, 847).—In nine out of ten cases of tuberculosis, the minimum excretion of nitrogen was from 0·041 to 0·093 gram per kilo. per day; in the tenth case, in which the basal metabolism was 30% above normal, the value was 0·267 gram per kilo. per day. Some cases could be brought into nitrogen equilibrium on diets containing from 37 to 44 grams of protein, of which half was from animal sources, so long as the energy content was from 1·7 to 2·4 times the energy requirement.

CHEMICAL ABSTRACTS.

The Mode of Action of Narcotic Gases : Nitrous Oxide and Acetylene. HERMANN WIELAND (*Arch. expt. Path. Pharm.*, 1922, **92**, 96—152).—The vital activities of the round-worm, and the phase of muscular contraction which is independent of the

presence of oxygen, are no more affected by nitrous oxide or acetylene than by indifferent gases, whereas the higher animals are rapidly narcotised. From these experimental results, and from the similarity between the symptoms of nitrous oxide intoxication and of anoxæmia, it is argued that the narcotic effect of nitrous oxide and acetylene is due to an interference with the uptake or utilisation of oxygen by the nerve-cells. The fact that these two gases in particular exert a narcotic effect is ascribed to their relatively great solubility in water, which permits a high concentration to be attained in the blood. It is claimed that the experiments emphasise the distinction between the true lipid-soluble narcotics such as chloroform and the narcotic gases of the type of nitrous oxide.

C. R. H.

The Physiological Action of Metallic Ammines and Allied Compounds. AD. OSWALD (*Biochem. Z.*, 1922, **127**, 156—167).—The action of a series of ammines of cobalt, nickel, and chromium and similar complexes of cobalt, iron, and chromium with ethylenediamine, pyridine, and phenanthroline and of complex oxalates and malonates has been studied on frogs, mice, and rats. A description of the physiological action of each is given, but in general the action of the ammines is that of ammonia or ammonia derivatives, that is initial stimulation of the motor centres followed by paralysis. The activity increases with the number of ammonia radicals. Unstable complex oxalates have the action of oxalic acid which is similar to that of the complex ammines, but the action of sodium chromomalonate has no similar action. The action of stable oxalates, for instance, potassium and rhodium oxalates, is therefore ascribed to their oxalate content and the action of ammines to their ammonia content.

H. K.

The Fate of Methyl and *iso*Propyl Alcohols in the Organism. JULIUS POHL (*Biochem. Z.*, 1922, **127**, 66—71).—The normal urinary content of formic acid of dogs is increased manyfold by oral administration on successive days of 3 grams of methyl alcohol. Similar administration of *isopropyl* alcohol to dogs or rabbits leads to a combustion of about 88% in the body and an excretion of about 12%, chiefly in the form of acetone with a little *isopropyl* alcohol in the expired air.

H. K.

The Physiological Action of β -Amino-4-ethylglyoxaline (Histamine). PAUL SCHENCK (*Arch. exp. Path. Pharm.*, 1922, **92**, 34—51).—Histamine is in general antagonistic to adrenaline (A., 1921, i, 640). Experiments on the surviving excised liver show, however, that histamine cannot antagonise the stimulating effect of adrenaline on the mobilisation of sugar; histamine itself, in fact, stimulates the latter process to some extent.

Anæmia could not be produced in guinea-pigs by prolonged administration of histamine.

C. R. H.

The Physiological Action of Melanin Acids. O. ADLER and W. WIECHOWSKI (*Arch. exp. Path. Pharm.*, 1922, **92**, 22—33).—Intravenous injection of a 1% solution of the sodium salts of the

melanin acids, obtained by the oxidation of tyrosine with hydrogen peroxide and ferric chloride, or from cabbages, in doses of about 1 mg. per c.c. of blood, produces a state of incoagulability of the blood which lasts for several hours. Simultaneously, changes are observed in the form elements of the blood; in particular, there is a great reduction in the number of the blood-platelets after an injection. C. R. H.

Physiology of the Phenols. II. Absorption, Conjugation, and Excretion. K. F. PELKAN and G. H. WHIPPLE (*J. Biol. Chem.*, 1922, **50**, 499—511).—After intravenous injection in dogs, phenols rapidly disappear from the blood, being converted, in part, into conjugated phenols. On the other hand, ingestion in sufficiently large doses is followed by the appearance, for a short time, of free phenols in the blood and an increase in the content of conjugated phenols, the latter reaching a maximum in about an hour. The authors conclude from their results that toxic phenols (phenol and *p*-cresol) produced in the intestine from tyrosine by bacterial action are to a large extent oxidised in the organism, the remainder being conjugated in the liver with sulphuric or glucuronic acid and finally excreted in this form. E. S.

[**Fate of Tetrahydronaphthalene in the Organism.**] W. RÖCKEMANN (*Arch. expt. Path. Pharm.*, 1922, **92**, 52—67).—Tetrahydronaphthalene, a volatile constituent of floor-polishes, may be absorbed in appreciable quantities by inhalation.

As a result of feeding this substance to rabbits there was isolated from the urine an optically active (dextrorotatory) compound of the composition $C_{10}H_{12}O$; evidence is adduced to show that this is probably ac- β -tetrahydronaphthol; from the urine of dogs treated similarly, the only product obtained was dihydronaphthalene, and it is assumed that in this case the earlier metabolic product was ac- α -tetrahydronaphthol, which substance would lose water with great ease to give dihydronaphthalene. C. R. H.

The Relative Toxicity of the Haloids and other Anions. A. T. CAMERON and M. S. HOLLENBERG (*J. Gen. Physiol.*, 1922, **4**, 411—421).—Experiments were made on the survival times of frog's heart and muscle-nerve preparations in modified Locke solutions in which part or the whole of the sodium chloride had been replaced by equimolecular amounts of the sodium salt of other halogen acids or by sodium nitrate.

When more than 5% of the sodium chloride was replaced, the relative toxicities of the replacing ions were found to be as follows: $F' > IO_3' > I' > NO_3' > ClO_3' > Br' > Cl'$.

Relatively the greatest toxic effect was produced by the first slight replacement of the sodium chloride. C. R. H.

The Toxicology of Arsine. II. Toxicity for Warm-blooded Animals. HERMANN FÜHNER (*Arch. expt. Path. Pharm.*, 1922, **92**, 288—301).—A series of experiments with white mice shows that a minimum concentration in the atmosphere of 0.1 to 0.2 mg. of arsine per litre causes death from acute poisoning in

two to three hours. In these cases, post mortem estimations of arsenic show a concentration of 0.013 to 0.020 mg. of As_2O_3 per gram of body-weight. Death from delayed poisoning is induced by exposure for thirty minutes to a minimum concentration of from 0.1 to 0.15 mg. of arsine per litre, and the slowly poisoned animals show a concentration per gram of body-weight of 0.007 to 0.013 mg. of As_2O_3 .

The toxicity of arsine is not markedly greater than that of corresponding doses of sodium arsenite administered by subcutaneous injection. C. R. H.

Toxicity of the Metallo-albumins. V. ARIOLA (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 31—32, 33—39).—The metallo-albumins, obtained by shaking egg-albumin with powdered metals, exert a toxic action on *Colpoda cucullus* and vinegar eels, the intensity of the action with different metals diminishing in the order: cobalt, copper, iron, antimony, nickel, arsenic. Prolongation of the shaking at first enhances, but, if carried beyond a certain point, diminishes the effect of the resultant product. T. H. P.

Toxicity of Metallic Powders. V. ARIOLA (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 75—80, 88—90; cf. preceding abstract.)—Powdered metals introduced under the skin of *Rana esculenta*, *Hyla arborea*, or *Bufo vulgaris* determine phenomena of paralysis, followed by death. In order of diminishing activity, the metals studied are arranged thus: antimony, copper, cobalt, and iron. Oxides of copper, cobalt, and iron also exhibit toxic effects, which are less than those of the corresponding metals. T. H. P.

Pharmacological Action of Magnesium Sulphate and its Application in Strychnine Poisoning. MANFREDI FERRARA (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 91—96, 97—98, 113—125).—Magnesium sulphate exerts a depressing action on the nervous system and when administered in large doses through the veins or spine produces complete paralysis and anæsthesia, often followed by death. The general effects produced by medium doses of the salt are of short duration. No true antagonism exists between the action of strychnine and that of magnesium sulphate, the latter exerting merely a retarding influence on the former. T. H. P.

Chemistry of Vegetable Physiology and Agriculture.

Fat Metabolism of the Timothy Grass Bacillus. MARJORY STEPHENSON and MARGARET DAMPIER WHETHAM (*Proc. Roy. Soc.*, 1922, [B], **93**, 262—280).—Timothy grass bacillus was grown on a medium consisting of inorganic salts, including ammonia as the sole source of nitrogen, together with dextrose and sodium acetate. Estimations were made from time to time of the amounts of fat,

phosphatide, and protein, respectively. In each case a maximum is shown which almost coincides in time with the disappearance of dextrose and acetate from the medium. The organism is unable to utilise acetate in the absence of dextrose. Lactic acid (as lactate) gives results similar to those with dextrose. Both are utilisable alone. The acetic acid utilised in the presence of lactic acid or dextrose only affects the proportion of lipid material formed and does not increase the general growth. Propionic and butyric acids gave results similar to those with lactic acid. A method for estimating acetic acid is described. G. W. R.

The Production of Carbon Dioxide by the Typhoid Bacillus and the Mechanism of the Russell Double Sugar Tube. H. J. NICHOLS (*J. Infect. Dis.*, 1921, **29**, 82—85).—The typhoid bacillus produces considerable amounts of carbon dioxide both from sugars and from proteins. The appearance of the Russell double sugar tube during the growth of the typhoid bacillus is not due to direct oxygen requirements, but (a) to the retention of carbon dioxide in the butt of the tube and its escape from the slant and (b) to alkaline reversion of other acids. CHEMICAL ABSTRACTS.

Rate of Formation and the Yield of Yeast in Wort. NORMAN A. CLARK (*J. Physical Chem.*, 1922, **26**, 42—60).—A number of experiments on the rate of growth of yeast in beer wort, and in a sucrose medium are described together with experiments on the influence of alcohol, lack of bios, and crowding on the rate of growth. It is shown that if wort be seeded with “normal” actively budding yeast-cells (*Sacch. cerev.* race F.) and the culture is properly shaken and aerated at 25°, the rate of reproduction follows the logarithmic formula $\log C/C_0 = 0.160t$, from the moment of seeding until the crop reaches one hundred million cells per c.c., whether the seeding be five cells or eight million cells per c.c. or even more. At this point the solution contains 1.8 grams of alcohol per 100 c.c. When the concentration of alcohol exceeds 1.8% the constant k of the logarithmic formula must be replaced by a function of the percentage of alcohol, namely, $k = 0.2774 - 0.0806(\%) + 0.008543(\%)^2$, which holds from 1.8 to 5.0%. The crop of yeast reaches its maximum, about three hundred and twenty-five million cells per c.c., in about twenty-four hours; this maximum is independent of the seeding up to twenty-five million cells per c.c.; but if the wort be seeded up to four hundred million cells per c.c. the crop may reach six hundred and seventy-five million; this difference is to be ascribed to the lower content of alcohol. If wort be diluted with an artificial medium made up from sucrose and salts, the rate of reproduction is the same as in pure wort; the maximum crop is also the same, provided that the culture medium contains at least 10% of wort. In solutions containing less wort the rate is the same as usual, but the maximum crop is less; this must be ascribed to lack of bios in the culture liquid. Quantitative measurements of the maximum crop may be used as a convenient means of estimating bios. Washed yeast-cake rapidly absorbs bios from

wort, and if enough yeast is used the removal is practically complete and the cells do not bud. Under the experimental conditions, the rate of reproduction is independent of the concentration of sucrose and of bios; it is independent of the concentration of alcohol until this reaches 1.8 gram/100 c.c. The assumptions underlying Carlson's formula for the rate of reproduction of yeast are therefore without foundation (A., 1913, i, 117). J. F. S.

Action of Saponins on Yeast-cells. FRIEDRICH BOAS (*Ber. Deut. bot. Ges.*, 1922, **40**, 32—38; cf. A., 1921, i, 294; A., 1922, i, 94).—The effect of different varieties of saponin on the alcoholic fermentation of sucrose by yeast was studied. Whilst with highly active saponins fermentation was inhibited owing to destruction of the yeast plasma, with less active saponins the rate of evolution of carbon dioxide was increased owing to increased permeability of the plasma membrane. The addition of salts generally inhibited fermentation. The action of different saponins on yeast may be correlated with their hæmolytic activity. The action of saponin is due to its effect on the colloidal state of the lipid complex of the plasma membrane. G. W. R.

Decomposition of Lactic Acid by Yeast and by Blood-cells. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Z.*, 1922, **128**, 144—168).—For the extraction of lactic acid the authors use and recommend Ohlsson's method (A., 1916, ii, 542), the removal of amyl alcohol by extraction with benzene being replaced by steam distillation. Yeast-cells and blood can destroy lactic acid, the most favourable condition in the case of yeast-cells being agitation of the medium in a brisk current of oxygen. Under such conditions 25—50 grams of press yeast destroy 0.2—0.3 gram of lactic acid in six to fourteen hours. The fate of the lactic acid is not known, but a portion appears as carbon dioxide. Yeast killed by acetone or heat cannot destroy lactic acid. H. K.

The Course of Alcoholic Fermentation in the Presence of Urea. MARTA SANDBERG (*Biochem. Z.*, 1922, **128**, 76—79).—Top and bottom yeasts ferment sucrose in the presence of large quantities of urea with production of about 4% less alcohol than in the absence of urea. The urea is unchanged at the end of the fermentation. H. K.

Formaldehyde as an Intermediate Step between the Real Assimilation and the Formation of Carbohydrate in the Plant. II. MARTIN JACOBY (*Biochem. Z.*, 1922, **128**, 119—121; cf. A., 1920, i, 800).—Leaves of *Tropæolum majus* exposed to formaldehyde vapour show an increased weight of dry material which is independent of the presence of oxygen. H. K.

The Resorption of Aluminium Ions by the Roots of Plants. JULIUS STOKLASA [with J. ŠEBOR, F. TÝMICH, and J. CWACHA] (*Biochem. Z.*, 1922, **128**, 35—47; cf. A., 1918, i, 475).—Hydrophytes, mesophytes, and xerophytes were grown in aqueous culture media

with and without addition of aluminium sulphate. Aluminium is absorbed by the first two groups, but only slightly by xerophytes, the roots taking up most. The amount absorbed falls off with increasing concentration of aluminium in the solution. Employing plants which absorb considerable amounts of aluminium, for instance, *Eriophorum vaginatum*, *Phragmites communis*, and *Carex riparia*, it was found that when aluminium or iron was absorbed, calcium, magnesium, and sodium appeared in the nutrient medium, and if both iron and aluminium were present together the absorption of either was partly inhibited and less of the other ions appeared.

H. K.

† Behaviour of certain Organic Compounds in Plants. XIV.

G. CIAMICIAN and A. GALIZZI (*Gazzetta*, 1922, 52, i, 3—20).—The authors have investigated the resistance to oxidation by pulped spinach of uric and dimethyluric acids; aniline, acetanilide, and methylacetanilide; salicylic acid, methyl salicylate, and *m*-hydroxy-*p*-toluic acid; pyrrole- and dimethylpyrrole-carboxylic acids; phthalic and tetrahydrophthalic acids; aniline, α -naphthylamine, pyridine, and quinoline; carbamide and guanidine; eugenol, vanillin, and benzilic acid (cf. A., 1921, i, 483). The results obtained confirm the previous conclusion that the chemical actions of organic compounds on plants are not determined solely by etherification of the hydroxyl, amino-, and imino-groups, but are dependent also on other differences of constitution. The most poisonous products are not necessarily those most resistant to oxidation by vegetable enzymes.

Immersion of the leaves of *Prunus laurocerasus* in boiling water for some minutes results in the inactivation of the emulsin, whilst the oxidising enzymes present retain their activity. Amygdalin and saligenin are largely, and salicin completely, destroyed by the oxidising enzymes of pulped spinach. Thus, the oxidation of dextrose appears to catalyse that of the aromatic compound combined with the sugar. Tannin is far more resistant than pyrogallol to the oxidising enzymes of spinach.

It was previously found that, in general, fundamental compounds harmless to plants yield innocuous derivatives, but the fact that xanthine and ammonia were regarded as non-poisonous whereas theobromine, caffeine, and the amines are poisonous did not accord with this conclusion; further experiment shows that xanthine and ammonia exert a deleterious action on the bean plant.

The observation that esters are more injurious to bean plants than the corresponding potassium salts is confirmed by the results of tests with ethyl and potassium succinates and oxalates. The influence of alcohols is similar to that of the amines, as far as the development of the plants is concerned, although the phenomena characteristic of the alkaloids do not appear. Further, the action diminishes as the number of carbon atoms in the normal chain increases, with the exception that methyl alcohol, like methylamine, is the least harmful of the series. Like *isoamylamine*, *isobutyl* and *isoamyl* alcohols exhibit abnormally high toxicity, probably

owing to the presence of a methyl group in the side-chain of the alcohol radicle.

For compounds containing equal numbers of carbon atoms, the series : amines, alcohols, aldehydes, acids, represents the order of diminishing toxicity towards plants, the toxicity increasing with the resistance offered to enzymic oxidation. Acetone, methyl ethyl ketone, *cyclohexanone*, and 2-methyl*cyclohexanone* appear to be without influence on bean plants. Experiments with glycollic and acetic acids, and with lactic and propionic acids, fail to reveal any specific influence of the substituted hydroxyl group. As regards the effect of a double linking, stearic and succinic acids are harmless to bean plants, whereas oleic, fumaric, and maleic acids retard development and cause darkening and ultimate drying of the leaves. T. H. P.

The Chemical Composition of the Ergot of Diss and of the Ergot of Oats. GEORGES TANRET (*Compt. rend.*, 1922, 174, 827—830).—The ergot of diss, *Ampelodesmos tenax*, Linck, from North Africa, and the ergot of Algerian oats contain the same principles as the ergot of rye, but the proportions are very variable in passing from one species to another. The ergot of diss is poor in crystallised ergotinine, whilst that of oats, on the other hand, is richer than the average for the ergot of rye. The ergot of oats, but not the ergot of diss, could apparently be substituted for that of rye in years of scarcity. W. G.

Proteins of the Adsuki Bean, *Phaseolus angularis*. D. BREESE JONES, A. J. FINKS, and C. E. F. GERSDORFF (*J. Biol. Chem.*, 1922, 51, 103—114).—The adsuki bean contains 21.13% of protein ($N \times 6.25$). By extraction with sodium chloride solution, an α - and a β -globulin were obtained which were separated by fractional precipitation with ammonium sulphate. Both globulins gave positive tests for tryptophan. They differed mainly in their sulphur content. Using Van Slyke's method, the following values were obtained for the diamino-acids: α -globulin—arginine 5.45, histidine 2.25, lysine 8.30, cystine 1.63; β -globulin—arginine 7.00, histidine 2.51, lysine 8.41, cystine 0.86%. The adsuki bean was also found to contain a small quantity of an albumin. E. S.

The Carbohydrate Content of the Seed of *Asparagus officinalis*, L. W. E. CAKE and H. H. BARTLETT (*J. Biol. Chem.*, 1922, 51, 93—102).—The reserve carbohydrates of the asparagus seed consist of hemicelluloses. After removal of oil from the seed they may be extracted by dilute alkali, from which they are precipitated by acidification or addition of alcohol. Obtained in this way, the dry substance forms blue adsorption compounds with iodine which readily decompose on washing with water. Estimations of the carbohydrates in the seeds gave the following results: pentosans 2.02, galactans 0.42, dextrose 3.3, lævulose 1.4, condensed mannose 21.8, condensed dextrose 15.1, condensed lævulose 6.4%. From the values obtained for condensed sugar it is con-

cluded that the hemicelluloses occur either as mixtures of glucomannans and fructomannans or as glucofructomannans. Cellulose, starch, and inulin are absent from the seeds. E. S.

Nitrogen Distribution of Proteins extracted by 0.2 per Cent. Sodium Hydroxide Solution from Cotton-seed Meal, the Soja Bean, and the Coconut. W. G. FRIEDEMANN (*J. Biol. Chem.*, 1922, **51**, 17—20).—The following results were obtained: Cotton-seed meal—amide-N 10.54, humin-N 2.09, cystine-N 1.11, arginine-N 23.48, histidine-N 4.94, lysine-N 5.10, amino-N of filtrate 51.26%. Soja bean—amide-N 11.31, humin-N 1.84, cystine-N 1.04, arginine-N 14.57, histidine-N 5.92, lysine-N 8.26, amino-N of filtrate 54.32%. Coconut—amide-N 7.40, humin-N 2.08, cystine-N 0.86, arginine-N 28.60, histidine-N 4.88, lysine-N 4.56, total-N of filtrate 51.35%. E. S.

The Rôle played by the Various Elements of the Wood of *Juniperus oxycedrus* in the Formation of Oil of Cade. R. HUERRE (*J. Pharm. Chim.*, 1922, **25**, 165—173, 214—221).—The various constituents of oil of cade are produced by the action of heat on certain well-defined constituents of the wood of *Juniperus oxycedrus*, of which two groups may be distinguished, namely, the water-soluble matter, the essential oil, a resin soluble in light petroleum and in ether, and a resin soluble only in ether, all of which contribute to the production of a pyrogenous oil lighter than water, and, secondly, a resin soluble in ethyl acetate, and the deresinified wood itself, both of which furnish a tarry distillate heavier than water. The above elements of the wood give the following percentages of their weights of distillate: matter soluble in water 9%, essential oil 100%, resin soluble in light petroleum 55%, resin soluble in ether 45%, resin soluble in ethyl acetate 33%, wood 2%. The light oil obtained from the first group of materials acts as a solvent for the tar produced by the distillation of the entire wood, and if this is poor in essential oil, but little oil of cade is produced, whilst if it is also poor in resins soluble in ether and in light petroleum only a trace is obtained, consisting of tar heavier than water. G. F. M.

Volatile Oil of Milfoil. R. F. KREMERS (*J. Amer. Pharm. Assoc.*, 1921, **10**, 252—261).—Dried *Achillea millefolium*, when distilled with steam, yielded 0.467% of oil, two specimens of which had respectively d_{20}^{25} 0.915, 0.913; acid number, 7.24, 4.27; ester number, 2.22, 5.65; saponification number, 9.44, 10.92; ester number after acetylation, 23.5, 17.8. The following substances were present: methyl alcohol, formaldehyde, ethyl alcohol, acetone, furfuraldehyde, valeric acid, formic acid, eugenol, pinene, nopinene, cineole, thujone, borneol, camphor, caryophyllene, and azulene.

CHEMICAL ABSTRACTS.

Spilanthol, the Pungent Principle of Para Cress. II. YASUHIKO ASAHINA and MICHIZÔ ASANO (*J. Pharm. Soc. Japan*, 1922, 85—97; cf. A., 1920, i, 654).—When hydrosphilanthol is strongly pressed on a clay plate, its melting point is raised to

36—37° and its boiling point to 171°/6 mm. The analytical results correspond with the formula $C_{14}H_{29}ON$, and the acid obtained from it by hydrolysis (*loc. cit.*) gave an amide, m. p. 98°, and an anilide, m. p. 67—68°, which proved to be identical with decoamide and decoanilide. The authors next proceeded to synthesise the *isobutylamides* of decoic and *n*-nonoic acids. According to Fittig's method (*Annalen*, 1885, **227**, 85), heptaldehyde was condensed with succinic acid, producing hexylparaconic acid, which when subjected to dry distillation yielded decenoic acid; this on reduction with hydrogen in the presence of platinum black gave decoic acid, m. p. 30—31°.

n-Nonoic acid was prepared by oxidising dihydroxystearic acid with chromic acid mixture. *Decoisobutylamide*, forms white needles, m. p. 37—38°, b. p. 171°/6 mm., and a mixture with hydrospilanthol melts at 36—37°. *Nonoisobutylamide*, forms white needles, m. p. 37—38°, b. p. 162°/6 mm., but a mixture with hydrospilanthol melts below 30°. It follows that hydrospilanthol is mainly composed of *decoisobutylamide*; the hay-like odour and bitter taste of the former depend on some impurities, which are not removed by mere distillation. K. K.

Constituents of the Seeds of *Pharbitis Nil Chois*. II.

YASUHIKO ASAHINA and TORAJI SHIMIDZU (*J. Pharm. Soc. Japan*, 1922, 1—18; cf. A., 1920, i, 360).—When pharbitin, a glucoside of the seeds, was hydrolysed with barium hydroxide, *d*- α -methylbutyric acid, b. p. 176°, $d_{4}^{26.5}$ 0.9303, $[\alpha]_D +19.33^\circ$, containing a small quantity of tiglic acid, was obtained. Nilic acid (*loc. cit.*) purified as its copper salt, $C_5H_8O_3Cu$, which forms blue crystals, was converted by distillation into tiglic acid and water, hence it is β -hydroxy- α -methylbutyric acid. In addition to pentose, rhamnose was isolated in crystalline form from the decomposition product of pharbitic acid. When ipurolic acid was warmed with hydriodic acid and red phosphorus in a sealed tube, a syrupy acid containing iodine was obtained, which gave myristic acid, m. p. 53.5°, when reduced with zinc and hydrochloric acid. The acid has therefore a normal carbon chain. When oxidised with nitric acid (d 1.35), ipurolic acid gave suberic and azelaic acids, whilst with hot chromic acid mixture, butyric acid and a *diketone*, white needles, m. p. 49° (*disemicarbazone*, aggregates of needles, m. p. 135°), were isolated in addition to the two acids above mentioned.

When ipurolic acid is boiled with acetic anhydride and sodium acetate, and the reaction product is saponified with alkali, an unsaturated monohydroxy-acid is produced, the reduction of which with hydrogen in the presence of platinum black gives a monohydroxymyristic acid, needles, m. p. 51°. When the acid is oxidised with chromic acid mixture, sebacic and butyric acids are obtained. From these results, the ipurolic acid is shown to be a β -hydroxy-acid of the formula :



K. K.

Pectinase produced by Different Species of *Rhizopus*. L. L. HARTER and J. L. WEIMER (*J. Agric. Research*, 1921, **22**, 371—377; cf. Harter and Weimer, *ibid.*, 1921, **21**, 609—625).—*Rhizopus* spp., parasitic on sweet potatoes, produce an enzyme which dissolves the middle lamellæ of the cells of the host plant. The relative activity of the pectinase produced was compared for nine parasitic and two non-parasitic species by noting the time required for maceration of disks of sweet potato. The results show considerable variation in the amount of mycelial enzyme and also in the amount excreted in culture solutions. Pectinase is produced even by the non-parasitic species. G. W. R.

The Efflorescences of *Rhodymenia palmata*; Presence of a Xylan in the Floridean Algæ. C. SAUVAGEAU and G. DENIGÈS (*Compt. rend.*, 1922, **174**, 791—794).—The authors have obtained from the alga, *Rhodymenia palmata*, a pentosan which they have definitely identified as a xylan. It is admixed with a certain amount of a methylpentosan, which they were not able to identify. They were not able to find any indication of the presence of either mannitol or trehalose. W. G.

Velocity of Reaction of Vegetable Enzymes. I. Influence of the Concentration of the Enzymes on the Velocity of Action of the Enzymes of Germinated Barley. DARIO MAESTRINI (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 40—48, 49—59).—Measurements of the velocities of action of the three principal enzymes of germinated barley, namely, amylase, protease, and lipase, yield results in contradiction with the law of Schütz and Borissow, which states that the velocity of peptic digestion is proportional to the square root of the amount of the enzyme. The amylolytic and proteolytic actions of extract of germinated barley may be completely inhibited by addition of dextrose and peptone respectively. During the final period of the enzyme action, the amount of hydrolytic products produced is greater with the smaller concentrations of the enzyme; this result appears to depend on accumulation of the products of the action, since removal of these results, in the case of amylase, in renewal of the hydrolysis. T. H. P.

Velocity of Reaction of Vegetable Enzymes. II. Effect of Hydrogen Ions and of Salts on the Velocity of Action of the Enzymes of Germinated Barley. DARIO MAESTRINI (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 99—112; cf. A., 1920, i, 273, 413; 1921, i, 152, 281, 628).—Treatment of germinated barley with 0.3% acetic acid solution having electrical conductivity $\lambda = 14 \times 10^{-4}$ yields an extract having very high amylolytic activity. As the concentration of the acid is increased, the activity diminishes until it becomes almost zero for 0.9% acid, having $\lambda = 45 \times 10^{-4}$. With proteases (lipases), the optimum activity is obtained with about 0.4% acetic acid solution, having $\lambda = 28(26) \times 10^{-4}$; 0.9% acid gives an extract of very low proteolytic and lipolytic activities. The enzymic activity of these extracts appears to be proportional, within certain limits, to the concentration of the hydrogen-ions.

The author's results with malt amylase furnish no support for Duclaux's statement that calcium chloride inhibits completely the action of vegetable enzymes. The activity of malt diastase may be enhanced by chlorides, such as those of sodium and calcium, provided that the hydrogen-ion concentration of the enzyme solution is not at its optimum value. Cadmium chloride inhibits the amylolytic action of germinated barley extracts. T. H. P.

Velocity of Reaction of Vegetable Enzymes. III. Effect of the Quantity and Volume of the Substrate on the Activity of the Amylase of Germinated Barley. DARIO MAESTRINI (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 126—128, 129—133).—The results of the experiments here described show that, as regards the absolute quantity of the substrate, the behaviour of malt amylase closely resembles that of ptyalin (cf. Bielfeld, A., 1901, ii, 561) and that of emulsin, the quantity of reducing sugars produced being directly proportional to the absolute quantity of substrate used. Increase in the amount of the latter without increase of its concentration does not greatly affect the production of reducing sugars by amylase under the experimental conditions employed. Gradual increase of the volume of the substrate by addition of water is accompanied by a corresponding diminution in the activity of the amylase. T. H. P.

Analysis and Composition of Maize Pollen. R. J. ANDERSON and W. L. KULP (*J. Biol. Chem.*, 1922, **50**, 433—453).—Pollen from three different varieties of maize was investigated. Considerable variations in composition, especially as regards starch and sucrose, were found, but it is possible that these were due to differences in the degree of ripeness. From the ripe pollen of the variety mainly examined were isolated: choline, *l*-proline, inositol, a substance melting at 88—89° which was probably myricyl alcohol, and an amorphous and a crystalline phosphatide. The amorphous phosphatide gave on hydrolysis choline and a small quantity of another base which formed an aurichloride containing Au 49.84% and having m. p. 132°, glycerophosphoric acid, a saturated fatty acid, m. p. 63°, which was probably palmitic acid, and a small quantity of an unidentified unsaturated fatty acid. It was also found to contain sulphur. The crystalline phosphatide was hygroscopic after drying over sulphuric acid, and contained nearly two atomic proportions of nitrogen to one of phosphorus. E. S.

Absorbent Power of Soils, and the Absorption by Plants of Nutritive Substances from the Soil. LUIGI CASALE (*Staz. sper. agr. ital.*, 1921, **54**, 65—113).—The causes determining the absorbent power of soils are the same as those which govern absorption by colloids. The colloidal constituents of the soil acquire a positive or negative charge by yielding anions or kations to the liquids moistening them; the positive colloids are considered to be absorbed by the mass of the negative colloids, and the absorption of kations to take place as soon as the necessary difference of

potential is established between a colloid particle and the zone of concentration of kations round it. The coagulating power of various electrolytes is given by the decreasing order: $\text{Fe} > \text{Al} > \text{Mg} > \text{Ca} > \text{K} > \text{NH}_4 > \text{Na}$; in general, the coagulating power of the electrolyte is the greater the lower the solution tension of the kation and the greater its relative velocity, sodium being an exception. The anion of electrolytes also influences the coagulating power. Absorption by colloids is exerted on the entire zone of concentration. From the complex solutions which moisten the soil, potassium and ammonium ions are more absorbed than those of calcium, magnesium, and sodium. The last to be absorbed form the outermost layers, and being most easily redissolved, are most easily replaced by other bases; the substitution is therefore not chemical, but electrical in character. In order that absorption can occur, the colloid must acquire a negative charge by sending positive ions into solution. Basic silicates and humates, after being treated with boiling hydrochloric acid and washed, cannot do so, and therefore lose their absorbent power. The behaviour of organic colloids is exactly identical with that of inorganic colloids treated with metallic salts of solution tension lower than that of hydrogen. The ectoplasm of the absorbent cells of a plant sends hydrogen-ions into solution and thus acquires a negative charge which is less than that of the colloids of the soil, so that there is a difference of potential between the plant and the soil; the colloidal particles are consequently attracted and adhere to the absorbent zone, and, in endeavouring to equalise their negative charge with that of the ectoplasm, send kations towards it, establishing a kind of continuity. Equalisation does not, however, occur, since the absorbed ions are attracted by the tonoplast in an identical manner; they thus pass through the protoplasmic mass and can be utilised. The passage of nutritive substance from cell to cell is governed by the same causes as those controlling absorption. The beneficial action of fertilisers is explained by the action which their kation has in lowering the negative charge of the colloids, thus raising the difference of potential between them and the plant.

CHEMICAL ABSTRACTS.

Factors affecting the Hydrogen-ion Concentration of the Soil and its Relation to Plant Distribution. W. R. G. ATKINS (*Sci. Proc. Roy. Dubl. Soc.*, 1922, **16**, 369—413).—A comprehensive survey is given of modern theories on soil reaction. The buffer system in soils is discussed. Whilst the maximum alkalinity due to calcium carbonate in the soil is P_H 9.01, in the presence of carbon dioxide lower alkalinities are obtained owing to the formation of calcium hydrogen carbonate. In the presence of magnesium carbonate, alkalinity up to P_H 10.0 is possible, a circumstance which may explain the supposed unfavourable effect of lime prepared from dolomitic limestone. Alkalinities of more than P_H 10.0 are possible where sodium carbonate is present in the soil. In such cases, the alkalinity may be reduced to P_H 8 by additions of calcium sulphate. A survey of soils derived from different rocks

shows the influence of geology on soil reaction. This relation is also modified by topographical factors. Records are given for the soil reaction of the habitats of a large number of native plants. Data are also given for the reaction of spring- and river-waters.

G. W. R.

Relation of the Hydrogen-ion Concentration of the Soil to Plant Distribution. E. A. FISHER (*Nature*, 1921, **108**, 306; cf. Atkins, this vol., i, 415, and preceding abstract).—The apparent p_H of the soil, as determined colorimetrically, is often influenced by the fineness of division of the sample. Moreover, the actual p_H of the soil at the moment of measurement is sometimes of less importance than the rate of change of the p_H under natural conditions. The buffer effects imposed by the nature of the soil on its reaction vary enormously in magnitude with different soils. It is suggested that measurements should be made, not merely of the p_H of soils, but also of the variations in p_H with addition of acids and alkalis; the titration curves could then be correlated with the magnitude of the buffer action of the soil.

A. A. E.

Factors in the Development of Soil Acidity. J. KÖNIG, J. HASENBÄUMER, and E. KRÖGER (*Z. Pflanz. Düng.*, 1922, [A], **1**, 3—12).—Estimations of the P_H of soil moisture were made in order to determine the effect of different soil dressings, the effect of the growth of individual species of plants with varying manurial treatment, and the effect of different species of plants on soil acidity. The experiments were carried out in zinc pots. Even without the addition of any dressing, there was a slight increase in acidity after eight months, probably owing to defective aeration. Slight increases of acidity were observed as the result of normal applications of superphosphate, potassium salts, and ammonium salts. Sodium nitrate, "nitrolime," and basic slag had little effect, whilst calcium carbonate decreased the soil acidity. Similar results were obtained when the soil carried a crop of oats. In the experiments with different crops, peas, lupines, and buckwheat produced a slight increase in acidity, whilst maize, grass, clover, and mustard gave slight decreases. These results are in agreement with observations on the acidities of the root sap of the plants used.

G. W. R.

Soil Acidity and its Effect on Germinating Plants. OTTO LEMMERMANN and L. FRESSENIUS (*Z. Pflanz. Düng.*, 1922, [A], **1**, 12—32; cf. A., 1921, ii, 516).—Three types of soil acidity may be distinguished, namely, the actual acidity of the soil moisture due to the presence of acids, the latent acidity developed in the presence of solutions of neutral salts due to base exchange whereby salts of iron and aluminium appear in the soil extract and produce acidity by hydrolysis, and the latent acidity developed in the presence of salts of weak acids and strong bases where the base is absorbed by the soil colloids and the acid remains in the extract. The greatest acidity is found in the latter case and is not considered as of importance from a plant physiological point of view. The

three types of acidity for a number of soils as measured by the titratable acidity and by the P_H were compared. Whilst the results show a general agreement, the order of acidity is not quite consistent between the three series. Experiments with seedlings grown in sand cultures with the addition of varying amounts of sulphuric acid in the water supplied show that cereals have differing toleration. Oats showed the greatest toleration of acidity, whilst wheat was the most sensitive. In the case of oats, a concentration of 0.05% of sulphuric acid was required to produce injury. The effect on the titratable latent acidity of the soil extract of the previous addition of varying amounts of sulphuric acid is shown by curves giving the relation between the amount of sulphuric acid added and the titratable latent acidity of the soil extract. The curves for soils treated with sodium acetate show higher acidities than in the case of soils treated with potassium chloride. In the case of the potassium chloride series, the amount of sulphuric acid required to produce a titratable acidity in the extract sufficient to cause injury (as shown by the sand culture experiments) gives an expression for the amount of added acid which will produce harmful effects on plant growth. Results obtained with sodium acetate and similar salts are not regarded as trustworthy criteria as to the acidity of the soil for plant physiological purposes. From the differing tolerations of plants to acidity, the acceptance of any particular degree of acidity, measured as P_H , as critical is not to be recommended. Soil acidity must be considered in relation with the manurial treatment. Soils may have little active acidity, but marked latent acidity. With such soils no injurious effect due to acidity is observable unless dressings of salts such as potassium chloride are given.

G. W. R.

Displacement Method for Obtaining Soil Solution. F. W. PARKER (*Science*, 1921, **54**, 438—439).—The method, which is essentially that of Itscherekov (*J. expt. Landw. [Russia]*, 1907, 8), consists in displacing the soil solution from soil packed in brass or glass cylinders, by means of ethyl alcohol. The latter, as it percolates through the soil, displaces some of the soil solution which forms a zone of saturation below the alcohol; this zone increases in depth as it is continually forced downwards by the alcohol, and is ultimately delivered free from alcohol. From 35 to 75% of the soil solution may be obtained by this method. Successive portions of the displaced solution have the same composition, and the results indicate that the true soil solution is secured.

A. A. E.

Basic Exchange in Soils. VON NOSTITZ (*Mitt. deut. landw. Ges.*, 1921, **36**, 608—610).—A review of the present state of knowledge regarding absorption and basic exchange in soils, with particular reference to the work of Ramann (A., 1917, ii, 468; 1919, i, 615; ii, 154; 1920, ii, 257), which is of importance inasmuch as permutite-like hydrated aluminium silicates are fairly widely distributed in soils. The author has shown that even crystalline silicates such as mica and feldspar can to a certain extent exchange

their potash for other bases; thus excessive liming may cause potash impoverishment. Certain soils can be deprived of all basic elements by repeated treatment with ammonium nitrate; after treatment of such a soil with a solution containing ammonium, calcium, and magnesium salts, plants die soon after germination with typical symptoms of potash-hunger, whereas appropriate addition of potassium salts restores the fertility.

CHEMICAL ABSTRACTS.

The Nature of certain Aluminium Salts in the Soil and their Influence on Ammonification and Nitrification. IRVING A. DENISON (*Soil Science*, 1922, **13**, 81—106).—By the analysis of dialysed extracts from some acid soils, it is shown that the soluble aluminium in soils is not in the form of salts but of colloidal aluminium hydroxide. Increased hydrogen-ion concentration brought about by the formation of mineral acids, by adsorption of basic ions from salts, may ultimately produce soluble aluminium salts. The presence of soluble aluminium salts is the result rather than the cause of soil acidity. Ammonification is stimulated by aluminium salts, but nitrification suffers a temporary check. Calcium carbonate is the most effective agent for the removal of soluble aluminium salts from soils.
A. G. P.

Substances Dissolved in Rain and Snow. SHERMAN SCHAFFER (*Chem. News*, 1922, **124**, 35—36).—Forty-five samples of rain and snow which fell between August 18th, 1920, and June 1st, 1921, have been analysed. The deposits consisted of 18·14 in. of rain and 34·0 in. of snow, which fell in Mount Vernon, Iowa. During the period 0·60126 lb. of nitrates, 0·03985 lb. of nitrites, 1·48045 lb. of free ammonia, 1·16022 lb. of albuminoid ammonia, 34·43179 lb. of chlorides, and 102·08035 lb. of sulphates calculated as SO_3 , fell per acre. Generally, the author finds no seasonal change in the amount of these substances deposited. The nitrates had an average value of 0·3 per million of rain with a maximum of 1·0 per million, the average for the nitrites was 0·0033 per million with a maximum of 0·03 per million; free ammonia had an average of 0·67 and a maximum of 2·1 per million, whilst the average for albuminoid ammonia was 0·38 and the maximum 2·0 per million. The chlorides had an average of 10·1 and a maximum of 49·7 per million. It is shown, from an analysis of the sodium and potassium in the chloride, that these do not come from ocean spray, but probably from coal smoke. The average for the sulphates was 29·9 and the maximum 101·2 per million. Sulphites were also estimated, seven samples showed no sulphite, whilst the remaining samples had an average of 1·43 parts per million with a maximum of 1·8 per million. The total nitrogen which fell in this period was 3·28178 lb. per acre and consisted of 5·74% nitric acid, 0·51% nitrous acid, and 93·73% ammonia.
J. F. S.

Organic Chemistry.

Natural System of Carbon Compounds. II. Empirical and Rational Allologous Series and their Graphical Representation as a System. HERMAN DECKER (*Helv. Chim. Acta*, 1922, 5, 285—299; cf. this vol., i, 417).—Series of compounds are termed allologous when the formulæ of members conform to a general expression. The special type of allology in which the formulæ of compounds differ by $(\text{CH}_2)_n$, is termed empirical homology. These definitions, however, permit the inclusion in one class of structurally different compounds. Rational homology, exhibited by compounds the interconversion of which may be conceived by addition or removal of $\cdot\text{CH}_2\cdot$ groups, may be direct or indirect, according as the relationship is analogous to that of direct descent or of cousinship in human genealogy. Irrational homology, exemplified by the acetylenes and the allylenes, is specially frequent among aromatic compounds. Among hydrocarbons, C_nH_m , the following types of rational allology (of which the respective series equations are indicated) are at present distinguishable:—*homologues*—paraffins ($n-m/2+1=0$), ethylenes ($n-m/2=0$), acetylenes ($n-m/2-1=0$), benzene homologues ($n-m/2-3=0$), naphthalene homologues ($n-m/2-6=0$); *centrologues*—acetylene, benzene, . . . ($n-m=0$); *phenylogues*—benzene, diphenyl, . . . ($n-3/2m+3=0$), toluene, diphenylmethane, . . . ($n-3/2m+5=0$), ethylbenzene, diphenylethane, . . . ($n-3/2m+7=0$); *benzologues*—benzene, naphthalene, . . . ($n-2m+6=0$), diphenyl, phenylnaphthalene, . . . ($n-2m+8=0$), pyrene, isoperilene, . . . ($n-2m+4=0$); and *perilogues*—naphthalene, pyrene, . . . ($n-3m+14=0$); anthracene, perilene, . . . ($n-3m+16=0$). The series equations show that each of these may be represented by straight lines, of which the angle of inclination to the n -axis is termed the specific constant of the type. The discussion of the results of this mode of representation does not lend itself to abstraction. J. K.

Some Compounds of Bivalent Carbon. ALFRED GILLET (*Bull. Soc. chim. Belg.*, 1922, 31, 126—131; cf. this vol., i, 213).—A development of the theory put forward in the previous paper. Various data are tabulated and the conclusion is drawn that, of all the known saturated isomerides, the compound which is most closely related in formula to the corresponding unsaturated compound differs least in boiling point from the latter. Some connexion between these differences and their variations in various series of compounds is deduced. H. J. E.

Oxidation of Aliphatic Hydrocarbons with Nitrogen Peroxide. II. CH. GRÄNACHER and P. SCHAUFELBERGER (*Helv. Chim. Acta*, 1922, 5, 392—395; cf. A., 1921, i, 2).—Neither palmitic nor stearic acid could be detected among the acids obtained by the oxidation of paraffin (m. p. 50—52°) with nitrogen peroxide

(cf. Bergmann, A., 1918, i, 285). The main fraction, b. p. 240—300°/23 mm., of the esterification product of the acid mixture furnished an *ester*, leaflets, m. p. 40·5°, from which a saturated *acid*, $C_{22}H_{44}O_2$, leaflets, m. p. 59—60°, was obtained. Since these are not the properties of behenic acid, the new acid must contain a branched chain structure, and it is concluded that paraffin contains considerable quantities of hydrocarbons, other than normal. From a fraction, b. p. 90—135°/12 mm., of the esterified product, a *lithium* salt, $C_{14}H_{27}O_3Li$, was obtained, corresponding with a saturated liquid hydroxy-acid, probably naphthenic acid or containing a branched chain structure. Another fraction, b. p. 135—155°/12 mm., similarly furnished a *lithium* salt, $C_{15}H_{29}O_3Li$, also derived from an analogous hydroxy-acid. J. K.

Preparation of Fatty Acids, Aldehydes, and Ketones from Mineral and Tar Oils. CARL HARRIES (D.R.-P. 339562; from *Chem. Zentr.*, 1921, iv, 1222).—The raw oils before oxidation with ozone are treated with liquid sulphur dioxide to remove the portions soluble therein. For example, the tar from bituminous coal is treated with liquid sulphur dioxide, whereby strongly unsaturated compounds are removed, less unsaturated compounds with double linkings remaining behind in the residue. This is cooled to the point of partial solidification and the portion remaining liquid, the so-called "Schwitz" oil, is run off and fractionated with steam. The fraction between 100 and 250°/10 mm. is treated with ozone until the increase in weight amounts to 8—12%. The oxidised oil is then treated with superheated steam to decompose the peroxides formed and the acids are separated from the un-attacked portion by hot concentrated potassium hydroxide. The resultant soaps are separated from the oil by treatment with superheated steam. The soaps thus obtained on hydrolysis give principally palmitic and stearic acids. The material after the removal of the soaps still contains unsaturated compounds and the portion containing aldehydes is again treated with ozone, steam, and potassium hydroxide, whereby aldehydes are converted into acids. The yield of fatty acids, for the most part crystalline, amounts to about 18—20% of the Schwitz oil. In order to obtain aldehydes and ketones, the ozonised material after treatment with steam is shaken with sodium hydrogen sulphite and the aldehydes and ketones are recovered by way of the bisulphite compounds. A large number of aldehydes and ketones are obtained boiling over a large range. A yield of aldehydes and ketones up to 80% may be obtained if the ozonides are treated with sodium hydrogen sulphite or potassium ferrocyanide in the presence of potassium hydrogen sulphate. The residual "Schwitz" oil after treatment with sulphuric acid is no longer oxidisable and has m. p. —6° to 1°, according to origin; b. p. 280—350°/760 mm. G. W. R.

Preparation of Diolefines and Polymerisation Products Thereof. H. OTTO TRAUN'S FORSCHUNGLABORATORIUM (Brit. Pat. 156116).—Diolefines are obtained by heating together for a suitable

time under pressure at a sufficiently high temperature molecular quantities of acetylene and ethylene hydrocarbons in presence or absence of a catalyst, for example, anhydrous alkali hydroxides, and if either the pressure or temperature or time of interaction be increased polymerisation products of the diolefines are obtained in a single operation. For example, a mixture of acetylene and propylene in approximately molecular proportions is forced into a thick-walled spiral or autoclave at 3–15 atmos. pressure and heated at 350–450°. The spiral is provided with a non-return inlet valve and an outlet valve which can be regulated to release the gases at any desired pressure. The escaping gases are cooled and the diolefine condenses, unchanged gas being recirculated through the apparatus. By using an indifferent gas as a diluent to increase the pressure to, say, 30 atmos. the yield of diolefine, in the present instance isoprene, can be increased to 85% of the theoretical. When the operation is performed in an autoclave and the heating is continued for ten to fifteen hours at 55–65 atmos. pressure the diolefine undergoes polymerisation to rubber-like substances together with intermediate products which can be utilised as varnish and turpentine substitutes.

G. F. M.

Preparation of Diolefines and Derivatives Thereof. H. OTTO TRAUN'S FORSCHUNGSLABORATORIUM (Brit. Pat. 156122).—Halogenated derivatives of diolefines are obtained by the pyrogenetic decomposition of hydrocarbons such as turpentine, dipentene, or limonene in presence of halogens or hydrogen haloids, the reactions being accelerated by catalysts such as silicon alloys, silicates, or metallic platinum. Similar diolefine derivatives are also produced by the chlorination of pentane or isopentane at 600–800°. From these stable derivatives the unstable diolefines may readily be obtained as required for use by splitting off hydrogen haloid. By way of example, a mixture of equal volumes of benzene and limonene vapours and hydrogen chloride is passed through a ferro-silicon tube heated at 550–600°, or, alternatively, a mixture of 1 vol. of gasolene vapour (b. p. 40–45°) and 4 vols. of chlorine is similarly treated at 600–800°, and the chlorinated products, consisting mainly of dichloropentanes, are led into a suitable water-cooled condenser and collected. The yield of compounds from which diolefines suitable for caoutchouc synthesis can be obtained amounts to 60–80% of the theoretical.

G. F. M.

Compounds of Acetylene with Silver Phosphate and Silver Arsenate. P. BENEDICT OBERDOERFER and J. A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1922, **44**, 837–840).—The formula assigned to their acetylene silver phosphate compound by Nieuwland and Maguire (*A.*, 1906, ii, 721) is now shown to be incorrect. The substance which they analysed contained small amounts of water and free phosphoric acid. Analytical results from the carefully purified substance give the following formula to the compound, $6(\text{Ag}\cdot\text{C}\equiv\text{CH})_2\cdot\text{Ag}_2\text{HPO}_4$.

An *acetylene silver arsenate* has also been prepared by the same

method, and the analytical data point to the constitution $2(\text{H}_3\text{AsO}_4), \text{Ag}_3\text{AsO}_4, 4\text{C}_2\text{Ag}_2$. Its properties are similar to those of acetylene silver phosphate (*loc. cit.*).
W. G.

The Interaction of Methyl Iodide and Potassium Plumbite. J. G. F. DRUCE (*Chem. News*, 1922, **124**, 215—217; cf. A., 1920, i, 426).—Contrary to the behaviour of alkaline solutions of stannous hydroxide, it is shown that no organo-metallic compounds are obtained with potassium plumbite and methyl iodide. The constitutional formulæ of the potassium hydrogen plumbites and stannites are discussed.
W. E. G.

Preparation of Vinyl Compounds and Polymerisation Products Thereof. H. OTTO TRAUN'S FORSCHUNGLABORATORIUM (Brit. Pat. 156117).—The addition of hydrogen haloids, methyl haloids, or organic carboxylic acids to acetylene hydrocarbons takes place smoothly and rapidly at 100—120° under a pressure of 1—2 atmos. By increasing the pressure and by raising the temperature when all the acetylene is absorbed, polymerisation products of the vinyl esters are obtained without the necessity of isolating the intermediate product. Although the reactions proceed quite satisfactorily without catalysts, they can be accelerated if desired by the addition of small amounts of certain metals or metallic compounds (other than mercury compounds, the use of which is already known, and involves troublesome regeneration processes) such as magnesium, tin, or copper, or their compounds, iodine, hydriodic acid, boron compounds, or organic acid anhydrides. If the acetylene is diluted with an inert gas such as nitrogen, or with benzene or petroleum vapour, the pressures can be increased to 10—15 atmos. or more and the reaction correspondingly accelerated without risk of explosion of the acetylene. Examples: (1) 40 parts of allylene and 36—38 parts of dry hydrogen chloride are heated at 120° at 1—2 atmos. pressure for ten to twenty-four hours. Yields of 80—85% of β -chloropropylene and 10—15% of another chloro-compound are formed, and the former can be completely polymerised by further heating at 150—200°. The polymerisation is accelerated by increasing the pressure to, say, 15 atmos. by the introduction of nitrogen. The polymerisation product can be employed for the preparation of varnishes, or can be transformed into rubber-like substances by the removal of the halogen by the action, for example, of sodium, calcium, or magnesium in presence of an inert organic liquid. (2) Twenty-six to twenty-eight parts of acetylene are gradually introduced into a mixture of 50 parts of acetic acid and 1 part of acetic anhydride. The mixture is heated at 40—60° and the pressure raised to 5 atmos. by the introduction of nitrogen. The product consists of 75 parts of vinyl acetate and 3—5 parts of ethylidene diacetate. If the temperature is then increased to 120—200° and the pressure to 10 atmos. or more, the esters are polymerised to products which vary in consistence from semi-liquids to more or less tough solids, according to the extent to which the polymerisation is allowed to proceed.

G. F. M.

Preparation of Vinyl Haloids. H. OTTO TRAUN'S FORSCHUNGS-LABORATORIUM (Brit. Pat. 156120).—Vinyl haloids are obtained in good yield without the intermediate isolation and purification of acetylene by the action of concentrated aqueous hydrogen haloids at 60–95° on calcium carbide in the presence of a catalyst, preferably a mixture of a mercury and a copper salt. The reaction occurs without catalysts if the pressure is increased above atmospheric, but some of the vinyl haloid is polymerised under these conditions. The vinyl chloride distils off as it is formed, and if a stream of hydrogen chloride is passed through the reaction mixture during the operation the yield is almost quantitative. Small quantities of zinc, aluminium, or tin chlorides accelerate the addition of hydrogen chloride to the nascent acetylene, but ferric chloride accelerates the reaction in the direction of the formation of dichloroacetaldehyde. G. F. M.

The Labile Nature of the Halogen Atom in Organic Compounds. II. Action of Hydrazine on Nitrogen-Halogen Compounds and on Bromomalonate Esters. EDMUND LANGLEY HIRST and ALEXANDER KILLEN MACBETH (T., 1922, **121**, 904–911).

The Labile Nature of the Halogen Atom in Organic Compounds. I. Titanium Reductions of Substituted Nitro-paraffins. THOMAS HENDERSON and ALEXANDER KILLEN MACBETH (T., 1922, **121**, 892–903).

The Surface Tension of Mixtures of Alcohol and Water at 25°. LOUIS LEIGHTON BIRCUMSHAW (T., 1922, **121**, 887–891).

Co-ordination Forms of Glycerides. I. KLIMONT (*Oesterr. Chem. Ztg.*, 1922, **25**, 63–64).—A reply to Grün (this vol., i, 420). H. W.

Properties of Mixtures of Ethyl Ether, Sulphuric Acid, and Water. JAMES ROBERT POUND (T., 1922, **121**, 941–945).

Preparation of Alkyl Sulphates. HENRY DREYFUS (Brit. Pat. 177189).—Ethyl sulphate or its homologues are obtained by heating alkali pyrosulphates (2 mols.) or chlorosulphonates (2 mols.) with ethyl alcohol or ethyl ether or their homologues (2 mols.) and after four to five hours, distilling off the ester, preferably in a vacuum. Alternatively, the alcohol vapours may be passed over sodium pyrosulphate heated at 150° in a vacuum, whereby ethyl sulphate together with unchanged alcohol distils off as fast as it is formed. G. F. M.

Preparation of Vinyl Sulphuric Acid and Homologues thereof. H. OTTO TRAUN'S FORSCHUNGS-LABORATORIUM (Brit. Pat. 156121).—Vinyl sulphuric acid is formed almost quantitatively according to the equation $\text{CH}:\text{CH} + \text{H}_2\text{SO}_4 = \text{CH}_2:\text{CH}:\text{SO}_3\cdot\text{OH}$, when cold anhydrous sulphuric acid (96 parts) is gradually saturated, at temperatures below 0°, with 26 to 28 parts of acetylene at

2 to 5 atmos. pressure, preferably in presence of small quantities of a catalyst such as mercuric sulphate. Homologues of acetylene can be used in a similar way.

G. F. M.

Trimethylene Dinitrate. F. BLECHTA (*Z. ges. Schiess-Sprengstoffw.*, 1922, **17**, 57—58).—Pure trimethylene glycol (b. p. 211—212°/741 mm., d^{15}_4 1.054) was nitrated in Schlögel's apparatus, the composition of the mixed acids being nitric, 25.26%, sulphuric, 66.55%, water, 8.19%. Ten grams of the glycol were slowly dropped into 200 grams of mixed acids cooled to 8° with violent agitation. The increase of temperature was much greater than in the nitration of glycerol, and drops hanging from the funnel on being splashed with the acids ignited regularly. The nitrate obtained was washed with cold water, 2% sodium carbonate solution, and finally several times with cold water and dried to constant weight in a vacuum over sulphuric acid. The nitrogen content was 16.7% (theoretical, 16.87%). The product was similar to glyceryl nitrate but less viscous; d^{15}_4 1.408. It was miscible in all proportions with methyl alcohol, ether, chloroform, benzene, or acetone, only slightly soluble in carbon bisulphide, solubility in 96% ethyl alcohol 1:5, solubility in water at 20° 1:410. No signs of crystallisation occurred on cooling for three hours at -20°. Tested by Abel's method at 83°, it showed slightly less stability than glyceryl nitrate. Its sensitiveness to impact is the same as that of the latter.

H. C. R.

Symmetrical Dibromopivalic Acid and 1-Methylcyclopropane-1-carboxylic acid. MORITZ KOHN and ANISSIM MENDELEWITSCH (*Monatsh.*, 1921, **42**, 227—244).—Symmetrical dibromopivalic acid and from it dihydroxypivalic acid were synthesised by the following steps. Two mols. of formaldehyde and 1 mol. of propaldehyde were condensed in aqueous potassium hydroxide to dihydroxy- $\alpha\alpha$ -dimethylpropaldehyde, which was converted into its oxime. The oxime, which readily decomposes on heating, was boiled with excess of acetic anhydride whereby it was converted into diacetoxypivalonitrile. By heating in a sealed tube at 125—130° for twenty hours with saturated hydrobromic acid, the nitrile was converted into *dibromopivalic acid*, $\text{CMe}(\text{CH}_2\text{Br})_2\cdot\text{CO}_2\text{H}$, m. p. 56—58°, crystallising from light petroleum in rhombic pyramids [$a:b:c=0.8949:1:0.7789$], d 2.078. By boiling with lead oxide and water, the dibromopivalic acid was converted into *dihydroxypivalic acid*, m. p. 179—182°, crystallising from water in small, acute rhombohedra or tetrahedra belonging to the trigonal-pyramidal class of the rhombohedral system, [$a:c=1:1.2549$], d 1.329. The product obtained by Koch and Zerner (*A.*, 1901, **i**, 633), m. p. 163—164°, was evidently impure.

Methyl dibromopivalate has b. p. 229—231°. *Methyl dihydroxypivalate* was prepared by alkylating dihydroxypivalic acid with diazomethane. It forms apparently rhombic, very deliquescent prisms, m. p. 40—45°, b. p. 145°/20—22 mm.

By reduction of the methyl ester of dibromopivalic acid in methyl alcohol with zinc dust, *methyl 1-methylcyclopropane-1-carboxylate*

was formed; it is a colourless, mobile liquid, b. p. 121—123°, with a camphor-like odour. The free acid crystallises from water in spear-shaped crystals, m. p. 28—31°, b. p. 183—185°/762 mm. The calcium salt, $(C_5H_7O_2)_2Ca$, crystallises in flat, rhombic needles; the silver salt, $C_5H_7O_2Ag$, forms thin needles or leaflets, apparently rhombic.

E. H. R.

Behaviour of Crotonic Acid in Ultra-violet Light. II.

R. STOERMER and E. ROBERT (*Ber.*, 1922, **55**, [B], 1030—1040; cf. Stoermer and Stockmann, A., 1914, i, 925).—It has been found previously that the transformation of crotonic into *isocrotonic* acid under the influence of the light from a Uviol lamp could not be established with certainty. By the use of the more powerful Heräus lamp, this transformation has been shown to occur to a small extent; on one occasion, it was found possible to isolate pure *isocrotonic* acid from the product, but, in general, the substance is separated as the corresponding amide. The experiments are rendered difficult by the restricted range of solvents available and the marked resinification which usually occurs, but is least obvious in toluene.

Under the influence of ultra-violet light, aniline and ammonia are very readily added at the double bond of $\alpha\beta$ -unsaturated acids. Thus crotonic acid and aniline give mainly β -anilinobutyric acid and anilinobutyranilide with minor amounts of croton- and *iso*-croton-anilides, whereas the chief products with ammonia are β -aminobutyric acid and iminodibutyric acid, and, in addition, very small quantities of crotonamide. Crotonic acid and *p*-toluidine give β -*p*-toluidinobutyric acid, which could not be caused to crystallise and was therefore analysed as its *ethyl* ester, b. p. 186—188°/30 mm.; the latter yields a *hydrochloride* which crystallises with difficulty.

Acetic, propionic, and (to a less extent) benzoic acids are converted into their anilides when mixed with aniline and exposed to the light of the Heräus lamp; the action is shown to be due to the radiation and not to the temperature of the lamp. The formation of amides takes place with considerably greater difficulty.

H. W.

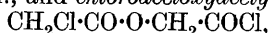
Erucic Acid and Erucic Anhydride. II. D. HOLDE and C. WILKE (*Z. angew. Chem.*, 1922, **35**, 186—187; cf. this vol., i, 217).—Historical. The authors give an account of attempts by earlier workers to isolate pure erucic acid from rape oil, the successful conclusion of which in their hands has been already described (*loc. cit.*).

G. F. M.

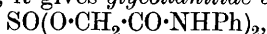
So-called Raptic Acid. ALFRED GRABNER (*Monatsh.*, 1921, **42**, 287—292).—The acid known as raptic acid was first isolated by Reimer and Will (A., 1887, 1030) and was shown by Zellner to have the formula $C_{18}H_{34}O_2$ (A., 1896, i, 592) and to be probably an isomeride of oleic acid. It has now been submitted to detailed comparison with oleic acid and shown to be identical therewith.

E. H. R.

Action of Thionyl Chloride on α -Hydroxy-acids. E. E. BLAISE and (MLLE) MONTAGNE (*Compt. rend.*, 1922, **174**, 1173—1174).—Thionyl chloride reacts with glycollic acid, giving two products, namely, *Chlorosulphonylacetyl chloride*, $\text{SO}_2\text{Cl}\cdot\text{CH}_2\cdot\text{COCl}$, b. p. 78—82°/16 mm., and *chloroacetoxyacetyl chloride*,



b. p. 99—101°/17 mm. The former compound is very unstable, and on heating at 180° it decomposes, giving sulphur dioxide and chloroacetyl chloride. It is also decomposed by water or methyl alcohol. With aniline, it gives *glycollanilide sulphite*,



m. p. 140—141°. This sulphite also loses sulphur dioxide when heated, giving glycollanilide, which, with thionyl chloride, regenerates the sulphite. Chloroacetoxyacetyl chloride gives with aniline an *anilide*, m. p. 119°. W. G.

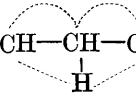
Oxidation of Dihydroxystearic Acid. YOSHIHIKO ASAHINA and YOSHITOYO ISHIDA (*J. Pharm. Soc. Japan*, 1922, 171—179).—Azelaic and *n*-nonoic acids are readily prepared from dihydroxystearic acid by oxidation. One part of dihydroxystearic acid (obtained by oxidation of oleic acid with potassium permanganate in potassium hydroxide solution) is added to a mixture of 2 parts of crystallised sodium dichromate and 25 parts of 25% sulphuric acid, and gradually heated on an oil-bath until the temperature has risen to 80°; the mixture is then distilled with steam, the temperature of the bath being maintained at 110—120°. The distillate is saturated with sodium chloride, extracted with ether, and rectified, when *n*-nonoic acid of b. p. 150°/20 mm. is obtained. The non-volatile residue is filtered while hot. On cooling the filtrate, impure azelaic acid crystallises. It is dissolved in concentrated sodium carbonate, or, better, sodium hydroxide solution, boiled until the accompanying coloured compound is destroyed, filtered, acidified, and crystallised, when white leaves, m. p. 128—132°, are obtained. From 504 grams of dihydroxystearic acid, 202·5 grams of azelaic acid and 130 grams of *n*-nonoic acid were obtained.

By the same method, 89 grams of azelaic acid and 41·5 grams of heptonic acid were prepared from 480 grams of the trihydroxystearic acid obtained from ricinolic acid by oxidation with potassium permanganate. K. K.

The Hydrolysis of the Mono- and Di-ethyl Esters of Diethyl-malonic Acid. PHILIPPE DUMESNIL (*Bull. Soc. chim.*, 1922, [iv], **31**, 320—324; cf. A., 1921, i, 391).—The author has repeated previous work (*loc. cit.*) under slightly different conditions, and has obtained confirmatory results. W. G.

Glutaconic Acid. II. P. E. VERKADE (*Rec. trav. chim.*, 1922, **41**, 208—223; cf. Verkade and Coops, A., 1920, i, 592).—A summary and extension of previously published work. Different methods of preparation of glutaconic acid (Conrad and Guthzeit, A., 1883, 311; Blaise, A., 1904, i, 10; Fichter and Dreyfus, A.,

1900, i, 426; von Pechmann and Jenisch, A., 1892, i, 147; von Pechmann, A., 1891, ii, 1457; Bucherer, A., 1890, i, 736) are shown to yield a substance of identical properties; no trace of the presence of an isomeride could be detected. Various methods of preparation of isomerides were attempted, but without success. The formula suggested by Perkin and Tattersall (T., 1905, 87, 361) and modified by Thorpe (T., 1912, 101, 871) is discussed and

the author suggests that $\text{CO}_2\text{H}-\text{CH}-\text{CH}-\text{CH}-\text{CO}_2\text{H}$ is the

 best representation of the experimental evidence. H. J. E.

Isomerism in the Glutaconic Acid Series. FRANZ FEIST (*Annalen*, 1922, 428, 25—40).—The evidence which has been accumulated by Thorpe and his co-workers during the past seventeen years is summarised. The author maintains his view that the isomerides in this series of acids are of the ordinary geometrical type, the difference, revealed by Thorpe's work, between the chemical relationship of these compounds and that subsisting between other maleoid and fumaroid acids being a difference of degree and not one of principle. The absence of a second form of glutaconic acid is readily explicable on the assumption that the double bond changes position (cf. following abstracts and this vol., i, 553). C. K. I.

The Two β -Methylglutaconic Acids. FRANZ FEIST and PAUL KARL BREUER (*Annalen*, 1922, 428, 59—68).—Both the *cis*- (labile) and *trans*- (normal) forms of ethyl β -methylglutaconate yield *ozonides* which on hydrolysis give ethyl acetoacetate and ethyl glyoxylate (also acetone and oxalic acid). *cis*-Ethyl β -methylglutaconate readily absorbs chlorine, giving a *dichloride* ($\text{C}_{10}\text{H}_{16}\text{O}_4\text{Cl}_2$), b. p. 159—161°/12 mm., and a *trichloro*-compound ($\text{C}_{10}\text{H}_{15}\text{O}_4\text{Cl}_3$), b. p. 116·5°/0·57 mm., 130°/0·96 mm., 142·0°/1·70 mm., 155·0°/2·70 mm. The *dibromide*, b. p. 108°/0·11 mm., 116°/0·66 mm., 133°/2·20 mm., 154—156°/11 mm., 159—160°/13 mm., on condensation with ethyl sodiomalonate gives ethyl ethanetetracarboxylate and *ethyl β -oxalyl-n-butyrate*, b. p. 125·3°/1·6 mm., 163°/5 mm. (cf. preceding abstract). C. K. I.

$\alpha\beta$ -Dimethylglutaconic Acid. FRANZ FEIST and (in part) PAUL KARL BREUER (*Annalen*, 1922, 428, 68—75).—Neither the *cis*- (labile) nor *trans*- (normal) forms of $\alpha\beta$ -dimethylglutaconic acid undergo optical resolution with the help of brucine, strychnine, or quinine. The quinine salt of the *cis*-acid is crystalline (needles), and has the composition $\text{C}_7\text{H}_{10}\text{O}_4 \cdot 2\text{C}_{20}\text{H}_{24}\text{O}_2\text{N}_2 \cdot 6\text{H}_2\text{O}$.

Ethyl *cis*- (labile) $\alpha\beta$ -dimethylglutaconate gives an oily *ozonide*, $\text{C}_{11}\text{H}_{18}\text{O}_8$, which on hydrolysis gives ethyl acetoacetate, ethyl methylacetoacetate, methyl ethyl ketone, and other products which were not identified. The *trans*- (normal) ester yields an oily *ozonide*, $\text{C}_{11}\text{H}_{18}\text{O}_{10}$, which on hydrolysis gives mainly ethyl acetoacetate, acetone, and acetic acid. To account for these

results it appears to be necessary to assume three-carbon tautomerism as in the case of the β -phenyl- α -methylglutaconic esters (cf. preceding abstracts and this vol., i, 553). C. K. I.

Aleuritic Acid. C. HARRIES and W. NAGEL (*Chem. Umschau*, 1922, 29, 135—137).—The acid was obtained as potassium salt in 30% yield by allowing 5*N*-potassium hydroxide to act in the cold for twelve hours on shellac. After purification, the acid gave figures corresponding with the formula $C_{16}H_{32}O_5$, and molecular weight determinations confirmed this. The acid has m. p. 100—101°, and yields a *methyl* ester (colourless needles, m. p. 69—70°) and a *triacetyl* derivative, $C_{15}H_{28}(OAc)_3 \cdot CO_2H$, and when reduced by hydriodic acid yields palmitic acid. The acid is therefore a trihydroxypalmitic acid as suggested by Endemann and not dihydroxytridecoic acid as stated by Tschirch and Farnier (A., 1899, i, 447). H. C. R.

Action of Acids on Ammonium Molybdomalate. E. DARMOIS (*Compt. rend.*, 1922, 174, 1062—1064).—The ammonium molybdomalate, $2MoO_3 \cdot C_4H_4O_5(NH_4)_2$, is very sensitive to the action of acids. On the addition of small amounts of hydrochloric acid to its solution the rotation rapidly decreases to a limit value which is the same if nitric or sulphuric acids is used in place of hydrochloric acid. The limiting value of the rotation corresponds with the formation of the compound, $MoO_3 \cdot 2C_2H_6O_5$. If acetic acid is used, the action is not so marked and the results with this acid and its chloro-derivatives indicate that, in these cases, the diminution in rotation is proportional to the total quantity of hydrogen-ions. It is suggested that this difference may serve as the basis of a method for detecting the presence of mineral acid in acetic acid. W. G.

Preparation of Formaldehyde and Methyl Alcohol. H. OTTO TRAUN'S FORSCHUNGLABORATORIUM (Brit. Pat. 156148).—Formaldehyde and methyl alcohol are obtained by the oxidation of methane, or natural gas containing methane, by means of carbon dioxide, the mixed gases being passed through a constricted pipe heated at 500—700° at the constriction, and the gaseous reaction products rapidly cooled. The tube may be made of copper, silver, or nickel, or alloys of these metals with one another or with tin, zinc, aluminium, etc., which metals catalytically assist the reaction. If iron pipes are used, they are advantageously packed with wire or turnings of the above metals or alloys. The following reactions apparently occur in the process: $2CO_2 = 2CO + 2O$ and $CH_4 + 2O = H \cdot CHO + H_2O$. The yield of formaldehyde under favourable conditions may amount to 56%, calculated on the methane employed. The yield of methyl alcohol is favoured by a slower passage of the gas through the tubes, and by the presence of hydrogen in the gas mixture. Saturation of the gases with alcohol vapour at 20—30° favourably influences the reaction. G. F. M.

Aptitude of Formaldehyde to Form Hydrocyanic Acid by Oxidation in Ammoniacal Silver Solutions. R. FOSSE and A. HIEULLE (*Compt. rend.*, 1922, **174**, 1021—1023; cf. this vol., i, 117).—By oxidising very small amounts of formaldehyde with excessive amounts of potassium permanganate in strong ammonium hydroxide in the presence of a silver salt and ammonium chloride the yield of hydrocyanic acid obtained may be as high as 37%. At the same time, however, a considerable amount of cyanic acid is produced. W. G.

Preparation of Acetaldehyde from Acetylene. SHUICHIRO OCHI, YOICHI ONOZAWA, and THE TOKYO INDUSTRIAL LABORATORY (Japan. Pat. 38752, 1921).—Acetaldehyde is prepared by introducing 10.3 litres of acetylene into 100 c.c. of a solution containing 25 grams of sulphuric acid, 1 gram of mercuric oxide, and 3.6 grams of ferric acetate, and heating at 40° for three hours, the product being then distilled with steam. K. K.

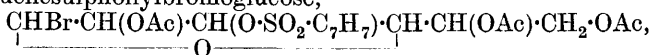
Researches on Residual Affinity and Co-ordination. VIII. Interaction of Tellurium Tetrachloride and β -Diketones. GILBERT T. MORGAN and HARRY DUGALD KEITH DREW [with E. A. COOPER] (*T.*, 1922, **121**, 922—940).

Electrolytic Reduction of Dextrose. ALEXANDER FINDLAY and VERNON HARCOURT WILLIAMS (*Trans. Faraday Soc.*, 1922, **17**, 453—456).—The method and apparatus used were those of Tafel (*A.*, 1900, ii, 588). A current density of 0.16 ampere per sq. dcm. was employed, the solutions contained 1—10% of dextrose in 3% of sulphuric acid, the rate of absorption of hydrogen fell rapidly almost to zero, and the total amount absorbed corresponded with a 2% reduction of dextrose. The current concentration was varied between the limits of 0.04 and 0.444 ampere per 100 c.c. With increase of current concentration the absorption of hydrogen increases but falls off rapidly. No appreciable change was effected by changing the temperature, substituting gas carbon or Acheson graphite for lead electrodes or changing the current density. The rapid falling off of the hydrogen absorbed was found to be due to a film of lead formate formed on the cathode. The products of reduction were found to be formic acid and a pentose (cf. Löb, *A.*, 1910, i, 94); contrary to the claims of O'Brien Gunn [*D.R.-P.* 140318 (1900)], no hexahydric alcohol was formed. W. T.

The Catalytic Hydrogenation of Dextrose. W. E. CAKE (*J. Amer. Chem. Soc.*, 1922, **44**, 859—861).—When dextrose is hydrogenated in $N/2$ -potassium hydroxide solution in the presence of platinum black, *d*-sorbitol and *d*-mannitol are obtained. W. G.

Syntheses of Mixed Acylated Halogen Sugars. KARL FREUDENBERG and OTTO IVERS (*Ber.*, 1922, **55**, [B], 929—941).—The authors have attempted the synthesis of substances of the type of acetobromoglucose in which the individual acetyl groups

are replaced by other acyl radicles. The preparation of triacetyl-*p*-toluenesulphonylbromoglucose,



is now described, the initial material being dextrosediacetone (cf. Fischer and Rund, A., 1916, i, 364).

A simplified method for the preparation of dextrosediacetone consists in shaking β -glucose (Behrend, A., 1907, i, 481; 1911, i, 14) with acetone containing a little hydrogen chloride at the atmospheric temperature and subsequent neutralisation of the acid by the addition of 5*N*-sodium hydroxide solution; the bulk of the acetone is removed by distillation on the water-bath and the remainder under diminished pressure. The dextrosediacetone is removed from the residue by treating it with warm light petroleum. It is converted by toluene-*p*-sulphonyl chloride in the presence of aqueous potassium hydroxide solution or pyridine into *toluene-p-sulphonyldextrosediacetone*, slender needles, m. p. 120—121°, $[\alpha]_D^{20} - 81.7^\circ$ in *s*-tetrachloroethane; the latter substance is remarkably stable towards warm concentrated alcoholic alkali hydroxide solutions and is unaffected by ammonia at 100°. Warm dilute sulphuric acid causes the successive removal of the acetone residues and the toluene-*p*-sulphonyl group, so that by interrupting the reaction at the requisite moment it is possible to isolate 3-*toluene-p-sulphonyldextrose* (the constitution assigned to this compound is necessarily dependent on the correctness of the formulation of dextrosediacetone); the substance crystallises as the monohydrate, m. p. (indefinite) 70—71° after softening at 65—66°, $[\alpha]_D^{19} + 39.64^\circ$ in aqueous solution. It is re-converted by acetone and hydrogen chloride into toluene-*p*-sulphonyldextrosediacetone. Treatment of toluene-*p*-sulphonyldextrose with pyridine and acetic anhydride leads to the formation of *toluene-p-sulphonyltetra-acetylglucose*, m. p. 170—171° (decomp.), $[\alpha]_D^{19} + 13.6^\circ$, when dissolved in *s*-tetrachloroethane. The tetra-acetyl derivative is converted by glacial acetic acid and hydrogen bromide or by liquid hydrogen bromide into *toluene-p-sulphonyltriacetylbromoglucose*, slender needles, m. p. 150—151°, $[\alpha]_D^{19} + 164.4^\circ$, which can also be prepared directly from toluene-*p*-sulphonyldextrosediacetone, glacial acetic acid, and hydrogen bromide; it is re-converted by a solution of thallium acetate in acetic acid and acetic anhydride into toluene-*p*-sulphonyl-tetra-acetyldextrose. *Toluene-p-sulphonyltriacetylmethylglucoside*, slender needles, m. p. 138°, $[\alpha]_D^{25} - 17.1^\circ$ in *s*-tetrachloroethane is prepared by agitating a solution of the bromo-compound in methyl alcohol with silver carbonate.

Benzoyltriacetylbromoglucose, m. p. 152°, $[\alpha]_D^{19} + 162.5^\circ$ when dissolved in *s*-tetrachloroethane, is prepared by the action of glacial acetic acid and hydrogen bromide on benzoyldextrosediacetone (Fischer and Noth, *loc. cit.*).

An improved method is given for the preparation of octa-acetyl-maltose. When dissolved in benzene, it is converted by a saturated solution of hydrogen chloride in anhydrous ether into a crystalline substance, m. p. 112—114°, $[\alpha]_D^{19} + 67.5^\circ$ in chloroform, which

appears to be an octa-acetylchloromaltose; the chlorine atom is displaced with unusual readiness.

The estimation of readily eliminable halogen is conveniently effected by boiling a solution of the substance in glacial acetic acid with a similar solution of thallium carbonate. The thallium haloid which is quantitatively precipitated is filtered through a Gooch crucible, washed with hot glacial acetic acid, dried at 135–140°, and weighed.

H. W.

Thioglucose. FRITZ WREDE (*Z. physiol. Chem.*, 1922, **119**, 46–59).—Boiling potassium disulphide solution converts tetra-acetylbromoglucose into octa-acetyldithiodiglucose (Wrede, A., 1920, i, 13), and this, on reduction at a temperature below 25° with sodium amalgam in alcohol containing acetic acid, gives *tetra-acetylthioglucose*, which crystallises in thick, compact masses, m. p. 75°, $[\alpha]_D^{15} - 13.57^\circ$, in 90% alcohol, after seven days, -6.78° ; $[\alpha]_D^{15} + 0.5^\circ$ in $\alpha\alpha\beta\beta$ -tetrachloroethane. Tetra-acetylthioglucose quickly changes Fehling's solution in the cold and gives a dark-coloured precipitate on boiling. On long exposure to the air, but quickly if hydrogen peroxide be added, it is reconverted into octa-acetyldithiodiglucose. With diazomethane in ethereal solution, tetra-acetyl- β -methylthioglucoside is formed, compact crystals from methyl alcohol, m. p. 95°, $[\alpha]_D^{18} - 16.18^\circ$ in $\alpha\alpha\beta\beta$ -tetrachloroethane. By acetic anhydride, it is converted into *penta-acetylthioglucose*, white, compact needles, m. p. 121°, $[\alpha]_D^{14} + 1.6^\circ$ in ethyl acetate. This substance is also obtained directly from octa-acetyldithiodiglucose on reduction with zinc dust and acetic anhydride. Penta-acetylthioglucose, on hydrolysis by methyl alcohol saturated with ammonia, is converted into *thioglucose*, which can also be obtained in a less pure condition by the reduction of octa-acetyldithiodiglucose with aluminium amalgam or sodium amalgam in alcoholic solution containing acetic acid. It has not been found possible to recrystallise thioglucose. After drying over phosphoric oxide in a vacuum, it is an amorphous, white powder, sintering at 70° and foaming at 105°. It shows mutarotation; $[\alpha]_D^{15} + 23^\circ$ in 50% alcohol when equilibrium is reached. Its solubility is similar to that of dextrose; its taste is unpleasant and scarcely sweet. Fehling's solution gives a green colour in the cold, which does not increase on heating. It forms a *silver salt*, $C_6H_{11}O_5SAg$, a yellowish-white non-hygroscopic powder, which can be decomposed by methyl iodide to give β -methylthioglucoside isolated as its tetra-acetyl derivative.

W. O. K.

The Polymerisation of Lævoglucosan. AMÉ PICTET and J. H. ROSS (*Compt. rend.*, 1922, **174**, 1113–1114; A., 1921, i, 647, 766).—When lævoglucosan is heated with a trace of zinc chloride at 140°, the reaction $nC_6H_{10}O_5 = (C_6H_{10}O_5)_n$ takes place in a few minutes, but the products of the reaction vary with the pressure. As the pressure increases the value of n increases. Thus at a pressure of 15 mm. the product is a *dilævoglucosan*, m. p. 135°, $[\alpha]_D + 28.2^\circ$; at the atmospheric pressure the product is *tetralævoglucosan*, $[\alpha]_D + 111.9^\circ$; at a pressure of 4.6 atmos. *hexalævoglucosan*,

$[\alpha]_D + 94.1^\circ$, is obtained, and at 13.3 atmos. *octalævoglucosan*, $[\alpha]_D + 72.8^\circ$, is the product. As the polymerisation increases, the products have properties more nearly approaching those of the dextrins.

W. G.

Celloisobiose. H. OST and G. KNOTH (*Cellulosechemie*, 1922, **3**, 25—38).—*Celloisobiose* is a well-characterised biose sugar the *octa-acetate* of which occurs in the products of acetolysis of cellulose, but readily undergoes conversion into the more stable cellobiose-octa-acetate. The octa-acetates are partly separable by extracting the crude product of acetolysis with ether and then extracting the extracts with alcohol. The *isobiose* acetate is concentrated in the fractions which are readily soluble both in ether and in alcohol. The biose itself is isolated by saponifying the acetate fraction with $N/2$ -barium hydroxide at 25° and submitting the syrup to a systematic fractionation with aqueous alcohol of 85—100% strength. The major portion occurs in the fractions soluble in 85% alcohol. A yield of 2.5 parts of purified *isobiose* per 100 of cellulose was thus isolated, but, owing to the instability of its acetate, the quantity originally formed must have been much larger. *Celloisobiose* crystallises in microscopic needles with $\frac{1}{2}H_2O$; after drying at 105° , the crystals break down to a powder. It is hydrolysed more slowly than most other bioeses into 2 mols. of dextrose. It shows multirotation, which arrives at a constant value of $[\alpha]_D^{20} + 24.6^\circ$ after six hours in 6—8% solution. It has a cupric-reducing value equivalent to 63.2% of dextrose, and forms an *osazone* melting at 165 — 167° , with a composition indicating one free aldehyde group. The authors consider that the cellulose molecule is probably built up entirely of bioese units, and that their crude acetates derived directly from the cellulose apparently contained 40% of cellobiose octa-acetate, 40% of *isobiose* octa-acetate, and about 15% of acetates of cellulose dextrins, which themselves would presumably have given further quantities of bioese acetates if the reaction had been more complete. J. F. B.

The Heat Developed by the Action of Sodium Hydroxide on Cotton ("Mercerisation"). THOS. BARRATT and J. W. LEWIS (*Trans. Text. Inst.*, 1922, **13**, 113—120).—As a contribution to the problem of the connexion between the concentration of sodium hydroxide employed and the "degree of mercerisation" produced, which has not yet received any satisfactory solution, the authors have measured the heat developed when well-scoured Egyptian cotton is immersed in solutions of sodium hydroxide of various concentrations. Since the heat developed is not great (the greatest rise in temperature being 0.5°) and equilibrium is only reached after several minutes in certain cases, an electrical system was elaborated by means of which heat development was measured directly and such factors as the specific heat of the liquid and the total thermal capacity of the calorimeter and its contents could be neglected. The apparatus is fully described, and it is stated that it would also serve for a study of heats of dilution.

A small correction was applied for the heat of dilution of the alkali by the water present in the cotton. This amounted to 5.1%, the material being kept for several months in a desiccator over sulphuric acid (d 1.345), at nearly constant temperature, in order to control the moisture content. The "heat of mercerisation" increases with the concentration of the sodium hydroxide solution, but is not proportional to it. The curve shows an inflection corresponding with a rapid increase in the heat produced when the concentration of alkali is between 10% and 15%, which is the lower limit of the commercial mercerising process. A second inflection, corresponding with a decrease, occurs at about 30%, which is near the upper limit of solutions usually employed in the industry. The rate at which heat is developed is greatest between about 10% and 18%, equilibrium being reached in solutions within these concentrations in about two minutes. J. C. W.

Compounds of Iodine with Constituents of Starch. H. VON EULER and KARL MYRBÄCK (*Annalen*, 1922, **428**, 1—24).—This paper records a large number of measurements of the partition coefficient of iodine between benzene and starch obtained from various sources and previously treated in different ways. The general inference is that two compounds are formed probably with the amylose, and the formulæ $(C_6H_{10}O_5)_{12}I_2$ and $(C_6H_{10}O_5)_{12}I_4$ are suggested with reservations. The formation of these substances is reversible, and is controlled by a dissociation pressure for each which is constant for a constant temperature, although above 40° the formation of hydriodic acid becomes perceptible.

Starch-iodide can be titrated with sodium hydroxide, one atom of iodine being equivalent to about 7NaOH. On back-titration with acids, the iodine is again liberated and forms starch-iodide, one atom of iodine being set free for each 4NaOH neutralised. C. K. I.

Amylocellulose considered as Composed of Silicic Acid and Amylose. G. MALFITANO and M. CATOIRE (*Compt. rend.*, 1922, **174**, 1128—1130).—The authors suggest that the resistance to the action of hot water or acids shown by that part of the starch grain known as amylocellulose is due to the presence of silicic acid and that this material is really a complex compound of amylose with silicic acid of the type $[SiO_3(C_6H_{10}O_5)_n]H_2$. They consider that the various amylaceous materials may be looked on as complexes of silicic acid, phosphoric acid, or simply water with the group $C_6H_{10}O_5$, and that this theory is in better accord with the experimental facts than that which demands varying stages of polymerisation and condensation. W. G.

Chlorites of Ammonium, Tetramethylammonium, and certain Amines. GIORGIO RENATO LEVI (*Gazzetta*, 1922, **52**, i, 207—209; cf. A., 1916, ii, 27).—*Ammonium chlorite*, NH_4ClO_2 , forms transparent, pale yellow, prismatic needles, is not deliquescent, decomposes rapidly when heated, and is exploded by percussion on an anvil. *Methylamine chlorite*, $NH_2Me.HClO_2$, is obtainable only in 66—67% aqueous solution, which detonates

slightly when poured on to a hot iron plate. *Dimethylamine chlorite*, $\text{NHMe}_2\cdot\text{HClO}_2$, and *trimethylamine chlorite*, $\text{NMe}_3\cdot\text{HClO}_2$, also obtainable only in aqueous solution, behave similarly to the previous compound, the tertiary compound exhibiting greater tendency to decompose on concentration. *Tetramethylammonium chlorite*, NMe_4ClO_2 , forms colourless crystals, is highly deliquescent, explodes on percussion, and forms neutral aqueous solutions.

T. H. P.

Preparation of Hexamethylenetetramine and Formaldehyde
H. OTTO TRAUN'S FORSCHUNGS-LABORATORIUM (Brit. Pat. 156136).—Formaldehyde can be obtained in satisfactory yield by the contact oxidation of methane (or natural gas containing methane) if the oxidation takes place in presence of ammonia whereby the more stable hexamethylenetetramine is formed and the aldehyde is thus saved from destruction. For example, a mixture of 6 vols. of methane, 12 vols. of oxygen, and 4 vols. of ammonia is passed through a reaction tube provided with a constriction, where it is heated at $300\text{--}500^\circ$, or even at 700° if the reaction is performed under reduced pressure. The tube itself may serve as the catalyst, or a steel or iron tube packed at the constriction with silver, nickel, or copper wire may be used. The reaction product is condensed and consists mainly of hexamethylenetetramine (70% yield), from which formaldehyde can be regenerated in known manner. The yields are favourably influenced by saturating the gases with methyl or ethyl alcohol vapour before passing them through the contact tube.

G. F. M.

The Two Modifications of Glycine. Methylation with Diazomethane. HEINRICH BILTZ and HANS PAETZOLD (*Ber.*, 1922, 55, [B], 1066—1073).—The occurrence of two modifications of glycine has been noted by Fischer (A., 1905, i, 863) and Falk and Sugiura (A., 1918, i, 292); according to the former, the yield of aminoacetyl chloride hydrochloride from glycine depends on whether the plate or needle variety of the latter is used, whilst, according to the latter, the two modifications behave differently when heated and have differing additive capacity towards bromine. The explanation is now found in the observation that the large plate-like crystals deposited from aqueous solution enclose mother-liquor which is not removed even when the finely divided material is heated at 100° . This can be effected at 130° , and the behaviour of both crystalline forms becomes then physically and chemically identical. Alanine behaves in a similar manner. When heated glycine decomposes at about 245° after becoming brown at about 220° and black at about 237° . Either form absorbs bromine vapour to an equal degree under identical conditions, but the actual amount depends greatly on the tension of the bromine vapour, and there does not appear to be any indication of the formation of a definite product. The absorbed bromine is evolved completely when the products are prepared over moistened potassium hydroxide.

Neither variety is methylated appreciably by an ethereal solution of diazomethane, such action as is observed being due to the

methylation of admixed methyl alcohol, which can also be catalysed by other agents. The addition of a small quantity of water causes the reaction to proceed vigorously with the formation of betaine in about 75% yield from either variety; the action of the water is attributed to its solvent power towards glycine.

H. W.

Preparation of Dialkylaminoalkyl Compounds. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 167781; from *Chem. Zentr.*, 1921, iv, 1223).—Halogen alkylalkylamines are allowed to react with alkali salts of compounds of the general formula $R\cdot CO\cdot CHR'\cdot X$, where R and R' are hydrogen or an organic radicle and X is a negative group such as $-\text{CO}_2\text{Et}$, $-\text{COMe}$, $-\text{Bz}$, or $-\text{CN}$. Such compounds are ethyl acetoacetate, ethyl cyanoacetate, ethyl malonate, ethyl acetonedicarboxylate, ethyl camphorcarboxylate, ethyl succinylsuccinate, or acetylacetone. Dialkylaminoalkyl compounds can also be prepared by the action of dialkylamines on halogen derivatives of the compounds mentioned. *Ethyl α -diethylaminoethylacetoacetate* is prepared from ethyl sodioacetoacetate and chloro- or bromo-ethyl-diethylamine, or from ethyl α -bromoethylacetoacetate and diethylamine. By similar methods, the following compounds are obtained: *methyl α -diethylaminoethylacetoacetate*; *ethyl α -dimethylaminoethylacetoacetate*; *ethyl diethylaminobutylacetoacetate*; *ethyl diethylaminoethylmalonate*; *ethyl diethylaminoethylcyanoacetate*; *ethyl bisdiethylaminoethyldiketocyclohexanedicarboxylate* (from diethylchloroethylamine and ethyl sodium succinylsuccinate); *ethyl diethylaminoethylacetonedicarboxylate*; *methyl diethylaminoethylcamphorcarboxylate*; *diethylaminoethylacetylacetone*. *Diethylchloroethylamine* is obtained by the action of thionyl chloride on diethylaminoethanol in chloroform solution and decomposition of the hydrochloride with potassium carbonate. *Diethylbromoethylamine* is obtained by heating diethylaminoethanol hydrobromide with 48% hydrobromic acid. *Diethylchlorobutylamine*, $\text{NEt}_2\cdot[\text{CH}_2]_2\cdot\text{CHMeCl}$, is obtained by the reduction of diethylaminobutanone to the corresponding alcohol and subsequent treatment with thionyl chloride. *Diethylpiperazine dichloroethylate* is obtained as a by-product in the preparation of ethyl α -diethylaminoethylacetoacetate. G. W. R.

Synthesis of Formamide from Carbon Monoxide and Ammonia. KURT H. MEYER and LUDWIG ORTHNER (*Ber.*, 1922, 55, [B], 857; cf. A., 1921, i, 775).—A correction in the calculation of the equilibrium constant.

H. W.

Synthesis with Cyanamide. Cyanamidoethyl Alcohol and Guanidoethyl Alcohol. EMIL FROMM and ERNST HONOLD (*Ber.*, 1922, 55, [B], 902—911).—*Cyanamidoethyl alcohol*, an oily liquid which could neither be caused to crystallise nor distilled without decomposition even in a vacuum, is prepared by the action of ethylene chlorohydrin on an aqueous solution of sodium cyanamide and is characterised by its benzoate and *p*-toluenesulphonate. The substance can react in the following forms, $\text{NC}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$,

$\text{HN}:\text{C}:\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, $\text{CH}_2\begin{smallmatrix} \text{O}---\text{C}\cdot\text{NH}_2 \\ | \\ \text{CH}_2\cdot\text{N} \end{smallmatrix}$, and $\text{CH}_2\begin{smallmatrix} \text{O}---\text{C}\cdot\text{NH} \\ | \\ \text{CH}_2\cdot\text{NH} \end{smallmatrix}$,

and its derivatives are constituted differently from one another. With toluene-*p*-sulphonyl chloride in the presence of alkali, a *mono-toluenesulphonate*, m. p. 128°, is obtained which doubtless has the

constitution $\text{CH}_2\begin{smallmatrix} \text{O}---\text{C}\cdot\text{NH} \\ | \\ \text{CH}_2\cdot\text{N}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7 \end{smallmatrix}$, since it is converted by cold

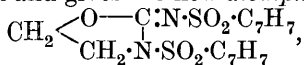
dilute sulphuric acid with loss of ammonia into 3-*p-toluenesulphonyl*-1:3-*oxazolid-2-one*, m. p. 193°, is transformed by aniline even in the absence of water into diphenylcarbamide, and yields with

benzoyl chloride the *derivative*, $\text{CH}_2\begin{smallmatrix} \text{O}---\text{C}\cdot\text{NBz} \\ | \\ \text{CH}_2\cdot\text{N}\cdot\text{SO}_2\cdot\text{C}_7\text{H}_7 \end{smallmatrix}$, small

needles, m. p. 117°, which is converted by cold dilute sulphuric acid into benzoic acid, ammonia, and the lactone, m. p. 193° (see above). Cyanamidoethyl alcohol is converted by benzoyl chloride in alkaline solution into a *dibenzoyl* derivative, colourless needles, m. p. 165°, to which the constitution $\text{NBz}:\text{C}:\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OBz}$ is assigned. It is completely stable towards dilute sulphuric acid, but is transformed by cold, concentrated sulphuric acid and subsequent addition of water into *benzoyl-β-benzoxylethylcarbamide*, $\text{NHBz}\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OBz}$, m. p. 176°. It is converted by aniline into benzanilide and *benzoylphenylcarbamide*, lustrous platelets, m. p. 204°. Finally, when a boiling alcoholic solution of dibenzoylcyanamidoethyl alcohol is treated with ammonia *dibenzoyl-β-hydroxyethylguanidine*, $\text{NHBz}\cdot\text{C}(\text{NH}_2):\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OBz}$, thin needles, m. p. 150°, is produced from which benzoylcarbamide is readily isolated by the action of dilute hydrochloric acid in the presence of alcohol; it is remarkable that the guanidine derivative cannot be benzoylated further by the Schotten-Baumann method.

Guanidoethyl alcohol is prepared by passing gaseous ammonia into the boiling alcoholic solution of cyanamidoethyl alcohol; like the latter, it cannot be purified by crystallisation or distillation. It can react in the following forms: $\text{C}(\text{NH}_2)_2:\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, $\text{HN}:\text{C}(\text{NH}_2):\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, and $\text{CH}_2\begin{smallmatrix} \text{O}---\text{C}(\text{NH}_2)_2 \\ | \\ \text{CH}_2\cdot\text{NH} \end{smallmatrix}$. With

benzoyl chloride, it gives a *tribenzoate*, $\text{C}(\text{NHBz})_2:\text{N}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OBz}$, m. p. 156°, which is hydrolysed smoothly by dilute hydrochloric acid in alcoholic solution to dibenzoylcarbamide, m. p. 197°. With toluene-*p*-sulphonyl chloride and sodium hydroxide, it yields a *disulphonate*, $\text{N}(\text{SO}_2\cdot\text{C}_7\text{H}_7):\text{C}(\text{NH}_2):\text{N}(\text{SO}_2\cdot\text{C}_7\text{H}_7)\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, lustrous platelets, m. p. 163°, which loses ammonia, without, however, adding the elements of water under the action of boiling dilute sulphuric acid and gives the new *disulphonate*,



m. p. 206°.

H. W.

The Action of Sulphuric Acid on Nitroguanidine. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1922, **44**, 868—872).—Nitroguanidine is decomposed quantitatively by hot concentrated

sulphuric acid, half of its nitrogen being liberated as ammonia and the whole of its carbon as carbon dioxide.

Solubility curves of nitroguanidine in sulphuric acid of varying strengths at 0° and 25° have been constructed. W. G.

Synthesis and Properties of Tetramethylenediguanidine.

ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **118**, 277—283).—In repeating the synthesis by Kossel (*A.*, 1910, i, 500, 625) of agmatine (α -amino- δ -guanidino-*n*-butane), by the action of cyanamide on tetramethylenediamine (putrescine), the author has improved the yield, and has obtained also from the product of the reaction *tetramethylenediguanidine*, $C_4H_8[NH \cdot C(NH) \cdot NH_2]_2$ as its *sulphate*, spherical aggregates of needles, m. p. 291° (decomp.). The following salts have also been prepared: *carbonate*, small, thick prisms or boat-shaped crystals; *hydrochloride*, thick, transparent prisms; *picrate*, small, thin, light yellow prisms, m. p. 253—254° (decomp.); *picrolonate*, yellow, amorphous, m. p. 278—279° (decomp.); *aurichloride*, small, lustrous needles, m. p. 172.5°, and *platinichloride*, orange, rhombic plates or feather-like, crystalline aggregates, m. p. 224° (decomp.). W. O. K.

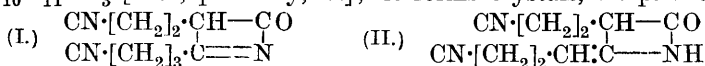
The Action of the Grignard Reagent on Thiocyanates.

ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, **44**, 873).—Certain structural formulæ given in a previous paper are now corrected (cf. *A.*, 1921, i, 5). W. G.

Preparation of Ethylene Cyanohydrin [β -Hydroxypropionitrile]. RÖHM and HAAS (*Fr. Pat.* 525539; from *Chem. Zentr.*, 1921, iv, 1222).—The reaction of ethylene halogen-hydrins and cyanide solutions takes place in aqueous solutions at temperatures below the temperature at which the cyanohydrin is decomposed by aqueous salt solutions. For example, *ethylene cyanohydrin* is formed by the reaction of ethylene bromohydrin with potassium cyanide solution at 55—60°. Ethylene chlorohydrin reacts similarly with sodium cyanide solution; 85—95% of the theoretical yield is obtained. G. W. R.

The Action of Organo-magnesium Compounds on Glutaronitrile. P. BRUYLANTS (*Bull. Acad. roy. Belg.*, 1921, [5], 7, 252—259; from *Chem. Zentr.*, 1921, iii, 1349; cf. Blaise, *A.*, 1921, i, 647).—By the action of magnesium ethyl bromide on glutaronitrile, ethane is evolved with the probable formation of a compound, $CN \cdot CH_2 \cdot CH_2 \cdot CH : C : N \cdot MgBr$, which when decomposed by acidified water gives exclusively glutaronitrile and glutaramide nitrile (?). By heating the nitrile (1 mol.) with magnesium ethyl bromide (2 mols.) and decomposing with water, small quantities of a *ketone*, probably $COEt \cdot [CH_2]_3 \cdot CN$, a liquid of camphor-like odour, b. p. 170°/17 mm., are obtained; the *semi-carbazone* has m. p. about 215°. The hydrolysis of the ketone with hydrochloric acid gives *propionylbutyric acid* (?). The decomposition with water of the magnesium compound formed from an equimolecular mixture of glutaronitrile with a mag-

nesium methyl, ethyl, or propyl haloid gives a *compound*, $C_{10}H_{11}ON_3$ [I or, probably, II]; it forms crystals, m. p. 149-6—



149-8°; molecular weight in acetic acid 100—110. It reacts energetically with 1 molecule of bromine, giving 1 molecule of hydrogen bromide. By hydrolysis with hydrochloric acid, an acid, $CO([CH_2]_3 \cdot CO_2H)_2$, is formed, having m. p. 91—93°.

G. W. R.

Crystal Structures of Complex Cyanides of Potassium with Zinc, Cadmium, and Mercury. ROSCOE G. DICKINSON (*J. Amer. Chem. Soc.*, 1922, **44**, 774—784).—The crystal structures of potassium zinc cyanide, $K_2Zn(CN)_4$, potassium cadmium cyanide, $K_2Cd(CN)_4$, and potassium mercury cyanide, $K_2Hg(CN)_4$, have been determined by X-ray spectral photographs and unsymmetrical Laue photographs. It is shown that the theory of space groups is extremely useful in interpreting the experimental data, and also that it was not necessary to make any quantitative assumptions as to the “normal decline” of intensity. All three substances have a cubic structure. The following data are recorded: potassium zinc cyanide, length of side of unit cube (d_{100}) = 12.54 Å.U., distance between potassium and cyanogen 3.20 Å.U., distance between zinc and cyanogen, 2.61 Å.U.; potassium cadmium cyanide, d_{100} = 12.84 Å.U., distance between potassium and cyanogen, 3.28 Å.U., distance between cadmium and cyanogen, 2.67 Å.U.; potassium mercury cyanide, d_{100} = 12.76 Å.U., distance between potassium and cyanogen, 3.25 Å.U., distance between mercury and cyanogen, 2.65 Å.U. The unit cube in all cases contains eight molecules. It is shown that these complex cyanides have the same structure as magnetite and spinel.

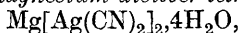
J. F. S.

Attempts to Prepare Pure Calcium Cyanide. HEINRICH PINCASS (*Chem. Ztg.*, 1922, **46**, 347).—Pure calcium cyanide cannot be prepared by Schulz's method, which consists in mixing concentrated solutions of potassium ferrocyanide and calcium chloride, ignition of the precipitate at a dull red heat, and extraction of the residue with water. The action of hydrocyanic acid on calcium hydroxide in aqueous solution gives a product containing about 33% of calcium cyanide. At the atmospheric temperature, gaseous hydrocyanic acid and solid calcium hydroxide give the substance $3Ca(OH)_2 \cdot 2Ca(CN)_2 \cdot 13H_2O$ with 41% of calcium cyanide, whereas at 600—700° they give carbon, and calcium cyanide and cyanamide. If carbonisation is excluded by working in a vacuum, calcium cyanide alone is formed. The absorption of gaseous hydrocyanic acid by lime increases up to 300°, and then falls; at 700°, the formation of cyanide does not take place.

H. W.

Magnesium Cyanide. FR. FICHTER and RICHARD SUTER (*Helv. Chim. Acta*, 1922, **5**, 396—400).—Solutions of magnesium cyanide are best prepared by solution of the metal in 10—15%

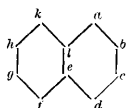
aqueous hydrocyanic acid solution, but they gradually deposit the hydroxide even when preserved in an atmosphere of hydrogen cyanide. Contrary to the statement of Schulz (1856), the cyanide cannot be obtained in the crystalline condition by concentration of its solution. By addition of silver nitrate solution until a permanent turbidity is produced, filtration, and concentration in a vacuum, leaflets of *magnesium disilver tetracyanide*,



are isolated. By recrystallisation of this salt, and accompanying it, needles of *magnesium silver tricyanide*, $\text{Mg}[\text{Ag}(\text{CN})_3]$, are obtained. Dry magnesium hydroxide does not react with an ethereal solution of hydrogen cyanide (cf. Meyer, A., 1921, i, 501); in presence of moisture, a product is obtained which has suffered almost complete hydrolysis. The preparation of the anhydrous cyanide by heating magnesium ferrocyanide (analytical data for which indicate its existence in varying degrees of hydration) (Eidmann, A., 1899, i, 317) is unsatisfactory, not only on account of the presence of iron carbide and carbon in the product, but also owing to simultaneous formation of magnesium nitride: $3\text{Mg}_2[\text{Fe}(\text{CN})_6] = 2\text{Mg}_3\text{N}_2 + 3\text{FeC}_2 + 7\text{N}_2 + 15\text{C}$. This decomposition occurs to an extent which rapidly increases with rise in temperature above 400° , so that at 800° it is the sole reaction. The most favourable yields of cyanide (4.6—5.7 per cent.) were obtained at 450° .

J. K.

The Atomic Vibrations in the Molecules of Benzenoid Substances. R. ROBINSON (*Nature*, 1922, 109, 476).—If, in the annexed formula, it is assumed (Bragg, *Proc. Physical Soc.*, 1921, 34, 33) that the centres of the carbon atoms at *h*, *l*, *b*, *g*, *e*, and *c* lie in a plane, whilst those at *k* and *a* lie above the plane, and those at *f* and *d* an equal distance below it, enantiomorphism



would result in the case of all mono-substituted and in the majority of the higher substituted compounds. It is suggested that the above conception represents merely a phase of an oscillation of the relatively unrestricted molecules of the fused or dissolved substance in which the pairs of carbon atoms, *k*, *a*, and *f*, *d*, appear alternately above and below the plane containing the six remaining atoms. An identical result is obtained if all the atoms are supposed to be in motion in such a way that adjacent atoms move in opposite directions and to an equal distance from the plane of the original ring.

A. A. E.

Configurations of Molecules of Benzenoid Substances. J. KENNER (*Nature*, 1922, 109, 581; cf. preceding abstract).—Recent investigations (T., 1922, 121, 614) indicate that in the case of 6:6'-dinitrodiphenic acid, the two benzene nuclei in separate molecules (as distinguished from their crystalline aggregates, to which Bragg's results apply) are not coplanar. If this be so, it follows that the direction of the valency of each of the carbon atoms through which these nuclei are united is not, as represented

in the usual formula for benzene, exerted in the plane of the benzene ring, and, further, that this condition is a stable one, rather than a phase of an oscillation as suggested by Robinson. It is pointed out that one phase of Bloch's formula for benzene corresponds closely with that deduced by Bragg from observations on diamond and on naphthalene and its derivatives. A. A. E.

Ethylenic Stereoisomerism. CH. DUFRASSE (*Ann. Chim.*, 1922, [ix], 17, 133—221).—A more detailed account of work already published (A., 1914, i, 845; 1920, i, 486; 1921, i, 17, 104, 114, 168; this vol., i, 39). W. G.

Oxidation of the Trinitroxylenes. M. GIUA (*Gazzetta*, 1922, 52, i, 183—188).—When oxidised by means of chromic acid, 3 : 4 : 6-trinitro-*o*-xylene and 2 : 3 : 5-trinitro-*p*-xylene yield, respectively, 3 : 4 : 6(or 3 : 5 : 6)-trinitro-*o*-toluic and 2 : 3 : 5-trinitro-*p*-toluic acids. By excess of chromic acid 2 : 4 : 6-trinitro-*m*-xylene in concentrated sulphuric acid solution is converted into 2 : 4 : 6-trinitroisophthalic acid.

3 : 4 : 6(or 3 : 5 : 6)-*Trinitro-o-toluic acid*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{HMe}(\text{NO}_2)_3$, crystallises in white needles, m. p. 201—202°, and gives a reddish-brown coloration with alkali; its *silver* salt deflagrates when heated.

2 : 4 : 6-*Trinitroisophthalic acid*, $\text{C}_6\text{H}(\text{NO}_2)_3(\text{CO}_2\text{H})_2$, forms white needles, m. p. 196—197° (evolution of gas), has a slightly bitter taste, and loses carbon dioxide with formation of *s*-trinitrobenzene when heated above its melting point or boiled with water.

2 : 3 : 5-*Trinitro-p-toluic acid*, $\text{C}_8\text{H}_5\text{O}_8\text{N}_2$, crystallises in lustrous, white lamellæ, m. p. 230—231°, and gives a brownish-red coloration with alkali hydroxides. Its *silver* salt, which deflagrates when heated, *methyl* ester, white needles, m. p. 114—115°, and *ethyl* ester, colourless prisms, m. p. 87—88°, were analysed.

Methyl 3 : 5-dinitro-2-amino-p-toluate, $\text{C}_9\text{H}_9\text{O}_6\text{N}_3$, prepared by the action of alcoholic ammonia solution on *methyl 2 : 3 : 5-trinitro-p-toluate*, forms lustrous, yellow needles, m. p. 139—140°, and *methyl 3 : 5-dinitro-2-ethylamino-p-toluate*, $\text{C}_{11}\text{H}_{13}\text{O}_6\text{N}_3$, similarly obtained by the action of ethylamine, in yellow needles, m. p. 103—104°, which are slowly reddened by the action of light.

T. H. P.

An Instance of the Apparent Effect of the Entering Group on the Position of Substitution in the Benzene Nucleus. WILLIAM DAVIES (T., 1922, 121, 806—815).

The Cumulative Effect of the Chlorine Atom and the Methyl and Sulphonyl Chloride Groups on Substitution in the Benzene Nucleus. III. WILLIAM DAVIES (T., 1922, 121, 785—791).

Determination of the Configuration of the Stereoisomeric Hexamethylenes. A. SKITA (*Annalen*, 1922, 427, 255—280).—Most of this work has already been described (cf. A., 1921, i, 503). *cis*-1-Amino-*cis*-2-*trans*-4-dimethylcyclohexane is characterised by an *acetyl* derivative, b. p. 149°/12 mm., m. p. 29°, a *phenylcarbamide*, m. p. 60°, a *s*-*thiocarbamide*, $\text{C}_{17}\text{H}_{32}\text{N}_2\text{S}$, m. p. 182°, a *picrate*,

leaflets, m. p. 176—177°, and a *hydrochloride*, needles, m. p. 223°. The five corresponding derivatives of *cis*-1-amino-*trans*-2-*cis*-4-dimethylcyclohexane have the following m. p.: 120°, 128°, 215°, 155—156°, and 235°, respectively. C. K. I.

Catalytic Preparation of Aniline. II. O. W. BROWN and C. O. HENKE (*J. Physical Chem.*, 1922, **26**, 272—287; cf. this vol., i, 445).—The reduction of nitrobenzene by hydrogen to aniline in the presence of various catalysts has been investigated. It is shown that cobalt is active at a lower temperature than nickel (*loc. cit.*), but it is to be noted that the cobalt contained a little nickel and the nickel a little cobalt. Iron is found to carry the reduction further than copper, but cannot be used below 300°, and at this temperature its action is too vigorous, the reduction being carried too far. Silver is an excellent catalyst, even better than copper prepared by ignition of the nitrate, because it may be used with a much higher rate of flow of nitrobenzene. Antimony, manganese, and chromium also act as catalysts in the reduction of nitrobenzene. The lower oxides of molybdenum, vanadium, uranium, tungsten, and cerium also catalyse the reduction. The activity of the oxides of molybdenum and vanadium is greater than that of the other three. Alumina has a slight activity, which is probably that of a dehydrating catalyst, as water is one of the products of the reaction. Commercial tellurium and the oxides of calcium, barium, and silicon have no appreciable activity. In the case of iron and antimony, a part of the reduction is due to the direct action of the metal, an oxide being formed. When antimony is used at a low temperature, the catalyst loses its activity, which is restored by heating at 450° in hydrogen. When, however, antimony is used at 320° it does not lose its activity with use. J. F. S.

Migration of the Methyl Residue into the Benzene Nucleus. The Transformation of Methylaniline Hydrochloride into Toluidine Hydrochloride. ERNST BECKMANN and ERICH CORRENS [with OTTO LIESCHE] (*Ber.*, 1922, **55**, [B], 852—856).—The conversion of methylaniline hydrochloride into toluidine hydrochloride has been regarded as an intramolecular change of the first order due to a direct exchange of position of the methyl group and a hydrogen atom, or, alternatively, as due to the preliminary production of methyl chloride and subsequent action of the latter on the aniline. The proof that a tertiary base is also produced greatly strengthens the latter conception.

Experiments with methylaniline hydrochloride show that the Hofmann-Martius reaction does not take place at 235°; at 260°, a mixture of primary and secondary amines in about equal proportions is produced whereas at 310° the tertiary amine is formed in considerable amount. The course of the reaction does not appear to be influenced to any considerable extent by the presence of aluminium chloride or zinc chloride, the temperature being the fundamental factor.

Methylaniline is not affected by treatment with concentrated

sulphuric acid at 100° or with a saturated solution of hydrogen chloride in glacial acetic acid and acetic anhydride at 150°; the Hofmann-Martius reaction does not therefore appear to be analogous to the Beckmann transformation. H. W.

2:3- and 2:5-Dinitro-*p*-toluidines. JAMES SCOTT and ROBERT ROBINSON (T., 1922, **121**, 844—846).

Complex Tautomerism. H. LEY and R. GRAU (*Z. physikal. Chem.*, 1922, **100**, 271—275).—When to a complex compound, formed between a nitrohydrocarbon, $\text{H}\cdot\text{R}(\text{NO}_2)_n$, and an aromatic amine, $\text{R}'\text{NA}_2$, of the type $\text{HR}(\text{NO}_2)_n \dots \text{R}'\text{NA}_2$, a salt-forming group, XH , is added, the hydrogen of which can form an ion, then the resulting compound may exist in two possible forms, $(\text{NO}_2)_n\text{RX}[\text{H} \dots \text{NR}'\text{A}_2]$ and $\text{HXR}(\text{NO}_2)_n \dots \text{R}'\text{NA}_2$. Evidence is advanced to prove that in the case of the complex formed between 3:5-dinitrobenzoic acid and diethylaniline, the two tautomerides actually exist. The complex forms light yellow crystals which dissolve in water to form a colourless solution. The solution has a marked electrical conductivity which points to the saline character of the dissolved substance. In chloroform, methyl alcohol, ethyl alcohol, amyl alcohol, and ethyl ether, the solution is yellow to yellowish-red. It melts at 93°, but when heated under water at 73°, brownish-red liquid drops are formed which on solidifying pass back to the white form, which again melts at 93°. J. F. S.

The Catalytic Reduction of Aromatic Nitro-compounds and a New Method for the Preparation of β -Arylhydroxylamines. I. K. BRAND and JOSEPH STEINER (*Ber.*, 1922, **55**, [B], 875—887).—Nord (A., 1920, i, 21) has studied the course of the catalytic reduction of nitrobenzene in the presence of a platinum catalyst and has thereby established the intermediate production of β -phenylhydroxylamine; he has, however, been led to the conclusion that the method does not allow ready control, and that the intermediate products are only present in such small amount as to render their isolation and identification a matter of extreme difficulty. It is now found, however, that under suitable conditions β -arylhydroxylamines, azoxy- and hydrazo-derivatives can be prepared in good yield. The compounds first named are obtained in neutral solution, whereby the possibility of the conversion of initially-formed β -arylhydroxylamines into azoxy-compounds, aminophenols, or chloroamines is practically excluded. Reduction is effected by hydrogen at the atmosphere pressure in the presence of palladised animal charcoal, the extent of the action being controlled by regulation of the volume of the hydrogen used; provided that the change does not occur too vigorously, there is little fear of the further reduction of β -arylhydroxylamine to primary amine so long as unchanged nitro-derivative is present. Under these conditions, nitrobenzene yields successively β -phenylhydroxylamine in 80% yield and (with a further supply of hydrogen) aniline in 90% yield. *m*-Dinitrobenzene yields 1-nitro-3-hydroxylaminobenzene [β -*m*-nitrophenylhydroxylamine], m. p. 118—119°

(cf. Brand, A., 1906, i, 80), *m*-nitroaniline, and *m*-phenylenediamine. 2:4-Dinitrotoluene is converted successively into 2-nitro-4-hydroxylaminotoluene (Brand and Zöller, A., 1907, i, 755) and 2:4-tolylenediamine, whereas 2:6-dinitrotoluene gives 2-nitro-6-hydroxylaminotoluene (Brand, A., 1911, i, 713), 2-nitro-6-aminotoluene, m. p. 92°, and 2:6-tolylenediamine.

The smooth formation of azoxy-compounds depends essentially on the alkalinity of the solution, which must be sufficient to promote the rapid production of the desired substance and thus to repress the further reduction of the β -arylhydroxylamine to primary amine. Palladised animal charcoal is used as catalyst. Under these conditions, nitrobenzene is transformed by the requisite quantities of hydrogen into azoxybenzene and hydrazobenzene, whereas with a smaller concentration of alkali hydroxide the main product is aniline, the formation of which is not due to fission of intermediately formed azoxybenzene; in aqueous alcoholic solution, azoxybenzene and azobenzene are converted by the requisite amounts of hydrogen into hydrazobenzene, aniline not being produced in more than minimal quantity. *m*-Dinitrobenzene gives 1:1'-dinitro-3:3'-azoxybenzene, m. p. 146.5° (cf. Brand, A., 1906, i, 80). 2:4- and 2:6-Dinitrotoluenes are transformed respectively into 2:2'-dinitro-4:4'-azoxytoluene, m. p. 164°, and 2:2'-dinitro-6:6'-azoxytoluene, m. p. 188° (cf. Brand and Zöller, A., 1907, i, 755).
H. W.

Semipinacolic Transposition in the Benzylcyclohexene Series; Migration of the Benzene Radicle. M. TIFFENEAU and M. PORCHER (*Bull. Soc. chim.*, 1922, [iv], 31, 324—334).—1-Benzylcyclo- Δ^1 -hexene, obtained by the dehydration of benzylcyclohexanol, gives, in ethereal solution with mercuric oxide and iodine, 2-iodo-1-benzylcyclohexan-1-ol, which when shaken in ethereal solution with silver nitrate yields a mixture of the original hexene, its oxide, and 1-benzylcyclohexan-2-one, b. p. 165—166°/18 mm., d_4^{20} 1.0733, giving a semicarbazone, m. p. 166—167°. 1-Benzylcyclohexan-2-one may also be prepared from cyclohexanone by the action of sodamide followed by the addition of benzyl chloride. A fourth product of the action of silver nitrate on the iodohydrin is 1-benzylcyclohexan-1:2-diol, m. p. 96—97°, which on dehydration gives benzylcyclohexanone.

4-Benzyl-1-methylcyclohexan-4-ol, b. p. 183—187°/25 mm., obtained by the action of magnesium benzyl chloride on 1-methylcyclohexan-4-one, on dehydration gives 4-benzyl-1-methylcyclo- Δ^3 -hexene, b. p. 160—165°/35 mm., from which 3-iodo-4-benzyl-1-methylcyclohexan-4-ol can be prepared. This iodohydrin does not give a ketone when shaken in ethereal solution with silver nitrate.
W. G.

Nitro-derivatives of *p*-Phenetidine. FREDERIC REVERDIN and H.-P. ANDRÉ ROETHLISBERGER (*Helv. Chim. Acta*, 1922, 5, 300—314).—The reactivity of the 2-nitro-group in 2:3:5-trinitro-*p*-phenetidine (Reverdin and Fürstenberg, A., 1913, i, 850) is preserved in its *p*-toluenesulphonyl derivative. In 2:3-dinitro-

p-phenetidine, however, it is the 3-nitro-group which exhibits reactivity, and this is enhanced by acylation, the benzoyl being more effective than the acetyl group in this respect. 2:3-Di- and 2:3:5-tri-nitro-*p*-phenetidines are best prepared by nitration of *p*-toluenesulphonyl-*p*-phenetidine (Reverdin and Fürstenberg, *loc. cit.*) or its 3-nitro-derivative (detailed directions for which are supplied), followed by hydrolysis. 2:5-Dinitro-*p*-toluenesulphonyl-*p*-phenetidine, $C_{15}H_{15}O_7N_3S$, prisms or rosettes, m. p. 152—154°, is a subsidiary product in the preparation of the 2:3-isomeride. The orientation of 2:5-dinitro-*p*-phenetidine, $C_8H_9O_5N_3$, scarlet needles, m. p. 139—139.5° (acetyl derivative, $C_{10}H_{11}O_6N_3$, yellow needles, m. p. 156—157°), follows from its conversion into 2:5-dinitrophenetole, m. p. 96—98° (cf. Andreae, A., 1880, 466), from which 2:5-dinitrophenol is obtained by means of concentrated sulphuric acid at 60—70°. Similarly, 2:5-dinitro-4-aminophenol, $C_6H_5O_5N_3$, violet-black needles, m. p. 166—167°, is produced from 2:5-dinitro-*p*-phenetidine, although the corresponding anisidine is stable under these conditions. 2:5-Dinitro-4-aminophenyl acetate, $C_8H_7O_6N_3$, m. p. 144—145°, exists in a yellow and a red form. Chromoisomerism is also exhibited by 3-nitro-*p*-toluenesulphonyl-*p*-phenetidine (large, pale yellow, cubic crystals, m. p. 104—105°; intensely yellow, fine needles, m. p. 94—95°), 2:3-dinitrotoluenesulphonyl-*p*-phenetidine (fine, pale yellow needles, m. p. 145—146°; almost colourless, cubic crystals, m. p. 162—163°; cf. Reverdin and Fürstenberg, *loc. cit.*).

p-Toluenesulphonyl-2:3-dinitro-N-methyl-*p*-phenetidine,

$C_{16}H_{17}O_7N_3S$, forms needles, or tablets, m. p. 152—152.5°. Benzoyl-2:3-dinitro-*p*-phenetidine, forms pale yellow plates, m. p. 182—183°. Benzoyl-2:3:5-trinitro-*p*-phenetidine, $C_{15}H_{12}O_8N_4$, forms pale yellow needles, m. p. 246—247° (decomp.). *p*-Toluenesulphonyl-2-nitro-3-anilino-*p*-phenetidine, $C_{21}H_{22}O_8N_4S$, crystallises in ruby-red needles, m. p. 111—111.5°. Acetyl-2-nitro-3-anilino-*p*-phenetidine, $C_{16}H_{17}O_4N_3$, brown plates, m. p. 151—152°; the benzoyl analogue, $C_{21}H_{19}O_4N_3$, dark brown crystals, m. p. 153—154°, furnishes benzoyl-2-nitro-3-methylamino-*p*-phenetidine, $C_{16}H_{17}O_4N_3$, dark brown crystals, m. p. 135—136°. *p*-Toluenesulphonyl-3:5-dinitro-2-anilino-*p*-phenetidine, $C_{21}H_{20}O_7N_4S$, forms yellow prisms, m. p. 198—199°. 3:5-Dinitro-2-methoxy-*p*-phenetidine, $C_9H_{11}O_6N_3$, forms orange needles, m. p. 120—121°. The following molecular compounds are described: *p*-Toluenesulphonyl-2:3-dinitro-*p*-phenetidine with methylamine, $C_{16}H_{20}O_7N_4S$, m. p. 148—149°; with dimethylamine, $C_{17}H_{22}O_7N_4S$, red crystals, m. p. 141°; with ethylamine,

$C_{17}H_{22}O_7N_4S$, orange needles, m. p. 146° (decomp.); with diethylamine,

$C_{19}H_{26}O_7N_4S$, red or yellow plates, m. p. 182—183°; with aniline, $C_{21}H_{22}O_7N_4S$, plates, m. p. 141—142°; with quinoline, $C_{24}H_{22}O_7N_4S$, yellow cubic crystals, m. p. 94—96°, and a potassium salt, $C_{25}H_{14}O_7N_3SK$, orange-yellow needles, m. p. 296—297°. *p*-Toluenesulphonyl-2:3:5-trinitro-*p*-phenetidine, gives with dimethylamine, $C_{17}H_{21}O_9N_3S$,

a red form, m. p. 164° , and an orange form, m. p. 184° ; with *trimethylamine*, $C_{18}H_{23}O_9N_5S$, canary yellow needles, m. p. $175-176^{\circ}$ (decomp.); and with *quinoline*, $C_{24}H_{21}O_9N_5S$, orange red needles, m. p. $102-103^{\circ}$ (decomp.). *p-Toluenesulphonyl-3-nitro-p-phenetidine* forms with *diethylamine*, $C_{19}H_{27}O_5N_3S$, red needles, m. p. $135-136^{\circ}$. *p-Toluenesulphonyl-2:5-dinitro-p-phenetidine*, gives with *dimethylamine*, $C_{17}H_{22}O_7N_4S$, red or yellow plates, m. p. $178-179^{\circ}$.
J. K.

Action of Nitric Acid on Phenol Ethers. KURT H. MEYER and HANS GOTTLIEB-BILLROTH (*Ber.*, 1922, 55, [B], 823-826; cf. A., 1920, i, 37).—A reply to Kehrmann, Decker, and Solonina (this vol., i, 32).
H. W.

The Oxidation of Quinol in the Presence of Aliphatic Amines. ROLLA N. HARGER (*Proc. Nat. Acad. Sci.*, 1922, 8, 57-59).—Quinol, dissolved in a strong aqueous solution of dimethylamine, takes up oxygen readily, and brilliant, red plates separate, m. p. 171° , which appear to be 2:5-di-dimethylaminoquinol (cf. Mylius, A., 1885, i, 803; Kehrmann, A., 1890, i, 756). Other products not yet identified are also formed in the reaction. Similar results have been obtained with methylamine.
W. O. K.

The Iodohydrin Derived from Allylbenzene and its Transformations. M. PORCHER (*Bull. Soc. chim.*, 1922, [iv], 31, 334-340).—Allylbenzene gives with mercuric oxide and iodine in moist ether α -iodo- γ -phenylpropan- β -ol, which under the influence of silver nitrate yields benzyl methyl ketone together with some allylbenzene oxide and some benzylethylene glycol as its nitrate. Allylbenzene oxide reacts with hydriodic acid to give a mixture of the above iodohydrin and its isomeride, β -iodo- γ -phenylpropan- α -ol, and if this mixture is treated with silver nitrate, phenylpropaldehyde is obtained in addition to benzyl methyl ketone.

Allylbenzene dibromide gives with alcoholic potassium hydroxide *benzylvinyl bromide*, $CH_2Ph\cdot CH:CHBr$, b. p. $217-221^{\circ}$, d_0 1.351. This reacts with magnesium in ethereal solution, giving phenylpropinene (cf. Lespieau and Garreau, A., 1920, i, 603), allylbenzene, and magnesium derivatives of these two hydrocarbons.
W. G.

Halochromic Phenomena with Carbinols. SIEGFRIED SKRAUP and LEO FREUNDLICH (*Ber.*, 1922, 55, [B], 1073-1080).—A preliminary communication induced by the recent publications of Hess and Weltzein (this vol., i, 35) and Ziegler (this vol., i, 151).

The basic character of carbinols is regarded as a consequence of the great valency demand on the central carbon atom. If this is the case, the hydroxyl of a carbinol must be the more readily removable from the central carbon atom by complex- or salt-forming agents (that is, the resulting halochromic salt must be the less sensitive towards hydrolysing agents) in proportion as the substituents make greater demands on the valency of the central carbon atom. It follows, therefore, that, in the presence of a suitable radicle, one or two phenyl residues in triphenylcarbinol can be replaced even by aliphatic groups without causing the disappear-

ance of halochromism, and ultimately that even primary and secondary alcohols may be halochromic. An intimate connexion exists between the halochromism and basicity of the carbinols and the radicle dissociation of the corresponding hexa-alkylethanes to substituted methyls; this is illustrated by a number of instances. The basicity of the carbinols is measured by treating their solutions in glacial acetic acid with a solution of concentrated sulphuric acid in the same solvent and titrating with alcohol (75%) until the colour is discharged. It is interesting to note that the method can be extended to benzoic acid and its esters, although in these cases the initial coloration, for some unexplained reason, is only developed when undiluted sulphuric acid is added to the solutions. The following series of basicities is recorded, that of triphenylcarbinol being adopted as unit in each series: (1) diphenyl-*p*-tolylcarbinol, 2.55; diphenyldiphenylcarbinol, 3.19; diphenyl-*p*-anisylcarbinol, 6.99; α -naphthyldiphenylcarbinol, 8.83; (2) benzhydrol, 0.330; diphenylmethylcarbinol, 0.361; diphenylethylcarbinol, 0.343; diphenylpropylcarbinol, 0.368; *p*-anisyl-dimethylcarbinol, 0.972; (3) benzoic acid, 0.806; methyl benzoate, 0.501; ethyl benzoate, 0.429.

The following substances are described incidentally: *diphenylpropylcarbinol*, m. p. 36°; *p*-anisyl-dimethylcarbinol, b. p. 130°/high vacuum; *triisobutylcarbinol*, which could not be isolated in the homogeneous state. H. W.

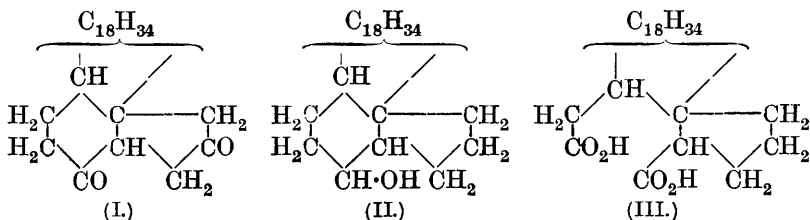
Carboligase. IV. CARL NEUBERG and HEINZ OHLE (*Biochem. Z.*, 1922, **128**, 610—618).—Improved experimental methods have confirmed and amplified the previous work (A., 1921, i, 480; this vol., i, 305) on the production of *l*-acetylphenylcarbinol from benzaldehyde during yeast fermentation. The *semicarbazone* of *l*-acetylphenylcarbinol has m. p. 194° and $[\alpha]_D^{25} + 215.78^\circ$ in pyridine. The *thiosemicarbazone* has now been obtained optically active by combination of the components in pyridine solution. It melts at 207° and has $[\alpha]_D + 228.78$ in pyridine. The formation of the thiosemicarbazone can be used for estimating the approximate content of the ketone-alcohol in the crude oil (ether extract). The value found was 27%. In the fractionation of the ketone-alcohol fraction, phenyldiketopropane was identified by its oxime and phenylhydrazone. H. K.

Diphenylstyrylcarbinol and Triphenylallene. KURT H. MEYER and KURT SCHUSTER (*Ber.*, 1922, **55**, [B], 815—819). *Diphenylstyrylcarbinol*, $\text{CHPh}:\text{CH}:\text{CPh}_2\text{-OH}$, colourless needles, m. p. 95°, is prepared in 14% yield by the action of magnesium β -styryl bromide on benzophenone in ethereal solution (cf. Ziegler, this vol., i, 151). Attempts to convert it into the corresponding chloride (and hence to an analogue of triphenylmethyl in which one phenyl group is replaced by an unsaturated residue) were unsuccessful, since it is transformed by acetyl chloride, acetic anhydride, or a solution of hydrogen chloride in ether into *triphenylallene*, $\text{CHPh}:\text{C}:\text{CPh}_2$, colourless, lustrous leaflets, m. p. 210°.

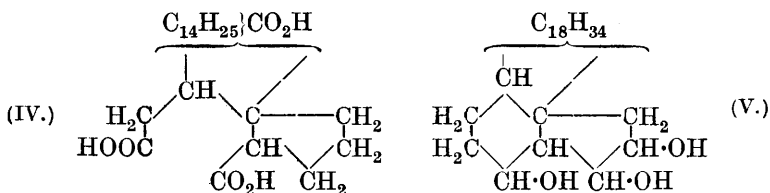
The preparation of the carbinol, $\text{CPh}_2\cdot\text{CPh}\cdot\text{CPh}_2\cdot\text{OH}$, could not be effected, since methyl triphenylacrylate could not be caused to react with magnesium phenyl bromide, even when dissolved in boiling *cyclohexyl* methyl ether.

H. W.

Cholesterol. A. WINDAUS (*Z. physiol. Chem.*, 1921, **117**, 146—158; cf. A., 1920, i, 41, 309, 434, 435; 1921, i, 507).—I. [With HARRY GRIMMEL.]—The ketodicarboxylic acid, $\text{C}_{27}\text{H}_{44}\text{O}_5$, formed by the oxidation of cholestan-4:7-dione (I) forms a *semi-carbazide* (slender needles, m. p. 240°) which with sodium ethoxide and alcohol yields an acid, $\text{C}_{27}\text{H}_{46}\text{O}_4$, identical with an acid obtained by the oxidation of dihydrocholesterol (II); it therefore has the constitution (III). This is confirmed by the fact that when heated, it forms a *diketone*, $\text{C}_{26}\text{H}_{42}\text{O}_2$, small plates, m. p. 148 — 149° (*dioxime*, m. p. 191°).



II. [With A. VON STADEN.]—From the dicarboxylic acid, $\text{C}_{27}\text{H}_{46}\text{O}_4$ (III), a *tricarboxylic acid*, $\text{C}_{24}\text{H}_{38}\text{O}_6$ has been prepared by oxidation with chromic acid, which crystallises from acetic acid in rosettes of slender needles, m. p. 238° , and forms a *trimethyl* ester, rectangular leaflets, m. p. 86 — 87° . This acid apparently has the constitution (IV.)



III. [With H. LÜDERS.]—On boiling α -cholestan-triol (V) (T., 1908, **93**, 1680; A., 1915, i, 884) with methyl alcoholic hydrogen chloride, it is converted into the *chlorohydrin* of α -cholesterol oxide, $\text{C}_{27}\text{H}_{47}\text{O}_2\text{Cl}$, long needles, m. p. 170 — 171° . With alcoholic potassium hydroxide, or with acid, β -cholesterol oxide is obtained, identical with that isolated by Westphalen (A., 1915, i, 885).

W. O. K.

Metacholesterol and its By-products. III. I. LIFSCHÜTZ (*Biochem. Z.*, 1922, **129**, 115—127).—The author amplifies the description of the properties and preparation of metacholesterol (A., 1920, i, 546). It has mol. wt. 369 and $[\alpha]_D -33.7^\circ$ in chloroform.

H. K.

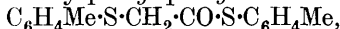
Derivatives of Dithioethylene and Dithioacetylene and the Additive Capacity of Multiple Bonds. EMIL FROMM and ERICH SIEBERT (*Ber.*, 1922, **55**, [B], 1014—1030).—The additive capacity of the double and treble linking in di-*p*-tolylthioethylene and di-*p*-tolylthiolacetylene is suppressed completely towards hydrogen and partly towards bromine; addition of the elements of water is, however, possible. The substances can also be oxidised, but the oxygen atoms become attached to sulphur. Since the activity of the multiple bond is lessened by the proximity of mercaptan residues, it would be expected that a still more marked effect would be produced by neighbouring sulphonyl radicles. This is actually the case with respect to the addition of bromine, but, on the other hand, the sulphonyl compounds are readily reduced by hydrogen; the apparent anomaly is explained by the observation of the presence of conjugated double bonds, whereby also the behaviour of the sulphones towards phenylhydrazine is explained.

Di-p-tolylthioethylene, $C_2H_2(S \cdot C_6H_4Me)_2$, long, lustrous needles, m. p. 93° , is prepared in 90% yield by the gradual addition of $\alpha\beta$ -dichloroethylene to a boiling alcoholic solution of *p*-tolyl mercaptan and potassium hydroxide. When dissolved in chloroform, it is converted by bromine into the corresponding *dibromide*, $C_2H_2Br_2(S \cdot C_6H_4Me)_2$, a somewhat unstable, colourless, crystalline powder, m. p. 72° , and by chlorine into the *dichloride*, m. p. 138° . The dibromide is transformed by boiling alcoholic potassium hydroxide solution into *di-p-tolylthiolacetylene*, long, lustrous needles, m. p. 101 — 102° , which combines with bromine in chloroform solution to give *di-p-tolylthiolacetylene dibromide*, $C_2Br_2(S \cdot C_6H_4Me)_2$, m. p. 99 — 100° ; the latter substance does not unite further with bromine. *Di-p-tolylthioethylene* is prepared by the action of zinc dust and boiling glacial acetic acid on *di-p-tolylthioethylene dibromide* or *di-p-tolylthiolacetylene dibromide*. *Di-p-tolylthioethylene* is converted by sulphuric acid (50%) in glacial acetic acid solution into the *p-tolylmercaptal* of *p-tolylthiolacetaldehyde*, $C_6H_4Me \cdot S \cdot CH_2 \cdot CH(S \cdot C_6H_4Me)_2$, colourless, unctuous leaflets, m. p. 62 — 63° . The course of the reaction is probably represented by the schemes: $C_6H_4Me \cdot S \cdot CH : CH \cdot S \cdot C_6H_4Me \rightarrow C_6H_4Me \cdot S \cdot CH_2 \cdot CH(OH) \cdot S \cdot C_6H_4Me \rightarrow C_6H_4Me \cdot S \cdot CH_2 \cdot CHO + HS \cdot C_6H_4Me$ and $C_6H_4Me \cdot S \cdot CH_2 \cdot CHO + 2SH \cdot C_6H_4Me = C_6H_4Me \cdot S \cdot CH_2 \cdot CH(S \cdot C_6H_4Me)_2 + H_2O$; this view is supported by the observation that the yield of the product is increased when the reaction takes place in the presence of added *p*-tolyl mercaptan. Oxidation of the *p-tolylmercaptal* with potassium permanganate leads to the production of the *p-tolylsulphonsulphidemercaptal* of *p-toluenesulphonylacetaldehyde*,

$C_6H_4Me \cdot SO_2 \cdot CH_2 \cdot CH(S \cdot C_6H_4Me) \cdot SO_2 \cdot C_6H_4Me$, slender, colourless needles, m. p. 119 — 120° , which is reduced by zinc dust in boiling glacial acetic acid solution to *di-p-toluenesulphonylethane*, $C_2H_4(SO_2 \cdot C_6H_4Me)_2$, m. p. 199 — 200° . If, however, the mercaptal is oxidised with hydrogen peroxide (30%), it is converted into the *p-tolylsulphonmercaptal* of *p-toluenesulphonyl-*

acetaldehyde, $\text{C}_6\text{H}_4\text{Me}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CH}(\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me})_2$, colourless needles, m. p. 222—223°, which is also reducible by zinc and acetic acid to di-*p*-toluenesulphonylethane.

Di-*p*-tolylthiolacetylene likewise unites with the elements of water when treated with sulphuric acid in glacial acetic acid solution, yielding thereby *p*-tolyl-*p*-tolylthiothioacetate,



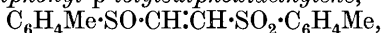
a liquid which could neither be caused to crystallise, nor distilled without decomposition; it is hydrolysed to *p*-tolyl mercaptan and *p*-tolylthiolacetic acid, m. p. 93°, which is readily oxidised to *p*-tolylsulphonylacetic acid, m. p. 117.5—118.5°.

Di-*p*-tolylthioethylene is not attacked by zinc dust and acetic acid, but is converted by sodium and alcohol into *p*-tolyl mercaptan.

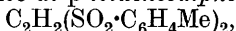
Oxidation of di-*p*-tolylthioethylene dissolved in benzene with potassium permanganate and dilute sulphuric acid leads to the formation of *p*-tolylsulphonyl-*p*-tolylthioethylene,



lustrous needles, m. p. 114—115°; the constitution of the substance is deduced from its reduction by zinc dust and glacial acetic acid to *p*-toluenesulphonyl-*p*-tolylthioethane, slender, colourless needles, m. p. 117—118°, and oxidation of the latter to di-*p*-tolylsulphonylethane, m. p. 199—200°. Oxidation of di-*p*-tolylthioethylene dissolved in cold acetic acid with hydrogen peroxide (30%) gives *p*-toluenesulphonyl-*p*-tolylsulphoxidethylene,

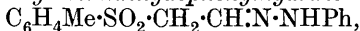


m. p. 122—123°, which, like other sulphoxides, gives a yellow coloration with alkali hydroxide and loses an oxygen atom when reduced, thus yielding *p*-toluenesulphonyl-*p*-tolylthioethane. Oxidation with hydrogen peroxide (30%) in warm solution transforms the dithio-compound into di-*p*-toluenesulphonylethylene,



long, lustrous needles, m. p. 149—150°, which is reduced by nascent hydrogen to di-*p*-tolylidisulphonylethane.

Di-*p*-toluenesulphonylethylene is converted by phenylhydrazine in alcoholic solution at the atmospheric temperature into the phenylhydrazine salt of toluene-*p*-sulphinic acid, m. p. 159—160°, and *p*-toluenesulphonylacetaldehydephenylhydrazone,



yellow needles, m. p. 144—145°. A similar change occurs with the sulphoxidesulphone, the products being *p*-toluenesulphonylacetaldehydephenylhydrazone and *p*-tolyl disulphide. H. W.

Interchange of Alcohol Radicles in Esters. AKIRA SHIMOMURA and JULIUS BEREND COHEN (T., 1922, 121, 883—887).

Preparation of Aromatic Esters in the Presence of an Organic Base. YOSHITARÔ SUZUKI and SANKYÔ KABUSHIKI KAISHA (Japanese Pat. 38647 [1921]).—Aromatic esters are easily prepared from aromatic alcohols and chlorides or bromides of aromatic acids in the presence of an organic base, such as pyridine.

with those of the compound obtained by Lossen by the action of potassium hydroxide and methyl iodide on benzhydroxamic acid (A., 1895, i, 37) and regarded by this author as having the oximic structure, $\text{OH}\cdot\text{CPh}\cdot\text{N}\cdot\text{OMe}$. Since, however, ethers are known in which both hydroxyls are undoubtedly etherified, for instance, $\text{OR}'\cdot\text{CPh}\cdot\text{N}\cdot\text{OR}$, and since also diazomethane is capable of etherifying feebly acid hydrogen atoms, such as the hydroxylic hydrogen atoms of phloroglucinol, Lossen's formula for the above compound is to be excluded, the true structure being either $\text{COPh}\cdot\text{NH}\cdot\text{OMe}$ or $\text{O} < \begin{smallmatrix} \text{N}\cdot\text{OR} \\ | \\ \text{CHPh} \end{smallmatrix}$. The salts of compounds of this class have, however, probably the oximic constitution.

T. H. P.

Free *o*-Aminophenylacetic Acid, its Esters and Transformations. P. W. NEBER (*Ber.*, 1922, 55, [B], 826—848).—The readiness with which *o*-aminophenylacetic acid passes by loss of water into oxindole has caused it to be regarded as a particularly unstable substance which cannot exist in the free state. It is shown, however, that this change is characteristic of solutions acidified with mineral acid; the substance can be isolated readily by the reduction of *o*-nitrophenylacetic acid in alkaline solution and behaves as a normally stable compound.

Barium *o*-aminophenylacetate is prepared readily by the addition of a hot, aqueous solution of barium hydroxide to a mixture of barium *o*-nitrophenylacetate and ferrous sulphate dissolved in hot water; the sodium salt ($+3\text{H}_2\text{O}$), *silver* salt, slender needles, and *copper* salt are described. The free *acid*, colourless, highly refractive needles, m. p. 119° (decomp.), is almost quantitatively precipitated by the addition of a slight deficiency of sulphuric acid to an aqueous solution of the sodium salt. The following derivatives are described: *o*-acetylaminophenylacetic acid (from the acid and acetic anhydride in the presence of ice and water), colourless crystals, m. p. 158° (when heated rapidly) after softening at 150° ; *o*-benzoylaminophenylacetic acid (from barium *o*-aminophenylacetate, aqueous sodium hydroxide, and benzoyl chloride), colourless needles, m. p. 179° after softening at 170° ; *methyl o*-benzoylaminophenylacetate (from the free acid and methyl sulphate), small colourless needles, m. p. 108° . *o*-Aminophenylacetic acid can be diazotised by the gradual addition of sulphuric acid to its aqueous solution in the presence of sodium nitrite; the diazonium compound couples with β -naphthol, giving *o*- β -naphtholazophenylacetic acid, $\text{C}_{18}\text{H}_{14}\text{O}_3\text{N}_2$, red needles, m. p. $211\text{--}213^\circ$ (the sodium salt is described). *o*-Nitrobenzylidene-*o*-aminophenylacetic acid, colourless needles, m. p. 146° after softening at 142° , is prepared from the acid and *o*-nitrobenzaldehyde in boiling alcoholic solution; the corresponding *m*-nitrobenzylidene compound, yellow needles, m. p. 147° , and *p*-nitrobenzylidene derivative, yellow needles, m. p. 157° , are prepared similarly. When heated together at 115° , *o*-nitrobenzaldehyde and *o*-aminophenylacetic acid give 3-*keto*-2-*o*-nitrophenyl-3 : 4-*dihydroquinoline* (or 3-*hydroxy*-2-*o*-nitrophenyl-

quinoline), yellowish-red needles, m. p. 227°. *Phenylacetic-o-sulphinic anhydride*, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{SO} - \text{O} \end{smallmatrix}$, colourless crystals, m. p. 185°

after softening at 177°, is prepared by the successive treatment of diazotised *o*-aminophenylacetic acid with sulphur dioxide and copper bronze. Reduction of the diazonium solution with stannous chloride and concentrated hydrochloric acid gives *o*-hydrazinophenylacetic acid, colourless needles ($? + H_2O$), m. p. 121°; this substance is converted by rapid distillation under atmospheric pressure into 1-amino-oxindole, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{N}(\text{NH}_2) \end{smallmatrix} \text{CO}$, colourless, lustrous leaflets, which is transformed by nitrous acid successively into oxindole and β -isatoxime, m. p. 220° (decomp.). *o*-Nitrobenzylideneamino-oxindole, yellow needles, m. p. 170° after softening at 163°, is prepared by the addition of *o*-nitrobenzaldehyde to a hot solution of *o*-hydrazinophenylacetic acid in acetic acid and water.

Somewhat unexpectedly, *o*-aminophenylacetic acid can be esterified by saturating a well-cooled solution of it in the requisite alcohol with hydrogen chloride. In this manner, *ethyl o*-aminophenylacetate is prepared as a pale red liquid which could not be caused to crystallise and decomposes with formation of oxindole when distilled under diminished pressure. It is transformed by acetic anhydride into *ethyl o*-acetylaminophenylacetate, colourless needles, m. p. 66°; *o*-acetylaminophenylacetamide crystallises in colourless needles, m. p. 203°. *Ethyl o*-benzoylaminophenylacetate, needles, m. p. 82°, is prepared from the amino-ester and benzoyl chloride in the presence of pyridine. Diazotisation of *ethyl o*-aminophenylacetate and subsequent coupling with β -naphthol yields *ethyl o*- β -naphtholazophenylacetate, red needles, m. p. 127°, which can also be prepared by esterification of the corresponding acid. The amino-ester is converted by *o*-nitrobenzaldehyde in boiling alcoholic solution in the presence of piperidine into *ethyl o*-nitrobenzylidene-*o*-aminophenylacetate, m. p. 58°; the corresponding *m*-nitrobenzylidene compound, pale yellow needles, m. p. 119°, and *p*-nitrobenzylidene derivative, yellow crystals, m. p. 125°, are also described.

Methyl o-aminophenylacetate is obtained as a liquid which could neither be caused to crystallise nor be distilled without decomposition. The following derivatives are described: *methyl o*-acetylaminophenylacetate, a colourless powder, m. p. 90° after softening at 87°; *o*-acetylaminophenylacetamide, m. p. 203°; *methyl o*-benzoylaminophenylacetate, colourless slender needles, m. p. 108°; *methyl o'*-nitrobenzylidene-*o*-aminophenylacetate, pale yellow needles, m. p. 79°; *methyl m'*-nitrobenzylidene-*o*-aminophenylacetate, yellow needles, m. p. 97° after softening at 91°; *methyl p'*-nitrobenzylidene-*o*-aminophenylacetate, yellow needles, m. p. 107° after softening at 105°; *methyl o*- β -naphtholazophenylacetate, brilliant red needles, m. p. 145°.

o-Azoxyphenylacetic acid, m. p. 250°, is obtained in small and

varying amount (up to 2%) by the reduction of *o*-nitrophenyl-acetic acid by ferrous sulphate and barium hydroxide. The corresponding *ethyl* ester, pale reddish-yellow needles, m. p. 69°, and *methyl* ester, yellowish-red needles, m. p. 114°, after previous softening, are described; they are very sensitive towards light.

H. W.

Higher Terpene Compounds. II. Abietic Acid. L. RUZICKA and JULES MEYER (*Helv. Chim. Acta*, 1922, **5**, 315—344; cf. A., 1921, i, 573).—Abietic acid, as it actually exists in American colophony, is best isolated in a 50% yield by distillation of this material at 200—210°/1 mm. (bath 255°), followed by crystallisation from methyl alcohol or acetone. It forms triangular leaflets, m. p. 158° when rapidly heated, $[\alpha]_D -68.5^\circ$; (*triozonide*, $C_{20}H_{30}O_2 \cdot O_9$, m. p. 91—93°, *methyl* ester, $C_{21}H_{32}O_2$, b. p. 168—172°/0.5 mm., d_4^{20} 1.049, n_D^{20} 1.5346). The acid at once decolorises alkaline permanganate and on catalytic reduction in alcoholic solution yields a mixture of presumably two *dihydro-acids*, of which one, $C_{20}H_{32}O_2$, m. p. 167—168°, $[\alpha]_D -12^\circ$, was isolated in the pure condition. This acid furnished a *diozonide*, $C_{20}H_{32}O_2 \cdot O_6$, m. p. 97—102° (decomp.), but was indifferent to alkaline permanganate (cf. Virtanen, A., 1920, i, 832), whilst the action of hydrogen bromide in glacial acetic acid solution yielded an *isomeride*, $C_{20}H_{32}O_2$, m. p. 130—131°, $[\alpha]_D$ about -2° , which is distinguished from all other isomerisation or reduction products of abietic acid by its sparing solubility in alcohol. It is stable towards alkaline permanganate, reacts with difficulty with ozone, the product, m. p. 112—116°, corresponding with the formula $C_{20}H_{32}O_2 \cdot O$. Catalytic reduction of abietic acid in ethyl acetate solution at the ordinary temperature, and more especially in amyl ether at 80°, resulted in the formation of notable quantities of the tetrahydro-acid, $C_{20}H_{34}O_2$, m. p. 167—169°, $[\alpha]_D +10^\circ$, the formation of which was complete in glacial acetic acid solution at 80°. This acid reacts with ozone with difficulty, forming somewhat indefinite products, for an account of which the original should be consulted.

The variation in the accounts of abietic acid given by earlier workers is due to the fact that, whilst in some cases [Mach, A., 1893, i, 582; 1895, i, 384; Maly (1861); Flückiger (1867); Tschirch and Studer, A., 1904, i, 79] the extraction of the acid was carried out by means of alcohol or weak alkali, and the products approximately agreed in melting point with that now described, in other instances (Levy, A., 1906, i, 870; Johansson, *Mon. sci.*, 1921, 73) methods were employed which caused isomerisation. This occurs to some extent if the distillation above described be carried out under 2 mm. pressure (bath temperature 275°); if the material is first heated for several hours at 290°, and subsequently distilled under 12 mm. pressure (bath 300°) the main product is an *isomeride*, $C_{20}H_{30}O_2$, m. p. 178—179°, $[\alpha]_D +3^\circ$, which yields a mixture of tetrahydro-acids. One of these, $C_{20}H_{34}O_2$, m. p. 169—171°, $[\alpha]_D +3^\circ$, has been definitely separated. When abietic acid was heated for

twenty-four hours at 300° in a stream of carbon dioxide and subsequently distilled, a considerable quantity of abietene, b. p. $160-170^{\circ}/0.5$ mm., accompanied the *isomerised acid*, b. p. $200-210^{\circ}/0.5$ mm., m. p. $170-172^{\circ}$, $[\alpha]_D +46^{\circ}$. The last furnished a mixture of di- and tri-ozonides, and a *tetrahydro-acid*, $C_{20}H_{34}O_2$, m. p. $116-118^{\circ}$, $[\alpha]_D +16^{\circ}$, from which what seemed to be a *monozonide of a peroxide*, $C_{20}H_{34}O_2, O_3$, m. p. $103-106^{\circ}$ (decomp.), was prepared. Abietic acid is quite stable towards boiling alcoholic sodium hydroxide solution, and is practically unchanged by glacial acetic acid, or after short treatment with alcoholic hydrogen chloride. After prolonged treatment with a hot solution of hydrogen chloride in glacial acetic acid, however, it melted at $176-177^{\circ}$, $[\alpha]_D -34^{\circ}$, and furnished a *diozonide*, $C_{20}H_{30}O_2, O_6$, m. p. 71° (decomp.), a *dihydro-acid*, $C_{20}H_{32}O_2$, m. p. $148-149^{\circ}$, $[\alpha]_D +27^{\circ}$ (from which a mixture of mono- and di-ozonides was obtained), and a *tetrahydro-acid*, $C_{20}H_{34}O_2$, m. p. $158-160^{\circ}$, $[\alpha]_D +9^{\circ}$. A further *isomeride* of abietic acid, $C_{20}H_{30}O_2$, m. p. $150-151^{\circ}$, $[\alpha]_D -10^{\circ}$, is obtained by heating its dihydrobromide, m. p. about 178° (cf. Levy, A., 1913, i, 620; Henze, A., 1916, i, 826) with quinoline at 240° . Since abietic acid is a methyldecahydroretene-carboxylic acid (Bamberger and Hooker, *Annalen*, 1885, 229, 102; Fortner, A., 1904, i, 729; Lux, A., 1908, i, 873; Bucher, A., 1910, i, 239; Vesterberg, A., 1904, i, 151), and a considerable group of the sesquiterpenes is derived from 1:6-dimethyl-4-isopropyl-naphthalene (see this vol., i, 560), abietic acid would seem to represent the extension of the sesquiterpene compounds in the higher natural series of terpenes.

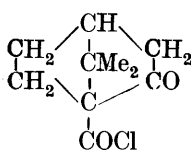
J. K.

The Action of Potassium Iodide and Iodate on some Hydroxy-acids. SRI KRISHNA and FRANK GEORGE POPE (T., 1922, 121, 798-800).

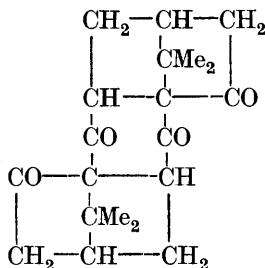
Neutral Homocamphoric Esters and their Products of Reduction. PALFRAY (*Compt. rend.*, 1922, 174, 1235-1238).—Ethyl hydrogen camphorate gives an acid chloride, which reacts with sodium phenoxide, giving *phenyl ethyl homocamphorate*, m. p. $51-51.5^{\circ}$, $[\alpha]_D^{19} +27.35^{\circ}$. This ester, on reduction with sodium and absolute alcohol, yields *homocamphoric glycol*, m. p. $63-63.5^{\circ}$, $[\alpha]_D^{21} +81^{\circ} 5'$, together with some *hydroxycampholic acid*, $C_8H_{14} \begin{matrix} \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH} \\ \text{CO}_2\text{H} \end{matrix}$, m. p. $130-131^{\circ}$, $[\alpha]_D^{21} +71^{\circ} 37'$. The glycol gives a *diphenylurethane*, m. p. $115-115.5^{\circ}$, $[\alpha]_D^{21} +31^{\circ} 29'$; a *diacetyl* derivative, b. p. $182-183^{\circ}/13$ mm., $[\alpha]_D^{21} +52^{\circ} 36'$; and a *dibenzoyl* derivative, b. p. $276-277^{\circ}/2$ mm., $295-300^{\circ}/12$ mm., $[\alpha]_D^{21} +34^{\circ} 41'$.

W. G.

Condensation Products from Acid Haloids. X. Action of Triethylamine on Ketopinyl Chloride. E. WEDEKIND and CL. WEINAND (*Ber.*, 1922, 55, [B], 945-951; cf. this vol., i, 234). The "tertiary base" reaction has now been applied to the chloride of a ketonic acid.



m. p. 98°.



Ketopinyl chloride (annexed formula), m. p. 109°, is readily prepared by the action of thionyl chloride on ketopinic acid (cf. Gilles and Renwick, T., 1897, 69, 1397, 1402), and is converted by triethylamine in the presence of benzene into a mixture of *ketopinic anhydride*, m. p. 182°, and *dinorcamphocyclohexanedione* (annexed formula), m. p. 226°.

The latter substance is stable towards bromine or permanganate, and does not react with hydrogen in the presence of palladium. It is not affected by boiling alkali hydroxide, but is slowly decomposed by boiling concentrated hydrochloric acid with re-formation of ketopinic acid. It reacts with phenylhydrazine and *p*-bromophenylhydrazine, without, however, yielding uniform products. It gives a *di-semicarbazone*, $\text{C}_{22}\text{H}_{30}\text{O}_4\text{N}_6$, m. p. 207—209° when crystallised from benzene, but this value rises to 207—209° when it is crystallised from alcohol.

H. W.

The Utilisation of Ethyl γ -Diethoxyacetoacetate for the Synthesis of Derivatives of Glyoxaline. An Attempt to Synthesise Histamine by a New Method. GEORGE W. PUCHER and TREAT B. JOHNSON (*J. Amer. Chem. Soc.*, 1922, 44, 817—826).—An attempt has been made to alkylate ethyl acetoacetate or ethyl γ -diethoxyacetoacetate by means of bromomethylphthalimide, as a first step in a new method of synthesising histamine, but without success. This bromophthalimide reacts abnormally with the sodium salts of β -ketonic esters, with formation of phthalimide, whereas the higher homologue reacts normally giving phthalimido-derivatives.

It was found that an almost quantitative yield of hydroxymethylphthalimide could be obtained by heating phthalimide under a reflux condenser with 10—15% formaldehyde solution. The hydroxy-compound is readily converted into bromomethylphthalimide by digesting it at 50—60° with 48% hydrobromic acid and concentrated sulphuric acid for two hours. The bromo-compound reacts with potassium thiocyanate in acetone, giving *phthalimidomethyl thiocyanate*, $\text{C}_6\text{H}_4(\text{CO})_2\text{N}\cdot\text{CH}_2\cdot\text{SCN}$, m. p. 147—148°, which is extremely irritant to the eyes. In the same solvent with potassium iodide, it gives iodomethylphthalimide, m. p. 150° (cf. Gabriel, A., 1908, i, 181).

Bromoethylphthalimide reacts with the sodium salt of ethyl

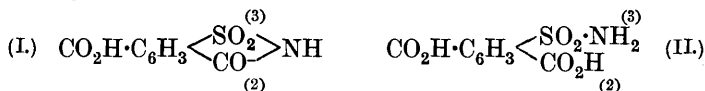
γ -diethoxyacetoacetate, giving *ethyl α -phthalimidoethyl- γ -diethoxyacetoacetate*.

W. G.

Sulphamidophthalic Acid and Sulphimidophthalic Acid.

TH. ZINCKE and H. GREUNE (*Annalen*, 1922, 427, 221—255).—

A considerable amount of confusion has arisen with regard to these two acids and their salts. For instance, all the salts of the imido-acid are described in "Beilstein's Handbuch" as salts of the amido-acid, which accords neither with the erroneous original literature nor with the truth. The two substances (formulae I and II) are dibasic acids of similar strength; both they and their salts are easily interconvertible, and the salts of the imido-acid frequently crystallise with H_2O , which makes it difficult to distinguish between them. The present paper places the whole chemistry of these substances for the first time on a correct basis.



The acid potassium salt which separates when the alkaline solution obtained by oxidising naphthalene-1-sulphonamide with alkaline permanganate is concentrated, cautiously acidified, and allowed to remain is the *N*-potassium salt of the imido-acid with $\text{1H}_2\text{O}$ which is quickly eliminated in a vacuum at 100° . The same substance is produced when the acid potassium salt (below) of the amido-acid is crystallised from warm water. When the *N*-potassium salt is treated with strong hydrochloric acid it gives the imido-acid (needles, decomp. $275\text{--}276^\circ$ when quickly heated), but if boiled with *N*-hydrochloric acid it yields the amido-acid. The latter crystallises in leaflets or needles with $\text{1H}_2\text{O}$ which is given up slowly at 100° but quickly at 120° , the dried acid passing into the imido-acid with elimination of a further molecule of H_2O at 194° . It is a slightly stronger acid than the imido-acid, into which it is converted on warming with concentrated hydrochloric acid. The carboxyl-*potassium* salt of the imido-acid is obtained by heating the acid potassium salt of the amido-acid at 150° ; it is easily soluble in water, but on warming its solution the less soluble *N*-potassium salt of the imido-acid is precipitated. The normal *barium* salt of the imido-acid (needles, with $2\text{H}_2\text{O}$ which is given up in a vacuum at 100°) is prepared by adding the imido-acid to excess of barium hydroxide. The *N*-*silver* salt of the imido-acid (needles, with $\text{1H}_2\text{O}$ which is eliminated in a vacuum at 100°) is prepared from the *N*-potassium salt, and the carboxyl-*silver* salt (amorphous) of the imido-acid by heating the acid silver salt of the amido-acid at 150° , or by precipitation from a solution of the carboxyl-*potassium* salt of the imido-acid. The normal *silver* salt of the imido-acid is obtained by precipitation from a neutralised solution of the *N*-potassium salt.

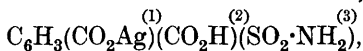
The *N*-methyl ester (needles, m. p. 189°) of the imido-acid is prepared from the *N*-potassium or *N*-silver salt and methyl iodide, but the reaction does not proceed very smoothly. It is rather

stable towards hydrolysing agents, but its constitution may be established by hydrolysis with concentrated hydrochloric acid at 150° , when methylamine is eliminated. The carboxyl-*methyl* ester (needles, m. p. $184-185^{\circ}$) of the imido-acid is prepared either from the carboxyl-*silver* salt and methyl iodide, or by heating the acid methyl ester (below) of the amido-acid, or by cautious alkaline hydrolysis of the dimethyl ester (below) of the amido-acid. Both this ester and the carboxyl-*ethyl* ester of the imido-acid give the imido-acid itself on hydrolysis by means of $2N$ -sodium hydroxide. The dimethyl ester (needles, m. p. 176°) of the imido-acid is prepared from the normal potassium or silver salt. An isomeric ester,

dimethyl ψ -sulphimidophthalate, $\text{CO}_2\text{Me}\cdot\text{C}_6\text{H}_3\text{C}(\text{OMe})\text{N}\overset{\text{SO}_2}{\text{>}}$ (small

tablets, m. p. 163°), is obtained by the action of methyl alcohol on *ψ -sulphimidophthalyl dichloride* (needles, m. p. 156°), which is prepared from the imido-acid by heating with phosphorus pentachloride at $150-160^{\circ}$. The *diethyl ψ -ester* (small tablets, m. p. $142-143^{\circ}$) is obtained in a similar way, using ethyl alcohol, and the *diamide* (fine needles, m. p. above 280°) using ammonia. These derivatives of the ψ -imide are all easily hydrolysed to the imido-acid.

The acid *potassium* salt, $\text{C}_6\text{H}_3(\text{CO}_2\text{K})^{(1)}(\text{CO}_2\text{H})^{(2)}(\text{SO}_2\cdot\text{NH}_2)^{(3)}$, of the amido-acid is prepared by cautious half-neutralisation of the acid with potassium hydroxide. On warming with water, it passes into the *N*-potassium salt of the imido-acid. The normal barium salt is precipitated when barium chloride is added to an ammoniacal solution of the amido-acid. The acid *silver* salt,



and the normal *silver* salt are obtained from the corresponding alkali salts.

The acid *methyl* ester, $\text{C}_6\text{H}_3(\text{CO}_2\text{Me})^{(1)}(\text{CO}_2\text{H})^{(2)}(\text{SO}_2\cdot\text{NH}_2)^{(3)}$ (small, glistening needles, m. p. 205°), may be prepared either by heating the amido-acid with methyl alcohol, or from the acid silver salt by heating with methyl iodide. On hydrolysis by alkalis or dilute acids, it yields the amido-acid; cold concentrated hydrochloric acid converts it into the imido-acid. The dimethyl ester (m. p. 148°) of the amido-acid may be obtained by esterifying either the amido-acid or the imido-acid by means of methyl alcohol and hydrogen chloride, or by heating the normal silver salt of the amido-acid with methyl iodide. The diethyl ester has m. p. $104-105^{\circ}$.
C. K. I.

The Configuration of the β -Phenylglyceric Acids and Phenylglycidic Acid. J. BÖESEKEN [and C. DE GRAAFF] (*Rec. trav. chim.*, 1922, **41**, 199-207).—Of the two isomeric forms of β -phenylglyceric acid, melting at 141° and 122° , respectively, the former shows a greater increase in conductivity under the influence of boric acid and the structure in which the hydroxyl groups are

most closely associated should therefore be assigned to it (cf. A., 1921, i, 843, 844). The dissociation constants of these acids are, for the former 2.35×10^{-4} and for the latter 2.54×10^{-4} ; it is probable that the phenyl and carboxyl groups are closer in the latter.

The oxidation of cinnamic acid by potassium permanganate to β -phenylglyceric acid takes place at a low temperature without molecular inversion. In β -phenylglycidic acid the phenyl and carboxyl groups are in the *trans*-position with respect to the tri-atomic ring. This acid in acid solution is hydrated, yielding the β -phenylglyceric acid of m. p. 141° ; in alkaline solution the isomeride (m. p. 122°) is formed and in this case molecular inversion occurs.

H. J. E.

The Action of Bromine on certain δ -Ketonic Esters. E. P. KOHLER (*J. Amer. Chem. Soc.*, 1922, **44**, 840—847).—It has previously been shown that methyl γ -benzoyl- β -phenylethylmalonate on bromination in methyl alcohol gives one monobromo-derivative and in chloroform a mixture of two monobromo-derivatives (cf. A., 1911, i, 984; 1917, i, 566, 568). The constitution of these two derivatives has now been determined, and a third isomeride has been prepared. The bromide, m. p. 113° (*loc. cit.*), is an α -bromo-derivative and the other bromide, m. p. 102° (*loc. cit.*, m. p. was given as 98°), and the new isomeride are stereoisomeric γ -bromo-derivatives. The γ -bromo-compound, m. p. 102° , on further bromination, yields three dibromides, two of which have already been described (*loc. cit.*), whilst the third, methyl $\gamma\gamma$ -dibromo- γ -benzoyl- β -phenylethylmalonate, has m. p. 126° , and when boiled with alcoholic potassium iodide yields methyl γ -bromo- γ -benzoyl- β -phenylethylmalonate, m. p. 76 — 77° .

On heating at from 150° to 200° , the two monobromo-derivatives, m. p. 102° and 77° , respectively, readily decompose, giving, amongst other products, methyl γ -benzoyl- β -phenylbutyrolactone- α -carboxylate, m. p. 93° , but the derivative, m. p. 113° , is much more stable and undergoes complex changes only at much higher temperatures.

If in these δ -ketonic esters prepared from malonic esters and $\alpha\beta$ -unsaturated ketones the α -position is blocked by a methyl group, the ester only gives one monobromo-derivative on bromination. Thus methyl γ -benzoyl- β -phenylethylmethylmalonate, m. p. 121 — 122° , obtained from phenyl styryl ketone and methyl malonate, gives methyl γ -bromo- γ -benzoyl- β -phenylethylmethylmalonate, m. p. 156 — 157° ; methyl γ -4-bromobenzoyl- β -phenylethylmethylmalonate, m. p. 89° , gives methyl γ -bromo- γ -4-bromobenzoyl- β -phenylethylmethylmalonate, m. p. 140° ; methyl γ -4-methoxybenzoyl- β -phenylethylmethylmalonate, m. p. 120 — 122° , gives methyl γ -bromo- γ -4-methoxybenzoyl- β -phenylethylmethylmalonate, m. p. 151° . On heating, methyl γ -bromobenzoyl- β -phenylethylmethylmalonate yields methyl γ -benzoyl- β -phenyl- α -methylbutyrolactone- α -carboxylate, m. p. 108° .

W. G.

$$\begin{array}{l} \text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{CPh}\cdot\text{CMe}\cdot\text{CO}_2\text{Et} \rightarrow \text{Me}\cdot\text{CO}\cdot\text{CO}_2\text{Et} + \text{Ph}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} \\ \text{CO}_2\text{Et}\cdot\text{CH}\cdot\text{CPh}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et} \rightarrow \text{Ph}\cdot\text{CO}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et} + \text{CHO}\cdot\text{CO}_2\text{Et} \end{array}$$

C. K. I.

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and precipitating with dilute hydrochloric acid, a mixture of the unsaturated acids is obtained. *apo*Cholic acid is separated by its relative insolubility in ether. The stronger unsaturated acids are obtained by dissolving the yellow, resinous residue after the evaporation of ether in sodium carbonate solution and precipitating with dilute hydrochloric acid. The unsaturated acids may also be prepared by heating cholic acid and oxalic acid at 100°.

G. W. R.

Preparation of Derivatives of Cholic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co., D.R.-P. 339561; from *Chem. Zentr.*, 1921, iv, 1227).—Paraformaldehyde intimately mixed with cholic acid is heated at 160—170° for half an hour. The cooled mass, after extraction with dilute sodium carbonate solution, is dissolved in ethyl alcohol, and the filtered solution mixed with ice-cold water. A *methylene* compound is thus obtained as a white, tasteless powder, m. p. 170°. It has therapeutic uses.

G. W. R.

Bile Acids. XI. The Oxidation of Cholic Acid. HEINRICH WIELAND and OTTO SCHLICHTUNG (*Z. physiol. Chem.*, 1922, **119**, 76—97).—Biloidanic acid, prepared by the oxidation of bilianic acid, has been given the formula $C_{19}H_{28}O_{10}$ by Letsch (A., 1909, i, 697) and by Schenck (A., 1921, i, 197). Borsche, Weickert, and Meyer (this vol., i, 255) found for it the formula $C_{18}H_{26}O_{10}$. The authors have prepared biloidanic acid, the neutral hexamethyl ester, the triethyl and monoethyl esters, trimethyl, dimethyl, and monomethyl esters, and the analytical results agree completely with the formula $C_{23}H_{34}O_{12}$ for the parent acid. Letsch has also described a hydrated form of biloidanic acid to which he assigned the formula $C_{19}H_{28}O_{10} \cdot 2H_2O$, but it is now found to be $C_{23}H_{34}O_{12} \cdot 2H_2O$. When heated in a vacuum at 115—125° this loses, however, $3H_2O$, pointing to anhydride formation from two of the carboxyl groups.

The constitution of the bile acids is considered in relation to these results.

W. O. K.

Preparation of Bile Acids. J. D. RIEDEL, AKT.-GES. (D.R.-P. 338736; from *Chem. Zentr.*, 1922, iv, 1226—1227).—The unsaturated acid (*apo*cholic acid) obtained by the elimination of water from cholic acid or its esters, is combined with hydrocarbons or their derivatives such as alcohols, bases, aldehydes, ketones, acids, and esters. For example, the unsaturated acid obtained by the elimination of water from methyl cholate is warmed with 96% acetic acid. On cooling, an *additive* compound crystallises, having an ill-defined m. p. 135—155°. The acetic acid is completely removed by excess of alkali or ammonia. The *additive* compound with 2 molecules of *apo*cholic acid and 1 molecule of naphthalene gives crystals having m. p. 173—174°; it is odourless and stable in air. A clear solution is given in water on addition of sodium carbonate and a small quantity of sodium *apo*cholate. The equimolecular *additive* compound of camphor and *apo*cholic acid is soluble in dilute alkalis and bases. Other *additive* compounds mentioned are *strychnine-apo*cholic acid, *ethyl acetate-apo*cholic acid, and

benzaldehyde-apocholic acid; the latter forms colourless needles, m. p. 156°. *apoCholic acid ethyl alcoholate* crystallises in needles which decompose in air with loss of alcohol. The compounds may also be prepared by way of the acetic acid compound. They have therapeutic uses.
G. W. R.

Vanillin Isomerides of the Resorcyl Series. ERWIN OTT and ERNST NAUEN (*Ber.*, 1922, 55, [B], 920—929).—Considerable uncertainty exists with regard to the constitution of the mono-methyl ethers of β -resorcylaldehyde [2 : 4-dihydroxybenzaldehyde], three substances, m. p. 41—42°, 62—63°, and 153°, respectively, having been thus described. The last-mentioned has been stated by Gattermann (*A.*, 1908, i, 28) to be the sole product of the action of hydrogen cyanide, hydrogen chloride, and aluminium chloride on resorcinyll monomethyl ether (this does not appear to be actually the case, since it is now found that the substance, m. p. 41—42°, is formed to a less extent); this substance is characterised as 4-hydroxy-2-methoxybenzaldehyde by its further methylation with methyl sulphate and cold alkali hydroxide to 2 : 4-dimethoxybenzaldehyde, m. p. 68°. The product, m. p. 41—42°, is also converted by the action of methyl sulphate on its sodium salt suspended in toluene at 40° into 2 : 4-dimethoxybenzaldehyde, and hence is shown to be 2-hydroxy-4-methoxybenzaldehyde. The aldehyde, m. p. 62—63°, is too sensitive towards alkali to permit its further methylation with methyl sulphate and, as in the case of the compound, m. p. 41—42°, diazomethane is found to be an unsuitable reagent for the methylation of difficultly substituted phenolic groups even at 100°. Friedländer's view (*A.*, 1908, i, 674) that the products, m. p. 41—42 and 62—63°, are actually identical is disproved by the observation that the corresponding oximes melt at 124—126° and 138°, respectively. The explanation of the difficulty is found in the fact that analysis of the aldehyde, m. p. 62—63°, obtained by the action of methyl iodide shows that it contains two methyl groups, of which only one is removable by hydriodic acid; the second methyl group must therefore be attached to the nucleus. The small amount of available material has precluded the exact elucidation of the constitution of the compound, but, by analogy, it is considered to be 2-hydroxy-4-methoxy-3-methylbenzaldehyde; the presence of substituents in the two ortho-positions to the hydroxyl group explains satisfactorily the impossibility of its further methylation and the non-appearance of acidic characteristics.

The following modification of Wegscheider's process is recommended for the oximation of hydroxyaldehydes, which are very sensitive towards alkali hydroxide. Hydroxylamine hydrochloride is dissolved in the minimum quantity of water, and the solution is treated with ammonia solution (20%) until it is just neutral towards litmus paper. An alcoholic solution of the aldehyde is added and the mixture is preserved at the atmospheric temperature until reaction is complete, after which the oxime is precipitated by addition of water.

The preparation of resorciny methyl ether is effected conveniently by the treatment of resorcinol with sodium hydroxide solution (10%) and methyl sulphate. The solution is made strongly alkaline and the dimethyl ether is removed by distillation with steam; subsequently the residue is acidified and again treated with steam, thus giving the monomethyl ether and leaving the non-volatile unattacked resorcinol. H. W.

Preparation of Protocatechualdehyde. S. HAMBURGER (D.R.-P. 339945; from *Chem. Zentr.*, 1921, iv, 1223—1224; cf. Schmidt, A., 1915, i, 682).—A modification of an earlier patent, whereby thionyl chloride is substituted for phosphorus pentachloride. Thionyl chloride and chlorine are allowed to act either successively or simultaneously on piperonal, with or without the use of solvents. For example, piperonal is treated with thionyl chloride and then warmed at 100°. Chlorine is passed in, the *dichloropiperonyl chloride* formed is decomposed with water, and the protocatechualdehyde formed is extracted with ether or obtained by evaporation. G. W. R.

Transformation of Tertiary Ethinylcarbinols into Unsaturated Ketones. KURT H. MEYER and KURT SCHUSTER (*Ber.*, 1922, 55, [B], 819—823).—Diphenylphenylethinylcarbinol, $\text{CPh:C}\cdot\text{CPh}_2\cdot\text{OH}$, is converted by acetyl chloride, acetic anhydride, thionyl chloride, hydrogen chloride dissolved in anhydrous ether, or concentrated sulphuric acid into phenyl β -phenylstyryl ketone, yellow prisms, m. p. 86—87° [Kohler (A., 1905, i, 215) gives m. p. 92°]; the constitution of the ketone is established by its oxidation to benzophenone and benzoic acid and hydrogenation to β -diphenylpropiofenone, m. p. 94—95°. The transformation might be due to the migration of a phenyl or a hydroxyl group; the latter is shown to be the case, since *di-p-chlorophenylphenylethinylcarbinol*, $\text{CPh:C}(\text{C}_6\text{H}_4\text{Cl})_2\cdot\text{OH}$, short, colourless prisms, m. p. 163—164°, is converted under similar conditions into *phenyl di-p-chloro- β -phenylstyryl ketone*, $\text{C}(\text{C}_6\text{H}_4\text{Cl})_2\cdot\text{CH}\cdot\text{COPh}$, yellow crystals, m. p. 103—104°, the constitution of which is established by its oxidation to 4:4'-dichlorobenzophenone and benzoic acid. The mechanism of the change has not been elucidated. H. W.

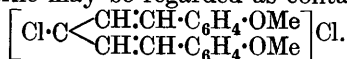
Halochromism and "Solvatochromism" of Distyryl Ketone and Simpler Ketones and of their Ketonic Chlorides. A. HANTZSCH (*Ber.*, 1922, 55, [B], 953—979).—In the so-called halochromism of ketones and ketonic chlorides two optically and chemically different processes are to be distinguished, (1) solvatochromism caused by the formation of additive products which involves a relatively small alteration in the absorption of light, and (2) the actual halochromism due to the formation of additive products with marked alteration in the absorption of light corresponding with the greater chemical change involved by the formation of complex carbonium salts under the transforming influence of acids. Generally, the two processes are closely related frequently in the sense that solvatochromism is the precursor of halochromism.

Thus, the solvatochromic additive products of certain ketones with stannic chloride are converted by hydrogen chloride into the halochromic carbonium salts, and hence the ketonic chlorides obtained from the ketones are directly converted by stannic chloride into the halochromic salts. The well-defined additive compounds which are constant in composition represent the extreme case of solvatochromism in the one direction (solid solvates), whereas the other extreme is represented by unsaturated substances which dissolve in such solvents as ether with deepening of colour and the formation of unstable compounds which either cannot be isolated in the solid state or in which the components appear to be present in indefinite ratio.

The absorption spectrum of distyryl ketone in ether differs considerably from that of triphenylcarbinol in ethyl alcohol, and it is therefore the more remarkable that the substances exhibit very similar absorption when dissolved in sulphuric acid. It appears therefore to be probable that the salts are similarly constituted and they may be formulated $\left[\text{Ph} \cdot \text{C} < \begin{smallmatrix} \text{Ph} \\ \text{Ph} \end{smallmatrix} \right] \text{X}$ and $\left[\text{R} \cdot \text{C} < \begin{smallmatrix} \text{CH}:\text{CHPh} \\ \text{CH}:\text{CHPh} \end{smallmatrix} \right] \text{X}$ or $\left[\begin{smallmatrix} \text{CHPh}:\text{CH}:\text{CR}:\text{CH} \\ \text{Ph} \end{smallmatrix} > \text{CH} \right] \text{X}$ (in which $\text{R} = \text{H}, \text{OH}, \text{Cl}$ or SO_4H).

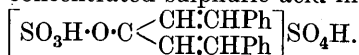
The choice between the two latter alternatives cannot be made definitely, but reasons are advanced for preferring the more symmetrical. The salts from benzophenone and benzophenone chloride are genetically intermediate between the triphenylcarbonium salts and those derived from distyryl ketone. Purely chemical evidence of the complex constitution of these halochromic salts can be adduced in the same manner as for the triphenylcarbonium compounds. The most important observation in this connexion is that the characteristic properties of the phenyl residue and of the $-\text{C}:\text{C}-$ group appear in them to be masked and, to some extent, completely lost. Thus the phenyl groups of triphenylcarbonium or distyryl ketone appear nearly indifferent towards concentrated sulphuric acid. Unsaturated ketones which instantly unite with bromine in glacial acetic acid are only very slowly attacked by bromine when dissolved in concentrated sulphuric acid; this is true even for the four ethylenic bonds of the dark violet salts of dicinnamylidenemethyl ketone, $\left[\text{HO} \cdot \text{C} < \begin{smallmatrix} \text{CH}:\text{CH}:\text{CH}:\text{CHPh} \\ \text{CH}:\text{CH}:\text{CH}:\text{CHPh} \end{smallmatrix} \right] \text{SO}_4\text{H}$.

The halochromism of the "abnormal" ketonic chlorides derived from styryl methyl ketone and similar substances which have been shown by Straus and Dützmann (this vol., i, 148) to have the constitution, $\text{CHAr}:\text{CH}:\text{CCl}:\text{CH}:\text{CHCl}:\text{Ar}$, is exactly analogous to that of the triphenylmethyl haloids, and the coloured solution formed, for example, by the chloride of dianisylidenemethyl ketone in phenylacetonitrile may be regarded as containing the salt



Since, however, the absorption spectra of the ketones in acid solution is exactly similar to those of the salts of the corresponding ketonic chlorides, the salts of the former may be regarded as having

initially the constitution $\left[\text{HO} \cdot \text{C} < \begin{smallmatrix} \text{CH} : \text{CHPh} \\ \text{CH} : \text{CHPh} \end{smallmatrix} \right] \text{SO}_4\text{H}$ and passing by further action of concentrated sulphuric acid into



Benzophenone when dissolved in concentrated sulphuric acid behaves like the almost completely ionised sulphate of sodium, dimethylpyrone or ethyl ether, and its salt is therefore formulated $[\text{Ph} \cdot \text{C}(\text{OH})\text{Ph}] \text{SO}_4\text{H}$, the hydroxyl group being in this case not appreciably esterified. The initially much more intensely yellow solution of benzophenone chloride in concentrated sulphuric acid contains the salt $(\text{Ph} \cdot \text{CCl} \cdot \text{Ph})\text{HSO}_4$, but rapidly becomes decolorised with liberation of hydrogen chloride and formation of the hydroxy-salt.

With regard to the solvatochromism of distyryl ketone and related ketones, it is pointed out that the optical changes are different from and generally more simple than those connected with halochromism. In these cases, compounds are being dealt with which are generally highly dissociated even in indifferent solvents such as chloroform. The characteristic absorption spectra are therefore obtained only when one component is added in such excess that optical constancy is induced. Thus, cinnamaldehyde, which forms a solid additive product, $(\text{CHPh} : \text{CH} \cdot \text{CHO})_2\text{SnCl}_4$, with stannic chloride, is but little affected optically when dissolved with twenty molecular proportions of stannic chloride in chloroform, and the spectrum gradually changes with further addition of stannic chloride, ultimately becoming constant when 8.50 molecular proportions of the latter have been added. Similar observations are recorded with salicylaldehyde, benzophenone, or distyryl ketone with stannic chloride in chloroform solution. H. W.

The Active Constituents of the True Coto-bark. The Synthesis of Cotoin. ERNST SPÄTH and KARL FUCHS (*Monatsh.*, 1921, 42, 267—272).—Attempts to synthesise cotoin, which is a monomethyl ether of 2 : 4 : 6-trihydroxybenzophenone, by methylation of the trihydroxy-compound with methyl alcohol and hydrochloric acid were unsuccessful, the only product isolated being methyl benzoate. The synthesis was accomplished by methylating with diazomethane in ethereal solution at -12° . Although less than one molecular proportion of diazomethane was used, the product contained 36% of cotoin, 26% of hydrocotoin (6-hydroxy-2 : 4-dimethoxybenzophenone), and 2% of the trimethoxy-compound. The synthesis does not establish the orientation of the methoxyl group in cotoin, although it is probable that methylation occurs first in the para-position. E. H. R.

The Hydroxybenzoylphloroglucinols. HIDEJIRO NISHIKAWA and ROBERT ROBINSON (*T.*, 1922, 121, 839—843).

Singular Formation of Ketodinitrones and their Behaviour. L. ALESSANDRI (*Gazzetta*, 1922, 52, i, 193—199).—At the ordinary temperature and best in a solvent which is indifferent to or at

least difficultly oxidised by nitrosobenzene, the latter (2 mols.) and toluene (1 mol.) react very slowly with formation of the *dinitrone*, $\text{O:NPh:CPh:CPh:NPh:O}$, which separates in pale yellow crystals decomposing with liberation of gas at 222° . When boiled with dilute sulphuric acid, the dinitrone yields benzil and *p*-aminophenol, the latter resulting from transposition of the β -phenylhydroxylamine originally formed. Reduction of the dinitrone by means of aluminium amalgam gives the dianil of benzil. The action of hydroxylamine on this ketodinitrone differs from that observed by Angeli, Alessandri, and Pegna with the aldonitrones (A., 1910, i, 552, 752) and is one of reduction, the product being either the semi-reduced compound, NPh:CPh:CPh:NPh:O , or an additive compound of the dinitrone with the dianil of benzil.

In the above formation of the ketodinitrone, the nitrosobenzene acts as an unsaturated compound, that is, as the phenyl ether of the anhydride of dihydroxyammonia, NPh:O .

The action of magnesium phenyl bromide on the aldodinitrone described by von Pechmann (A., 1898, i, 75, 187) might be expected to yield the corresponding $\beta\beta$ -dihydroxylamine, and this by oxidation the ketodinitrone, thus: $\text{O:NPh:CH:CH:NPh:O} + 2\text{MgPhBr} \rightarrow [\text{OH:NPh:ChPh}]_2 \rightarrow \text{O:NPh:CPh:CPh:NPh:O}$. The first of these reactions gives a small yield of a colourless compound, m. p. about 156° , which may be the $\beta\beta$ -dihydroxylamine, but the oxidation of the latter appears to give phenyl-*N*-phenylnitron or the *N*-phenyl ether of benzaldoxime, CHPh:NPh:O , this being obtained in appreciable yield. The latter compound is obtainable also by oxidation of the simpler β -hydroxylamine, $\text{CH}_2\text{Ph:NPh:OH}$ (cf. Cusmano, "Catalytic Reduction of Nitrones," to be published later).

Nitrosobenzene reacts on phenylpropionic acid with extreme slowness, if at all. With acetylene compounds containing unreplaced hydrogen, the action of nitrosobenzene appears to follow a different course. With acetylene itself in acetone solution, the reaction is very slow, but may be catalysed by alcoholic potassium hydroxide, and then yields a very small proportion of oxanilide, which is isomeric with the aldodinitrone, O:NPh:CH:CH:NPh:O , expected.

T. H. P.

Derivatives of 2-Hydroxybenzanthrone. I. GEOFFREY GORDON BRADSHAW and ARTHUR GEORGE PERKIN (T., 1922, 121, 911—922).

Preparation of Anthraquinone and its Derivatives. CHEMISCHE FABRIK WORMS AKT.-GES. (Brit. Pats. 156215 and 156538).—Anthraquinone or its derivatives are obtained by passing oxygen under pressure into a solution or suspension of anthracene (or its derivatives) in the presence of a small proportion of fuming nitric acid or an oxide of nitrogen at 80 — 90° . An additional oxygen carrier, for example, cobalt nitrate, may also be added if desired. The oxygen is rapidly absorbed and the operation is complete in three to five hours. When nitric acid is employed and the water formed in the reaction is not removed, nitro-compounds and other

impurities from which the anthraquinone can only be freed with difficulty are formed. This can be avoided and anthraquinone of 99—100% purity obtained if the nitric acid is replaced by sodium nitrite and the reaction is carried out in presence of a dehydrating agent such as acetic anhydride or anhydrous sodium acetate [cf. *J. Soc. Chem. Ind.*, 1922, 407A]. G. F. M.

Manufacture of Hydroxy- and Sulphohydroxy-derivatives of Anthraquinone. DAVID SEGALLER, DAVID HENRY PEACOCK, and BRITISH DYESTUFFS CORP., LTD. (Brit. Pat. 176925).—1-Hydroxyanthraquinone-4-sulphonic acid is obtained by the condensation of phenol or phenol-*p*-sulphonic acid with phthalic anhydride by means of a sulphuric acid solution of boric acid at about 200°. On further treatment of this substance, either after isolation, or in the sulphuric acid solution in which it is obtained, at a temperature of about 240—250°, it is converted into 1:4-dihydroxyanthraquinone (quinizarin). If phenol-2:4-disulphonic acid is used as starting material, the final product consists essentially of 1:2:4-trihydroxyanthraquinone (purpurin), whilst if *o*- or *m*-cresols are employed, β -methylquinizarin is produced. From *p*-cresol, 1-hydroxy-4-methylanthraquinone is obtained. G. F. M.

Preparation of Borneol. FABRIQUES DE PRODUITS CHIMIQUES DE THANN ET DE MULHOUSE (Brit. Pat. 164302, addn. to 144604; cf. A., 1921, i, 425).—In the preparation of bornyl tetrachlorophthalate from turpentine in presence of an organic solvent, the secondary products obtained from previous operations consisting of unchanged pinene mixed with dipentene may advantageously be used as diluent instead of ether, etc. A similar yield of borneol is obtained, and as the dipentene takes no part in the reaction the amount present in the recovered hydrocarbon increases from operation to operation until the quantity is such that it may easily be separated by fractional distillation from the crude secondary product. G. F. M.

Higher Terpene Compounds. III. The Naphthalene Hydrocarbons Cadalene and Eudalene. Two Aromatic Fundamental Compounds of the Sesquiterpene Series. L. RUZICKA, JULES MEYER, and M. MINGAZZINI (*Helv. Chim. Acta*, 1922, 5, 345—368; cf. this vol., i, 547).—The previous position of sesquiterpene chemistry is shortly reviewed. The method of removing hydrogen from cadinene by heating it with sulphur (A., 1921, i, 573) has been applied to other cases. The relative arrangement of the carbon atoms in a compound is unchanged by this treatment, since limonene and terpinene are each converted by its means into *p*-cymene, the respective yields being 15% and 50%. This result suggests that compounds containing cyclic double bonds may in general be more easily dehydrogenated than those with unsaturated side chains. Further, all the sesquiterpene fractions of a given oil yield the same product, and in no case is evidence observed of the formation of mixtures. Hence even

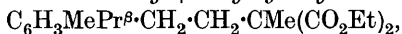
if, in any such case, the oil itself should be a mixture, the same carbon skeleton is present in each component. The hydrocarbon from cadinene (*loc. cit.*) is now termed *cadalene*; it has also been obtained from tetrahydrocadinene, from calamenol and its degradation product calamene, from calamenene, from *isozingiberene*, and from the sesquiterpene alcohol from Javanese citronella oil. Its smooth formation from the monocyclic zingiberene shows that the formation of a naphthalene derivative by this reaction is to be understood as evidence that the compound under examination has a potential, rather than an actual, bicyclic structure. Eudesmol and selinene apparently react according to the respective equations: $C_{15}H_{26}O + 3S = C_{14}H_{16} + H_2O + 2H_2S + CH_3 \cdot SH$; $C_{15}H_{24} + 3S = C_{14}H_{16} + 2H_2S + CH_3 \cdot SH$; the same hydrocarbon, eudalene, being produced in each case. This exceptional behaviour suggests that these compounds each contain a methyl group which cannot survive the transition into an aromatic compound and that the cadinene group of sesquiterpenes (Semmler and Becker, A., 1913, i, 742; Semmler and Stenzel, A., 1915, i, 427) must be sub-divided into the eudalene and cadalene classes. *Eudalene*, b. p. 280—281°, d 0.9734, R_D 63.31, ER_D 3.21, $E\Sigma_D$ 1.74 (*picrate*, $C_{20}H_{19}O_7N_3$, orange-yellow needles, m. p. 90—91°; *stypnate*, $C_{20}H_{19}O_8N_3$, yellow needles, m. p. 119—120°), is stable towards bromine and cold potassium permanganate, and its physical constants agree well with those of a naphthalene hydrocarbon. The synthesis of cadalene (see following abstract) shows it to be 1:6-dimethyl-4-isopropyl-naphthalene. Further, the close relationship of cadinene to copaene, and the loss of three carbon atoms from the molecule of copaneketonic acid by oxidation with sodium hypobromite (Semmler and Stenzel, *loc. cit.*) indicate that one double bond in cadinene is situated at the carbon atom carrying the isopropyl group. Corresponding with the contrast between retene and its parent phenanthrene in respect of the lability of the primary oxidation products of the former, those of cadalene are less stable than those of naphthalene. The quinone formed by the oxidation of cadalene could only be detected by means of its *oxime*, $C_{15}H_{17}O_2N$, m. p. 178—179° (decomp.); 6-methyl-4-isopropyl-1-naphthoic acid, $C_{15}H_{16}O_2$, leaflets, m. p. 161—162°, and possibly a hydroxyquinone, with other products were also formed. The relationship of the open-chain compound farnesol (Kerschbaum, A., 1913, i, 739) to cadalene is that of the aliphatic terpenes, for example, ocimene, to *p*-cymene. Further, the close relationship of cadalene not only to bicyclic, but also to monocyclic (zingiberene) and to tricyclic (copaene) sesquiterpenes reveals for the first time the analogous structure of a considerable number of sesquiterpenes, not only among themselves, but also with those of the terpenes. The common factor in the two series is the union of isoprene molecules, usually to a *p*-cymene skeleton. Probably a number of monocyclic sesquiterpenes represent a transition from farnesol to cadinene. The cadinene type is intermediate between the simple terpenes and the diterpenes (from which abietic acid is derived) and caoutchouc, which constitutes the highest member of the terpene series, and is

related to the others in being built up from isoprene molecules. Santonin, as a derivative of 1:4-dimethyl-6-isopropyl-naphthalene (Cannizzaro and Gucci, A., 1893, i, 665) is to be included with cadinene in the hydronaphthalene sub-group of bicyclic sesquiterpenes.

J. K.

Higher Terpene Compounds. IV. Synthesis of Cadalene.

L. RUZICKA and C. F. SEIDEL (*Helv. Chim. Acta*, 1922, 5, 369—375; cf. preceding abstract).—On the assumption that cyclic sesquiterpenes might have the same carbon chain as the open-chain alcohol, farnesol, it appeared that cadalene would be 1:6-dimethyl-4-isopropyl-naphthalene. The accuracy of this deduction has now been verified by the identity of the synthetic hydrocarbon with cadalene. Ethyl 2-cymylacetate, prepared from carvone by means of ethyl bromoacetate and zinc (Wallach, A., 1901, i, 156), was reduced by Bouveault's method to β -2-cymylethyl alcohol, $C_6H_3MePr^{\beta} \cdot CH_2 \cdot CH_2 \cdot OH$, b. p. 145—150°/12 mm. Condensation of its bromide, $C_{12}H_{17}Br$, b. p. 145—148°/12 mm., with ethyl methylmalonate furnished methyl β -2-cymylethylmalonate,



b. p. 200—210°/12 mm., from which β -2-cymyl- α -methylbutyric acid, $C_6H_3MePr^{\beta} \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CO_2H$, b. p. 200—201°/11 mm., was prepared. From its chloride, b. p. 165°/11 mm., and aluminium chloride, 5-keto-1:6-dimethyl-4-isopropyltetrahydronaphthalene, b. p. 160—170°/12 mm., was obtained. Reduction of this compound in alcoholic solution with sodium furnished as chief product, with a certain proportion of the pinacone, the corresponding secondary alcohol. Finally, a mixture of this compound with the hydrocarbon, resulting from its partial dehydration on distillation, was dehydrogenated at 180—210° by means of sulphur. The identity of the synthetic product with cadalene followed from a comparison of physical constants, picrates, and styphnates.

J. K.

The Action of Concentrated Sulphuric Acid on Natural and Artificial Caoutchoucs. II. F. KIRCHOF (*Kolloid Z.*, 1922, 30, 176—187; cf. A., 1921, i, 116).—Plantation pale crepe rubber is believed to have the composition $C_{20}H_{34}$. Under the action of cold concentrated sulphuric acid on its carbon tetrachloride solution for two hours, it undergoes conversion into an amorphous product of the composition $C_{10}H_{15}$, d 1.093—1.096, insoluble in chloroform. Gutta percha under similar conditions is converted into a product of unaltered composition, $C_{10}H_{16}$, soluble in chloroform. The behaviour of the former product towards bromine and sulphur with formation of compounds of the composition $C_{20}H_{30}Br_2$ and $C_{20}H_{30}S$ indicates the disappearance of three double bonds during the action of the acid. African rubber of the composition $C_{10}H_{16}$ gives rise to a similar series of products to plantation rubber. The latter type of rubber is believed to consist of spirally arranged closed chains, $C_{20}H_{32}$ or $C_{30}H_{48}$, which are held together in aggregates by partial valencies. To plantation rubber, a similar structure is attributed, consisting of aggregated, open-chain spirals

of the composition $C_{20}H_{34}$. The disappearance of the characteristic properties of rubber when the raw material is exposed to the action of sulphuric acid, or when vulcanised rubber hardens spontaneously, is ascribed to the development of tetramethylene rings, with loss of double bonds, by bridging.

On prolonged treatment in the undissolved state with cold sulphuric acid, plantation rubber is oxidised to a product, $C_{10}H_{14}O$, which is probably identical with the main product in the spontaneous oxidation of vulcanised rubber. Oxidation of the rubber by prolonged contact in benzene solution into sulphuric acid gives rise to an aldehydic acid, $C_{20}H_{30}O_3$, m. p. $95-96^\circ$ (crystalline phenylhydrazone, m. p. $120-124^\circ$). D. F. T.

The Essential Oil from *Blumea Malcomii*. JOHN LIONEL SIMONSEN and MADYAR GOPAL RAU (T., 1922, **121**, 876—883).

Constituents of Saffron. I. Picrocrocin. E. WINTERSTEIN and J. TELECKY (*Helv. Chim. Acta*, 1922, **5**, 376—381; *Z. physiol. Chem.*, 1922, **120**, 141—166).—Picrocrocin (Kayser, A., 1885, 59) forms colourless crystals, m. p. $154-155^\circ$, $[\alpha]_D -50.3^\circ$, and on hydrolysis with 1% sulphuric acid solution furnishes 54% of sugar (calculated as dextrose), with a ketone, $C_{10}H_{14}O$, b. p. $93^\circ/14$ mm., n_D 1.5240, $n_F - n_C$ 0.02283, d 0.985 (semicarbazone, $C_{11}H_{17}ON_3$, m. p. $162-163^\circ$). Its physical constants suggest that the latter belongs to the terpene series, and, like carvone, it furnishes an additive compound with hydrogen sulphide, m. p. 80° (decomp.). The sugar produced by hydrolysis furnishes an osazone, m. p. 205° , a phenylmethylhydrazone, m. p. 128° , and a corresponding osazone, m. p. 150° . Mannose, galactose, pentoses, and methyl-pentoses could not be detected, but tests for lævulose gave a positive result. The specific rotation was that of a mixture of 81.7% dextrose with 18.3% *d*-fructose, but the analytical results from picrocrocin could not be reconciled with this conclusion. Crocin, the colouring matter of saffron, contrary to earlier statements, furnishes on hydrolysis not an essential oil, but dextrose and a deep red, insoluble compound, crocetin (Decker, A., 1914, i, 979). Oxalic acid and a colourless unknown compound have been obtained from the oxidation of this compound. J. K.

Salicin Thiocyanate and Disalicin Sulphide. GÉZA ZEMPLÉN and ALEX. HOFFMANN (*Ber.*, 1922, **55**, [B], 992—997).—Tetra-acetylsalicin bromide is converted by ammonium thiocyanate in the presence of anhydrous acetone into *tetra-acetylsalicin thiocyanate*, $C_6H_7O_5Ac_4 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot SCN$, well-developed prisms, m. p. 135° , $[\alpha]_D^{25} +48.35^\circ$ when dissolved in chloroform. Somewhat unexpectedly, it is converted by methyl alcoholic ammonia into *disalicin disulphide*, $S_2(CH_2 \cdot C_6H_4 \cdot O \cdot C_6H_{11}O_5)_2$, m. p. 193° after slight previous softening, $[\alpha]_D^{25} -46.8^\circ$ when dissolved in glacial acetic acid; the substance can occasionally be isolated directly in the crystalline state, but, in general, is so prepared by the action of methyl alcoholic ammonia on the readily crystalline *octa-acetate*, long, slender needles, m. p. 188° , $[\alpha]_D^{20} +45.6^\circ$ in chloroform solu-

tion. The latter is hydrolysed by hydrochloric acid in the presence of alcohol to *di-o-hydroxybenzyl disulphide*, $S_2[CH_2 \cdot C_6H_4 \cdot OH]_2$, small prisms, m. p. 103° .
H. W.

New Derivatives of Salicin containing Nitrogen and Polynuclear Hydroxybenzylamines. GÉZA ZEMPLÉN and ALPHONS KUNZ (*Ber.*, 1922, **55**, [B], 979—992).—An investigation of the products obtained by the action of ammonia or amines on tetra-acetylsalicin bromide (cf. Zemplén, A., 1920, i, 559).

Tetra-acetylsalicin bromide, $C_6H_7O_5Ac_4 \cdot O \cdot C_6H_4 \cdot CH_2Br$, reacts readily with ammonia in ethyl or methyl alcoholic solution, exchanging its bromine atom initially for the amino-group and suffering de-acetylation; as with alkyl haloid and ammonia, however, the reaction proceeds further with the formation of secondary and tertiary amines. In the present instance, the isolation of a pure primary amine was not found possible, but the solution of the reaction product slowly deposits *disalicinamine*, $NH(CH_2 \cdot C_6H_4 \cdot O \cdot C_6H_{11}O_5)_2$, colourless needles, m. p. 205° (decomp.) after becoming yellow at 200° , $[\alpha]_D^{25} -45.82^\circ$ in aqueous *N*-hydrochloric acid solution, which is hydrolysed by boiling hydrochloric acid to dextrose and *di-o-hydroxybenzylamine*, colourless needles, m. p. 168° . The mother-liquors from the secondary amine contain *trisalicinamine*, which is isolated as the *dodeca-acetyl* derivative, $N(CH_2 \cdot C_6H_4 \cdot O \cdot C_6H_7O_5Ac_4)_3$, microscopic needles, m. p. $173-175^\circ$, $[\alpha]_D^{24} -45.13^\circ$ when dissolved in chloroform. It is hydrolysed by dilute hydrochloric acid to dextrose, acetic acid, and *tri-o-hydroxybenzylamine hydrochloride*, small, coarse needles, incipient decomp. 110° .

The reaction between tetra-acetylsalicin bromide and methylamine proceeds in an analogous manner, yielding (with de-acetylation) a non-crystalline syrup which, after re-acetylation, is readily separated into two fractions. The first of these consists of *penta-acetylsalicinmethylamine*, $C_6H_7O_5Ac_4 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot NMeAc$, coarse platelets, m. p. 165° , $[\alpha]_D^{23} -38.49^\circ$ in chloroform solution, which is hydrolysed by acids to *o-hydroxybenzylmethylamine* (isolated as the *phosphotungstate* and analysed as the *hydrochloride*, $OH \cdot C_6H_4 \cdot CH_2 \cdot NHMe, HCl$, slender needles, m. p. 130°). The second fraction is composed of *octa-acetyldisalicinmethylamine*, $NMe(CH_2 \cdot C_6H_4 \cdot O \cdot C_6H_7O_5Ac_4)_2$, colourless needles, m. p. $198-200^\circ$, $[\alpha]_D^{24} -35.40^\circ$, $[\alpha]_D^{31} -33.75^\circ$ when dissolved in chloroform, from which a uniform material could not be prepared by hydrolysis with acids.

Tetra-acetylsalicin bromide and ethylamine, under similar treatment, give *penta-acetylsalicinethylamine*, small, colourless needles, m. p. $96-97^\circ$, and *octa-acetyldisalicinethylamine*, long, colourless needles, m. p. $151-153^\circ$.

Tetra-acetylsalicin bromide is converted by diethylamine into *salicindiethylamine*, $C_6H_{11}O_5 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot NEt_2$, small, colourless needles, m. p. $102-103^\circ$, $[\alpha]_D^{30} -26.05^\circ$ in chloroform solution. With methylaniline in boiling methyl alcoholic solution, it gives *tetra-acetylsalicinphenylmethylamine*, long, colourless needles, m. p.

140—141°, $[\alpha]_D^{30} -19.78^\circ$ in chloroform, which is transformed by methyl alcoholic ammonia into *salicinphenylmethylamine*, small crystals, $[\alpha]_D^{30} -36.23^\circ$ when dissolved in acetone.

Tetra-acetylsalicin bromide is converted by trimethylamine in absolute alcoholic solution into *tetra-acetylsalicintrimethylammonium bromide*, $C_6H_7O_5Ac_4 \cdot O \cdot C_6H_4 \cdot CH_2 \cdot NMe_3Br$, colourless needles, m. p. 68° after softening at 65°, $[\alpha]_D^{26} -42.28^\circ$ in aqueous solution. It is hydrolysed by hydrochloric acid (5%) to *o-hydroxybenzyltrimethylammonium chloride*, slender needles (+H₂O), m. p. 96°; anhydrous, m. p. 200° (decomp.). H. W.

Saponins. VII. A. W. VAN DER HAAR (*Ber.*, 1922, 55, [B], 1054—1066; cf. this vol., i, 160).—It is shown that several sapogenins, such as hederagenin and others, are closely related to one another and to the terpene hydrocarbons (for example, sesquiterpenes) on the one hand and to phytosterols (sitosterol), cholesterol, and phytosterol-like substances (urson, oleanol) on the other. Hederagenin is decomposed by distillation with zinc dust in a current of hydrogen into sesquiterpenes, carbon dioxide, and water, in accordance with the equation $C_{30}H_{47}(OH)_2 \cdot CO_2H + H_2 = 2C_{15}H_{24} + CO_2 + 2H_2O$. The sesquiterpene volatile with steam which gives the violet coloration of sapogenins and saponins with sulphuric acid is to be regarded as the primary product of the distillation of hederagenin with zinc dust. During the process it undergoes partial conversion into terpene hydrocarbons which are not volatile with steam; the violet glacial acetic-sulphuric acid reaction passes to bluish-green. The volatile sesquiterpenes consist of a mixture of structurally different sesquiterpenes. The distillation of hederagenin with zinc dust in an atmosphere of hydrogen is most conveniently effected rapidly from a small retort heated on a sand-bath. H. W.

The Optical Activity of Catechins. K. FEIST and A. FUTTERMENGER (*Ber.*, 1922, 55, [B], 942—944; cf. Feist and Schön, A., 1921, i, 117; Freudenberg, A., 1921, i, 576, 577).—The observation of the optical activity of catechins in water, alcohol, or aqueous acetone is rendered very difficult by the inability to use any but very dilute solutions. Exact values can only be obtained when the hydroxyl groups of the catechin are protected by esterification or etherification. H. W.

Preparation of Coumarins. WOLFGANG PONNDORF (D.R.-P. 338737; from *Chem. Zentr.*, 1921, iv, 1224—1225).—Phenols or phenol ethers are condensed with fumaric or maleic acids or their derivatives at temperatures above 120°. In the condensation of fumaric acid with phenols, the ortho-hydrogen atom of the phenol unites with a carboxyl group of the acid, giving formic acid; ring closure and formation of coumarin follows the elimination of water from the coumaric acid thus formed. Zinc chloride or, preferably, 73% aqueous or alcoholic sulphuric acid may be used as condensing agents. By condensation of *p*-cresol with fumaric acid

in the presence of sulphuric acid at 130—180° 6-methylcoumarin, m. p. 72—73°, is formed.

G. W. R.

Dyes Containing the Furan Ring. R. R. RENSHAW and NELLIE M. NAYLOR (*J. Amer. Chem. Soc.*, 1922, **44**, 862—864).—The authors have repeated the work of Fisher (cf. A., 1878, 51) on the furan analogue of malachite-green. Contrary to the results of Fisher, they find that the product obtained by the oxidation of tetramethyldiaminodiphenylfurylmethane has a deeper colour than malachite-green and that it is an equally stable dye, giving handsome effects on silk and wool. Its *oxalate* and its zincochloride were prepared.

Pyromucic acid was condensed with pyrogallol, giving a yellowish-brown powder, m. p. 160°, which is presumably the furan analogue of alizarin-yellow-A. It gives a dark tan colour on cotton mordanted with turkey-red.

W. G.

The System Furfuraldehyde-Water. GERALD H. MAINS (*Chem. and Met. Eng.*, 1922, **26**, 779—784, 841—843).—The corrected boiling point of pure furfuraldehyde is 161·7° at 760 mm., and d_4^{20} 1·1598 or d_4^{25} 1·1545, both values corrected to vacuum. The composition-specific gravity tables for solutions of furfuraldehyde in water up to the saturation concentration were determined at 20° and 25°, and were subsequently used as a method of analysis, accurate to $\pm 0\cdot02\%$, in the determination of the mutual solubility and boiling-point and condensation-point curves for the system furfuraldehyde-water. The solubility of furfuraldehyde in water rises from 8·12% at 16° to 8·72% at 27° and 17% at 92°, whilst that of water in furfuraldehyde rises from 3·5% at 8° to 5·4% at 26·5° and 15·5% at 96°. The most important data emerging from the boiling-point curves of furfuraldehyde-water mixtures are as follows. With increasing amount of furfuraldehyde in the solution the boiling point gradually falls from 100° to a minimum of 97·9°, which is reached at the composition 18·4% furfuraldehyde, at which point two layers commence to be formed. Through the whole of this range the vapour phase contains a much higher percentage of furfuraldehyde than the liquid, rising to 35% at the minimum boiling point. From this point during the whole range in which there are two liquid layers, that is, up to 84% of furfuraldehyde, the boiling point and composition of the vapour phase remain constant. With higher concentrations than 84%, the boiling point rapidly rises until at 161·7° pure furfuraldehyde only remains. From the above data it is evident that by taking advantage of the great divergence in the boiling-point and condensation-point curves in this system, it is possible to effect readily a separation of furfuraldehyde from dilute aqueous solutions by fractional distillation, whereby a fraction containing furfuraldehyde and water in two layers boiling at 97·9—100° first distils. The aqueous furfuraldehyde layer is separated and the residual aqueous layer returned to the still. The aqueous high percentage furfuraldehyde is then dried by redistillation, water passing over first

and then furfuraldehyde of constant boiling point. In conclusion, the mathematical relations for the distillation of mixtures, as developed by Lord Rayleigh, are discussed with reference to the furfuraldehyde-water system. G. F. M.

Preparation of Thionaphthencarboxylic Acids. GESELLSCHAFT FÜR TEERVERWERTUNG M. B. H., RUDOLF WEISSGERBER UND OTTO KRUBER (D.R.-P. 341837; from *Chem. Zentr.*, 1921, iv, 1225).—Sodium thionaphthen is treated with carbon dioxide in the absence of water, and the carboxylic acids thus obtained are separated by their varying acidities or by the fractionation of their esters. For example, anhydrous thionaphthen is treated with sodamide at 140–150° for five hours in a shaking vessel. A stream of dry carbon dioxide is then passed without lowering the temperature or interrupting the shaking. By treatment of the cooled products of reaction with water and toluene, the sodium salts are obtained in aqueous solution and the unchanged thionaphthen in toluene solution. The thionaphthencarboxylic acids are liberated by acidifying. By dissolving in sodium carbonate solution and partial acidification, the more strongly acid, *thionaphthen-2:3-dicarboxylic acid* is separated from the weaker acid, *thionaphthen-2-carboxylic acid*. The acids may also be separated by fractionation of their methyl esters (Weissgerber and Kruber, A., 1920, i, 754). *Methyl thionaphthen-2-carboxylate* has b. p. 176–180°/13 mm. *Methyl thionaphthen-2:3-dicarboxylate* has b. p. 214–218°/13 mm. G. W. R.

Space Structural Formulæ of Chemical Substances in General, and of some Alkaloids in Particular. J. J. LYNST ZWIKKER (*Chem. Weekblad*, 1922, 19, 158–162).—Asymmetric as well as symmetric molecules may be regarded as harmonious groupings of atoms in space, building up constellations of simple and regular form.

In the cases of the alkaloids cinchonine, quinine, berberine, hydrastinine, and narceine, this form is the trigonal bipyramid, the 18 carbon atoms being regularly spaced in pairs along the nine edges. It is probable that the simplest and most stable form of this constellation is represented by the hydrocarbon retene.

S. I. L.

The Anhalonium [Cactus] Alkaloids. III. The Constitution of Anhaline. ERNST SPÄTH (*Monatsh.*, 1921, 42, 263–266).—The identity of anhaline with hordenine (A., 1919, i, 548) has been confirmed by a direct comparison of the two bases and of a number of their derivatives. The picrate has m. p. 139–140°, the picrolonate, m. p. 219–220°, the quaternary ammonium compound with methyl iodide, m. p. 230–231°, and the hydriodide of the acetylated base, m. p. 176–177°. E. H. R.

Preparation of Tropinonecarboxylic Acid Esters. E. MERCK and OTTO WOLFES (Brit. Pat. 153917).—Ethyl tropinonecarboxylate is obtained by the condensation of succinaldehyde, methylamine, and ethyl acetoacetate (cf. T., 1917, 111, 762). A

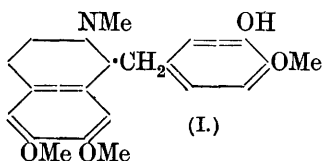
mixture of 8.6 parts of succinaldehyde, an alcoholic solution of 10 parts of methylamine, and 13 parts of acetoacetic ester dissolved in 30 parts of alcohol is kept for three days, the product is neutralised, freed from alcohol, rendered alkaline with aqueous potassium carbonate solution, and extracted with chloroform. The tropinone-carboxylic ester is then transferred to dilute sulphuric acid solution, and back to chloroform, and finally the chloroform is distilled, leaving the ester as an oil which gradually solidifies on keeping in contact with the air.

G. F. M.

Preparation of Tropinonecarboxylic Acid Esters. E. MERCK, OTTO WOLFES, and HORST MAEDER (Brit. Pat. 164757).—Ethyl tropinonecarboxylate is obtained by the hydrolysis of one ester group in diethyl tropinonedicarboxylate (cf. T., 1917, 111, 762) and simultaneous elimination of carbon dioxide. Twenty-eight parts of the diethyl ester in 50 parts of alcohol are heated to boiling with 22 parts of potassium hydroxide solution (1:1). After cooling, ice is added, the liquid is acidified with sulphuric acid, supersaturated with ammonia, and extracted with ether or a chlorinated hydrocarbon. Ethyl tropinonecarboxylate is an oil forming a crystalline hydrate, m. p. 63°.

G. F. M.

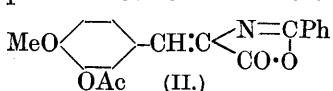
The Synthesis of Laudanine. ERNST SPÄTH and NORBERT LANG (*Monatsh.*, 1921, 42, 273—285).—Laudanine was shown by Späth (A., 1921, i, 50) to have the annexed formula (I). This



has now been confirmed by synthesis of the alkaloid. The synthesis depended on the known method of preparing isoquinoline derivatives by effecting ring-closure in *N*-acyl derivatives of *o*-phenylethylamine. Homoveratrylamine, β -aminoethyl-3:4-di-

methoxybenzene was prepared by Rosenmund's method (A., 1911, i, 34) by condensing 3:4-dimethoxybenzaldehyde with nitromethane, followed by reduction of the *o*-nitrostyrene in two stages.

3-Hydroxy-4-methoxyphenylacetic acid (homoisovanillic acid) is prepared by condensing isovanillin with hippuric acid in presence of sodium acetate and acetic anhydride, whereby the

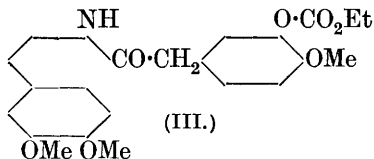


lactone of α -benzoylamino-3-acetoxy-4-methoxycinnamic acid (II) is formed, yellow needles from alcohol, m. p. 134—136°.

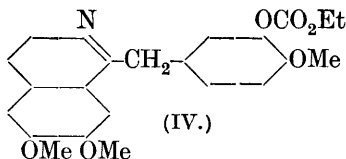
When this is warmed with 15% sodium hydroxide solution, the acetyl group is removed and the lactone ring opened. The resulting α -benzoylamino-3-hydroxy-4-methoxycinnamic acid forms colourless crystals, m. p. 213.5—215.5° (decomp.). When the lactone is boiled with 23.5% potassium hydroxide, the desired 3-hydroxy-4-methoxyphenylpyruvic acid is obtained, along with resinous products. This compound forms a voluminous precipitate when light petroleum is added to its ethereal solutions; it has m. p. 183—184.5° (decomp.), and decomposes gradually on exposure to air. The ethylcarbonato-derivative, in which the hydroxyl group is replaced by the ethyl-

carbonato-group, is crystalline, m. p. 143—146°. By oxidation of its sodium salt in aqueous solution with hydrogen peroxide, 3-hydroxy-4-methoxyphenylpyruvic acid was converted into 3-hydroxy-4-methoxyphenylacetic acid in 80—90% yield; the product forms long needles from ether, m. p. 122·5—124·5°. For condensation with homoveratrylamine, it was converted into its *ethylcarbonato*-derivative, m. p. 112—113°.

The 3-ethylcarbonato-4-methoxyphenylpyruvic acid was converted into the acid chloride and the crude product condensed in benzene solution with the above β -aminoethyl-3 : 4-dimethoxybenzene. The product (III) could not be purified, but was treated directly with phosphoric oxide in toluene



solution. From the products of the reaction was isolated 1-[*ethylcarbonatoisovanillyl*]-6 : 7-dimethoxy-3 : 4-dihydroisoquinoline (IV), which forms a crystalline *hydrochloride*, m. p. 193·5° (decomp.). The base was converted into the methylisoquinolinium iodide, which could not be obtained pure, and thence into

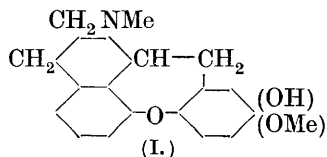


the corresponding *chloride*, which forms a well-characterised, yellow, crystalline double salt with platinum chloride. The methylisoquinolinium chloride was reduced with tin and hydrochloric acid, giving a mixture of laudanine and its ethylcarbonato-derivative, not all of which was hydrolysed during the reduction. The laudanine was proved to be identical with natural laudanine. E. H. R.

Alkaloids of the Pareira Root. II. *isoChondodendrine*.

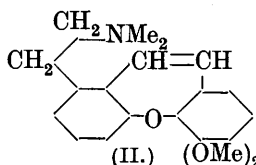
FRANZ FALTIS and FELIX NEUMANN (*Monatsh.*, 1921, 42, 311—376; cf. Faltis, A., 1912, i, 796; Scholtz, A., 1913, i, 87, 385; 1915, i, 450).—A long historical account is given of the alkaloids of the pareira root, which have been known as bebeerines. It is shown that these alkaloids are different from that obtained from the bark of *Nectandra Rodiæi*, the so-called bebeerin tree, and that the true source of pareira root is *Chondodendron platyphyllum*. For this reason, it is proposed to substitute the names α -, β -, and *isochondodendrine* for the alkaloids formerly known as α -, β -, and *isobebeerine*, respectively.

isoChondodendrine (and probably α - and β -chondodendrine) has the composition $C_{18}H_{19}NO_3$, which has been resolved into $OH \cdot C_{16}H_{12}ONMe \cdot OMe$. Starting from the hypothesis that *isochondodendrine* is related to lauda-



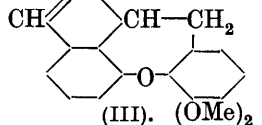
nosine, it may have the following configuration (attached formula, I). Methylation in the hydroxyl group, without formation of a quaternary ammonium compound, was only accomplished with diazomethane. *Methyl-*

isochondodendrine forms a crystalline crust, m. p. 256—257°, $[\alpha]_D^{19}$ —36·8° in alcohol. Its methiodide has $[\alpha]_D^{16}$ —7° in 50% alcohol. De-



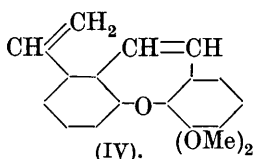
composition of the quaternary ammonium compound by Hofmann's method (heating with aqueous sodium hydroxide), gave an α - and a β -methine differing in some respects from those described by Scholz (*loc. cit.*). The α -methine (annexed formula [II]), according

to the above hypothesis is optically inactive, m. p. 204—205°. It forms tabular, triclinic crystals [$a : b : c = 1.6996 : 1 : 1.2908$; $\alpha = 91^\circ 5\frac{1}{2}'$; $\beta = 103^\circ 27'$; $\gamma = 91^\circ 20'$]. The β -methine (III), m. p. 167—168·5°, has $[\alpha]_D^{19} +353^\circ$ in pyridine, $+359^\circ$ in alcohol.



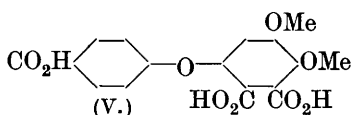
With sulphuric acid, the α -methine gives a deep red solution on warming, suddenly changing to blue. Scholz attributed this reaction to the active β -methine, which does not show it. The α -methine by reduction with sodium and alcohol gave the α -dihydromethine, m. p. 211·5—212°, which was also obtained by reduction of methylisochondodendrine methochloride with sodium amalgam. It forms small tetragonal crystals [$a : c = 1 : 0.38257$]. Its hydrochloride forms a double chloride with gold chloride, $C_{20}H_{25}O_3N, HAuCl_4$.

By reduction of the methiodides of the mixed α - and β -methines with powdered sodium hydroxide in methyl alcohol, a nitrogen-free compound, $C_{18}H_{16}O_3$, containing two ethylene linkings, was obtained; tabular six-sided monoclinic crystals [$a : b : c = 0.8271 : 1 : 0.8416$; $\beta = 99^\circ 35'$]; it does not melt below 312°. The

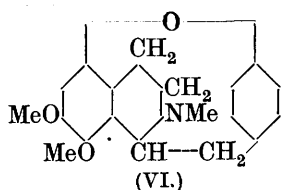


formula IV is suggested. Reduction of the α -dihydromethine gave a similar compound, $C_{18}H_{18}O_3$, containing only one double bond. This has no m. p. and forms tabular, monoclinic crystals [$a : b : c = 0.8470 : 1 : 0.6160$; $\beta = 97^\circ 45\frac{1}{2}'$]. The constitution suggested is that of IV with the $-CH:CH-$ bridge reduced.

Oxidation of the compound $C_{18}H_{16}O_3$ with potassium permanganate gave a tricarboxylic acid, $C_{12}H_5O(OMe)_2(CO_2H)_3$, m. p. 177·5—178°, which forms an *anhydride*, m. p. 244—245°, and a *trimethyl ester*, m. p. 100—102°. Demethylation of the tricarboxylic acid gave a dihydroxydicarboxylic acid showing the colour reactions of catechol, and therefore having the two hydroxyl groups in the ortho-position to each other. By fusion with potassium hydroxide, the tricarboxylic acid gave a good yield of *p*-hydroxybenzoic acid, and after methylation of the residue a trimethoxybenzoic acid,



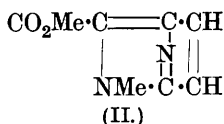
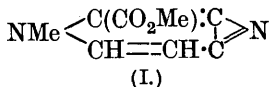
m. p. 141—143°, was isolated, which appears to be the hitherto unknown 2 : 3 : 5-trimethoxybenzoic acid. In all probability, therefore, the above tricarboxylic acid has formula V. This leads unexpectedly to the formula (VI) for methylisochondodendrine,



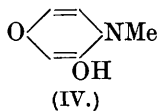
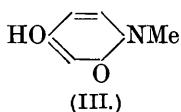
salicylic acid into *p*-hydroxybenzoic acid under similar experimental conditions gave negative results. Confirmation of the formula was obtained by distilling *isochondodendrine* with zinc dust when *p*-cresol was obtained. The formula of *isochondodendrine* will be similar to VI with (OH) in place of one of the (OMe) groups, but there is no evidence to show which.

E. H. R.

The Constitution of Ricinine. ERNST SPÄTH and ERICH TSCHERNITZ (*Monatsh.*, 1921, 42, 251—262).—Ricinine has generally been regarded as the methyl ester of ricinic acid, and different



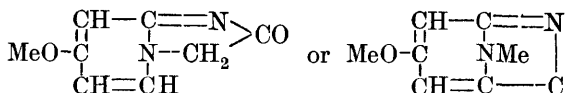
formulæ have been proposed for it, (I) by Maquenne and Philippe (A., 1905, i, 80) and (II) by Böttcher (A., 1918, i, 304). To throw more light on the structure of this alkaloid, the synthesis of the decomposition products, $\text{C}_7\text{H}_9\text{O}_2\text{N}$, obtained by Winterstein and others (A., 1919, i, 500) by boiling ricinine with 57.4% sulphuric acid, and $\text{C}_6\text{H}_7\text{O}_2\text{N}$ obtained by Maquenne and



Philippe by heating ricinic acid with hydrochloric acid, has been attempted and successfully accomplished. The latter compound is shown to be identical with a pyridone of formula (III) or (IV), whilst the compound $\text{C}_7\text{H}_9\text{O}_2\text{N}$ is the *O*-methyl derivative of either III or IV. The synthesis was accomplished as follows. 2:4-Dihydroxypyridine was converted into the corresponding dimethoxy-derivative by treating it with silver salt with methyl iodide in ethereal solution. The dimethyl ether was characterised by the preparation of its picrolonate, m. p. 148—149°. By further treatment of this compound with methyl iodide, it was converted directly into 4-methoxy-1-methyl-1:2-dihydropyrid-2-one or 2-methoxy-1-methyl-1:4-dihydropyrid-4-one identical with the ricinine derivative, $\text{C}_7\text{H}_9\text{O}_2\text{N}$, m. p. 113—114°. It forms a picrate, long, yellow, felted needles, m. p. 154—155°, and a picrolonate, golden-yellow crystals, m. p. 126.5° (decomp.). When heated with fuming hydrochloric acid at 140° in a sealed tube, the compound is demethylated, forming a compound, $\text{C}_6\text{H}_7\text{O}_2\text{N}$, identical with that obtained by Maquenne and Philippe from ricinic acid. A comparison of the boiling point of the compound $\text{C}_7\text{H}_9\text{O}_2\text{N}$, 161—162°/16 mm., with those of 1-methyl-1:2-dihydropyrid-2-one, 126.5°/14.5 mm., and of the corresponding pyrid-4-one, 223—224°/15 mm., leads to the

conclusion that the compounds under consideration correspond with formula (III) rather than (IV).

The methyl groups of ricinine being thus accounted for in the decomposition product $C_7H_9O_2N$, it follows that ricinine cannot be, as hitherto supposed, the methyl ester of a carboxylic acid, and the formulæ hitherto proposed must be rejected. The ease of hydrolysis of the methoxyl group may be accounted for by fusion of the pyridine ring with another ring, in all probability a glyoxaline ring, as suggested by Böttcher. These and other properties of ricinine may be summarised in either of the two formulæ :



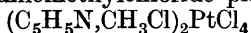
E. H. R.

Taxine, the Alkaloid from the Yew, *Taxus baccata*. I. E. WINTERSTEIN and D. IATRIDES (*Z. physiol. Chem.*, 1921, **117**, 240—283).—Taxine, obtained in yield of 0.7—1.4% from dried yew-needles, has the formula $C_{37}H_{51}O_{10}N$. It has not been possible to obtain it or its salts in a crystalline condition. The amorphous base sinters at 97° and melts at 105—110°, $[\alpha]_D +53.15^\circ$ in 1% sulphuric acid, $+51.52^\circ$ in absolute alcohol. With dilute organic and inorganic acids, cinnamic acid, acetic acid, a substance having reducing properties, and a resinous product are formed. With sodium hydroxide in the cold, cinnamic acid is produced in small amounts. When heated by itself, taxine gives rise to a product containing nitrogen. On reduction, it unites with two molecules of hydrogen, forming a compound, $C_{37}H_{55}O_{10}N$; thus indicating the presence of two double bonds. Similarly, a yellow, amorphous compound, $C_{37}H_{51}O_{10}NBr_4$, m. p. 125—130° (decomp.), is formed on bromination. Acetic anhydride produces an acetyl derivative of uncertain constitution, which with alcoholic potassium hydroxide yields a molecular proportion of cinnamic acid. Methyl iodide gives a white *methiodide*, $C_{37}H_{51}O_{10}N, CH_3I$, m. p. 122—125°, which with alkali hydroxide yields a white, flocculent product, $C_{37}H_{48}O_{10}$, m. p. 120—140°, methylamine being eliminated. Oxidation with hydrogen peroxide results in the formation of a reducing compound which with phloroglucinol and hydrogen chloride gives a crystalline compound, light brown needles, m. p. 123°. With potassium permanganate, benzamide, benzoic acid, acetic acid, oxalic acid, and benzonitrile are formed and also a substance which with phenylhydrazine yields a compound, $(C_4H_5ON)_x$, white, glistening scales, m. p. 185°.

W. O. K.

Additive Compounds of s-Trinitroanisole with Tertiary Bases. M. GIUA (*Gazzetta*, 1922, **52**, i, 182; cf. A., 1921, i, 592; Kohn and Grauer, A., 1914, i, 83; 1915, i, 836; Walther, A., 1915, i, 836, 993).—When treated with alcoholic platinum

chloride solution, the additive compound of *s*.-trinitroanisole with pyridine yields pyridinemethylchloride platinichloride,



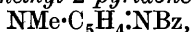
(cf. Bally, A., 1888, 964).

T. H. P.

Pyridinium Salts derived from some Chloroacetyl amino-compounds. EDWARD DE BARRY BARNETT and JAMES WILFRED COOK (T., 1922, 121, 792—797).

The Products of the Benzoylation of 2-Aminopyridine.

A. E. TSCHITSCHIBABIN and J. S. BYLINKIN (*Ber.*, 1922, 55, [B], 998—1002).—The action of benzoyl chloride or benzoic anhydride on 2-aminopyridine under very varied conditions leads to the production of a mixture of dibenzoylaminopyridine, slender needles, m. p. 166—167°, and 2-benzoylaminopyridine, $\text{C}_5\text{H}_4\text{N}\cdot\text{NHBz}$, large, colourless needles, m. p. 87° (*platinichloride*, orange-coloured needles, m. p. 230° [decomp.], *picrate*, yellow needles, m. p. 193°). The constitution of the substance is deduced from the observation that it is converted by the successive action of methyl iodide and alkali hydroxide into 1-methyl-2-pyridone-2-benzoylimide,



golden-yellow, granular crystals, m. p. 70° (*picrate*, small, yellow prisms, m. p. 157°), which is identical with the product obtained by the direct benzoylation of 1-methyl-2-pyridoneimide (A., 1921, i, 450). Dibenzoyl- α -aminopyridine appears to be identical with the substance described as benzoylaminopyridine by Marckwald. It is almost devoid of basic properties, and is characterised by the ease with which it loses a benzoyl group and passes into benzoylaminopyridine, m. p. 87°. When treated with platinum chloride in concentrated aqueous hydrochloric acid solution, it yields the platinichloride of the monobenzoyl derivative. It is not possible at present to decide between the alternative formulæ $\text{C}_5\text{H}_4\text{N}\cdot\text{NBz}_2$ and $\text{NBz}\cdot\text{C}_5\text{H}_4\text{NBz}$.
H. W.

4 : 6-Diphenyl-2-methylpyridine. C. GASTALDI (*Gazzetta*, 1922, 52, i, 169—175; cf. this vol., i, 367).—The author has investigated the interaction of acetophenone and acetic anhydride in presence of sublimed ferric chloride, the product of which is regarded by Dilthey (A., 1916, i, 829) as a ferric chloride compound of 2 : 6-diphenyl-4-methylpyrylium chloride of the constitution $\text{FeCl}_4\cdot\text{O}\langle\begin{smallmatrix} \text{CPh}\cdot\text{CH} \\ \text{CMe}\cdot\text{CH} \end{smallmatrix}\rangle\text{CPh}$. The author considers that this reaction is analogous to that occurring between dyponone and benzoyl chloride in presence of sublimed aluminium chloride with formation of 2 : 4 : 6-triphenylpyrylium chloride, and that the acetic anhydride, acting as a condensing agent, first converts the acetophenone into dyponone. This view is supported by the fact that the action of acetic anhydride on dyponone yields the ferric chloride compound of 4 : 6-diphenyl-2-methylpyrylium chloride. The constitution attributed to this compound by Dilthey is, therefore, erroneous, the mistake being the result of an earlier one made by von Meyer

and Irmscher (A., 1908, i, 911), who wrongly described as 4:6-diphenyl-2-methylpyridine, a compound of another structure. Thus the action of ammonia on the pyrylium salt obtained from either acetophenone or dypnone by the action of acetic anhydride yields 4:6-diphenyl-2-methylpyridine, m. p. 185°, which Dilthey regarded as 2:6-diphenyl-4-methylpyridine. Further, the compound which Dilthey considered to be the ferric chloride compound of 2:6-di-*p*-anisyl-4-methylpyrylium chloride is probably the corresponding compound of 4:6-di-*p*-anisyl-2-methylpyrylium chloride.

4:6-Diphenylpyridine-2-carboxylic acid, $N \begin{smallmatrix} \diagup C(CO_2H) \cdot CH \\ \diagdown CPh \end{smallmatrix} = CH \rangle CPh$, obtained by the action of potassium permanganate on 4:6-diphenyl-2-methylpyridine in presence of acid, crystallises in colourless needles, m. p. 150°; when the *sodium* salt is heated in a vacuum with the calcium oxide, it yields 2:4-diphenylpyridine, which forms a dense, pale yellow liquid, and gives the *hydrogen sulphate*, $C_{17}H_{13}N, H_2SO_4$, needles, m. p. 245° (slight browning). T. H. P.

2-*p*-Dimethylaminostyrylpyridine Methiodide, a New Photographic Sensitiser. WILLIAM HOBSON MILLS and WILLIAM JACKSON POPE (T., 1922, 121, 946—947).

Preparation of Hydrogenated 2-Phenylquinoline-4-carboxylic Acid, its Homologues, and their Salts. FRITZ ZUCKMAYER (D.R.-P. 342048; from *Chem. Zentr.*, 1921, iv, 1225—1226).—2-Phenylquinoline-4-carboxylic acid, or its derivatives containing alkyl or alkoxy in the quinoline group, are treated with reducing agents and the tetrahydroquinolinecarboxylic acids thus obtained are changed into their alkali or alkaline-earth salts. Acid, alkaline, or electrochemical reducing agents may be used. The resulting phenyltetrahydroquinolinecarboxylic acids are more soluble in dilute acids than their parent compounds and form slightly soluble nitroso-derivatives. They can be acetylated. The reduction of 2-phenylquinoline-4-carboxylic acid, either by iron and hydrochloric acid, by sodium amalgam, or electrochemically in alkaline solution, gives 2-phenyltetrahydroquinoline-4-carboxylic acid, white, felted needles, m. p. about 149°; *lithium* salt, white tasteless powder. Reduction of 8-methoxy-2-phenylquinoline-4-carboxylic acid by zinc and sodium hydroxide solution gives 8-methoxy-2-phenyltetrahydroquinoline-4-carboxylic acid; it crystallises in white needles, m. p. 185—186°. The acids and their salts have therapeutic uses as antipyretics and eliminators of uric acid. G. W. R.

Polynuclear Heterocyclic Aromatic Types. I. Some Indenoquinoline Derivatives. JAMES WILSON ARMIT and ROBERT ROBINSON (T., 1922, 121, 827—839).

Benzoxazole Derivatives. SIEGFRIED SKRAUP and MARIE MOSER (*Ber.*, 1922, 55, [B], 1080—1101; cf. Skraup, A., 1919, i, 598).—A description of attempts to prepare benzoxazol phenyl

ketone and a further account of the influence of substituents on the opening of the benzoxazole ring.

Attempts to prepare benzoxazyl phenyl ketone by converting 2-aminobenzoxazole into the corresponding nitrile and treatment of the latter with the requisite Grignard reagent were rendered unsuccessful by the apparent impossibility of diazotising the amino-substance.

Benzoxazole-2-carboxylic acid, colourless crystals, m. p. 85°, is obtained in small amount by the action of potassium permanganate on 2-methylbenzoxazole, but is more conveniently prepared by the oxidation of 2-*o*-hydroxyphenylbenzoxazole (long, pale pink needles, m. p. 123°, obtained by heating *o*-aminophenol with salicylamide); the *potassium, silver, mercurous, mercuric, lead, and copper* salts are described. The potassium salt is converted by thionyl chloride into *benzoxazole-2-carboxyl chloride*, m. p. 85°. The latter substance mainly suffers reduction when treated with magnesium phenyl bromide; in cold solution it is possible to obtain *benzoxazyl-diphenylcarbinol*, $\text{C}_6\text{H}_4\langle\text{N}\rangle_{\text{O}}\text{C}\cdot\text{CPh}_2\cdot\text{OH}$, colourless crystals, m. p. 157°, in small amount, but the main product is 2-*hydroxymethylbenzoxazole*, $\text{C}_6\text{H}_4\langle\text{N}\rangle_{\text{O}}\text{C}\cdot\text{CH}_2\cdot\text{OH}$, m. p. 125°, and this is formed exclusively when the action is carried out in warm solution. *Benzoxazole-2-carboxyanilide*, m. p. 156–157°, is reduced in a similar manner by magnesium methyl iodide with the formation of *benzoxazole-2-aldehydeanil*, $\text{C}_6\text{H}_4\langle\text{N}\rangle_{\text{O}}\text{C}\cdot\text{CH}\cdot\text{NPh}$, m. p. 153°.

Greater success was met in a series of experiments which depend on the reactivity of the methylene hydrogen atoms of 2-benzylbenzoxazole. The latter is converted by *p*-nitrosodimethylaniline into the compound, $\text{C}_6\text{H}_4\langle\text{N}\rangle_{\text{O}}\text{C}\cdot\text{CPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, slender, lustrous needles, incipient decomp. 150°, by 2 : 4-dinitrophenyldiazonium sulphate into the substance, $\text{C}_6\text{H}_4\langle\text{N}\rangle_{\text{O}}\text{C}\cdot\text{CPh}\cdot\text{N}\cdot\text{NH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, yellow crystals, m. p. 140°, and by amyl nitrite and sodium ethoxide into *benzoxazyl phenyl ketoxime*, m. p. 193°. The latter substance is converted by absolutely anhydrous acetic acid at 190° into the desired *benzoxazyl phenyl ketone*, but the reaction appears to be influenced to an unusual extent by the presence of traces of moisture.

2-*Ethylbenzoxazole*, from *o*-aminophenol and propionitrile at 205–210°, has b. p. 210°, d^{20}_4 1.081. 2- β -*Naphthylbenzoxazole* has m. p. 115–116°, 2-*p*-nitrophenylbenzoxazole, long needles, m. p. 260°, is obtained from *o*-aminophenol and *p*-nitrobenzonitrile at 135–140°; the preparation of the corresponding *m*- and *p*-nitro-compounds in this manner does not appear to be possible, but 2-*m*-nitrophenylbenzoxazole, m. p. 207°, is obtained from *o*-aminophenol and *m*-nitrobenzoyl chloride.

The velocity of hydrolysis of benzoxazole and its 2-substituted derivatives by hydrochloric acid (20.2%) has been measured at 61° and 108°. The reaction is apparently unimolecular, since

water is present in large excess; its velocity depends greatly on the substituent and gives a measure of the valency demands of the latter.

H. W.

Thiazoles. I. Derivatives of 2-Phenylbenzthiazole. Synthesis of an Analogue of Cinchophen (Atophan). MARSTON T. BOGERT and EMANUEL M. ABRAHAMSON (*J. Amer. Chem. Soc.*, 1922, **44**, 826—837).—The most satisfactory method of preparing 2-phenylbenzthiazole is by the fusion of benzanilide or benzylidene-aniline with sulphur. The product obtained by its nitration is shown to be the 6-nitro-derivative (cf. Nägeli, A., 1895, i, 347). When reduced, the nitro-derivative yields 6-amino-2-phenylbenzthiazole, giving an *acetyl* derivative, m. p. 214° (corr.). On fusion with potassium hydroxide, the amine gives benzoic acid and no aminobenzoic acid. Further, it couples only once with diazotised *p*-nitroaniline, giving *p*-nitrobenzeneazo-6-amino-2-phenylbenzthiazole, m. p. 196° (corr.), and its *acetyl* derivative, m. p. 203° (corr.). Finally, 6-aminophenylbenzthiazole gives a *benzylidene* derivative, m. p. 151° (corr.), which when fused with sulphur yields 2:2-diphenylbenzbisthiazole (cf. Green and Perkin, T., 1903, **83**, 1207). These facts establish the position of the amino- and consequently of the nitro-group. On nitration the bisthiazole yields 4-nitro-2:2-diphenylbenzbisthiazole, m. p. 262° (corr.), which on reduction gives 4-amino-2:2-diphenylbenzbisthiazole, m. p. 285—287° (corr.), giving an *acetyl* derivative, m. p. 250—253° (corr.). The positions of the nitro- and amino-groups in these compounds were established by the fact that, on fusion with potassium hydroxide, the amine did not give any aminobenzoic acid.

6-Amino-2-phenylbenzthiazole on methylation under pressure with methyl alcohol and hydrochloric acid gives 6-*dimethylamino*-2-phenylbenzthiazole, m. p. 185° (corr.), but no 'quaternary salt could be obtained. On bromination 2-phenylbenzthiazole gives a *tetrabromide*, m. p. 125° (decomp.), which when boiled with dilute acetic acid loses bromine and hydrogen bromide, yielding 6-*bromo*-2-phenylbenzthiazole, m. p. 152° (corr.), which was also obtained by the Sandmeyer reaction from 6-amino-2-phenylbenzthiazole. Similarly, by the Sandmeyer reaction 6-*cyano*-2-phenylbenzthiazole was prepared and this, on hydrolysis, yields 2-phenylbenzthiazole-6-*carboxylic acid*, m. p. 261—263° (corr. decomp.), giving a *methyl ester*, m. p. 153—154° (corr.). With iodine in acetic acid 2-phenylbenzthiazole gives a very unstable *di-iodide*, m. p. 84.5° (corr.). With acetyl chloride 2-phenylbenzthiazole gives an additive *compound*, which readily loses acetyl chloride again on warming or on shaking with water.

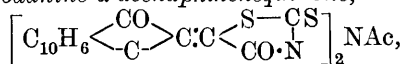
The 6-carboxylic acid mentioned above is structurally analogous to cinchophen (α -phenylcinchoninic acid), and it is hoped that it may show useful therapeutic properties.

W. G.

Rhodanine. II. CH. GRÄNACHER, H. REIS, and E. POOL (*Helv. Chim. Acta*, 1922, **5**, 382—391).—The red dye resulting from the oxidation of rhodanine by means of ferric chloride (A., 1920,

i, 252) is of the indigoid type. Thus the product obtained from *N*-phenylrhodanine was purified by conversion into a soluble reduction product by means of sodium hyposulphite, followed by oxidation with air. Analytical data, but no formula, are supplied for the magenta-like powder, with a green reflex, so prepared. It, and the following condensation products of rhodanines with α -diketones, are very easily converted by alkali into compounds only slightly coloured. *N*-Phenylrhodanine- α -acenaphthenequinone, $\text{PhN} \cdot \text{CO} \begin{array}{c} \diagup \\ \text{CS} \cdot \text{S} \end{array} > \text{C} : \text{C} < \begin{array}{c} \text{CO} \\ \diagdown \\ \text{C}_{10}\text{H}_6 \end{array}$, needles, yields a dinitro-

derivative, $\text{C}_{21}\text{H}_9\text{O}_2\text{NS}_2(\text{NO}_2)_2$, m. p. 342° (decomp.). Rhodanine- α -acenaphthenequinone, $\text{C}_{15}\text{H}_7\text{O}_2\text{NS}_2$, forms red needles. Imidoacetyldi-N : N-rhodanine- α -acenaphthenequinone,



forms scarlet leaflets. Iminodi-N : N-rhodanine- α -acenaphthenequinone, $\left[\text{C}_{10}\text{H}_6 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{C} \end{array} > \text{C} : \text{C} < \begin{array}{c} \text{S}-\text{CS} \\ \diagdown \text{CO} \cdot \text{N} \end{array} \right]_2 \text{NH}$, crystallises in dark red needles.

α -Oximino-N-phenylrhodanine, $\text{C}_9\text{H}_6\text{O}_2\text{N}_2\text{S}_2$, forms golden-yellow needles, m. p. 181° ; its silver salt exists in two forms, respectively yellowish-brown and reddish-orange; ethyl ether, $\text{C}_{11}\text{H}_{10}\text{O}_2\text{N}_2\text{S}_2$, is yellowish-orange, m. p. 130° . α -Nitro-N-phenylrhodanine,

$\text{PhN} \cdot \text{CO} \begin{array}{c} \diagup \\ \text{CS} \cdot \text{S} \end{array} > \text{CH} \cdot \text{NO}_2$, from the preceding oximino-compound and nitric acid, forms light yellow needles, m. p. 207° (decomp.).

α -Oximinorhodanine, $\text{NH} \cdot \text{CO} \begin{array}{c} \diagup \\ \text{CS}-\text{S} \end{array} > \text{C} : \text{NOH}$, forms yellow needles, m. p.

$151-153^\circ$; the silver salt exists in two forms. Reduction of the oximino-compound with zinc dust and acetic acid would seem to yield a rhodanine-purpuric acid (cf. Knorr, *Annalen*, 1887, **238**,

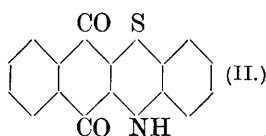
192). α -Oximino-N-phenylthiohydantoin, $\text{PhN} \cdot \text{CO} \begin{array}{c} \diagup \\ \text{HN} : \text{C}-\text{S} \end{array} > \text{C} : \text{NOH}$, forms yellow needles, m. p. $199-200^\circ$. J. K.

Linear Benzonaphthaparathiazine [$\beta\beta$ -Naphthaphenthiazine]. K. FRIES and F. KERKOW (1922, **427**, 281—302;

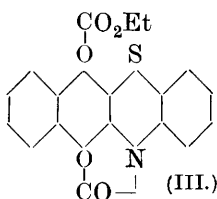
cf. Kehrman and Christopoulos, A., 1921, i, 449; Ludwig-Semelić, 1921, i, 448, 689). —This (I) is the only one of the three possible naphthaphenthiazines which has not previously been prepared. Its preparation is now described and general methods

for obtaining its substitution products are indicated.

3-Chloro-2-anilino-1 : 4-naphthaquinone (prepared from 2 : 3-dichloronaphthaquinone and aniline) reacts with sodium sulphide, giving 2-anilino-3-mercapto-1 : 4-naphthaquinone, which is characterised by an S-methyl derivative, m. p. 143° . The mercaptan undergoes oxidation when air is led through a boiling alcoholic



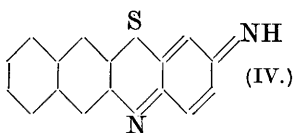
solution, and gives $\beta\beta$ -*naphthaphenthiazine-6:11-quinone* (II), which forms steel-blue crystals, m. p. 308°. On further oxidation by means of hydrogen peroxide, this substance yields a *sulphoxide*, an amphoteric substance melting above 360°, and a *sulphone*, an orange-red, acidic compound, which also melts above 360°. 12-*Methyl- $\beta\beta$ -naphthaphenthiazine-6:11-quinone*, reddish-blue needles, m. p. 197°, is prepared by directly methylating the thiazine (II) with methyl sulphate in the presence of magnesium oxide. Halogen derivatives of the thiazine containing the halogen atom in the 3-position are prepared by isomeric change of the halogen salts of the sulphoxide. 3-*Chloro- $\beta\beta$ -naphthaphenthiazine-6:11-quinone* forms small, stout, blue needles, m. p. 303°, and 3-*bromo- $\beta\beta$ -naphthaphenthiazine-6:11-quinone*, steel-blue needles, m. p. 309°. 6:11-*Dihydroxy- $\beta\beta$ -naphthaphenthiazine*, small, colourless crystals,



m. p. 192° (*diacetyl* derivative, m. p. 258°; *dimethyl ether*, m. p. 134°), is obtained by reducing the quinone with stannous chloride and acetic acid or with alkaline hyposulphite; atmospheric oxidation reconverts it into the quinone. The action of ethyl chloroformate on the sodium salt of the quinol gives rise to the 11:12-*lactam* of *ethyl $\beta\beta$ -naphthaphenthiazine-6:11-dicarboxylate* (III), which forms greenish-yellow needles, m. p. 203° (decomp.). Complete reduction of the quinone with stannous chloride yields $\beta\beta$ -*naphthaphenthiazine*, yellow needles, m. p. 277°.

A corresponding series of compounds containing an amino- or acetylamino-group in position 3 is described; these substances are obtained by a similar series of reactions starting from 2:3-dichloronaphthaquinone and *p*-phenylenediamine (or monoacetyl-*p*-phenylenediamine) instead of from 2:3-dichloronaphthaquinone and aniline. 3-*Chloro-2-p-aminoanilino-1:4-naphthaquinone* forms bluish-violet crystals, m. p. above 360°. 3-*Chloro-2-p-acetylaminoanilino-1:4-naphthaquinone* forms small, purplish-red crystals, m. p. 271° (decomp.). 2-*p-Acetylamino-3-mercapto-1:4-naphthaquinone* gives a *S-methyl ether*, m. p. 243°. 3-*Acetylamino- $\beta\beta$ -naphthaphenthiazine-6:11-quinone* forms green needles which decompose above 290° (*sulphoxide*, m. p. 330°, decomp., *sulphone*, m. p. above 360°). 3-*Amino- $\beta\beta$ -naphthaphenthiazine-3:10-quinone* sinters at 240°, m. p. 290° (decomp.). 3-*Acetylamino-6:11-dihydroxy- $\beta\beta$ -naphthaphenthiazine* is characterised by its green hydrochloride, and by acetylation to 3-*acetylamino-6:11-diacetoxy- $\beta\beta$ -naphthaphenthiazine*, m. p. 257° (decomp.). 3-*Amino- $\beta\beta$ -naphthaphenthiazine* is a yellow powder, m. p. 280° (decomp.) [*hydrochloride* is pale olive-green; the *acetyl* derivative forms greenish-yellow crystals, m. p. 285° (decomp.)].

When a current of air is passed through a boiling solution of 3-amino- $\beta\beta$ -naphthaphenthiazine oxidation occurs and the 3-



imino-compound (IV) is precipitated. It forms small, dark blue crystals, m. p. 290° (decomp.), and on warming with alkaline hyposulphite passes back into the aminothiazine. C. K. I.

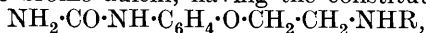
Preparation of Intermediate Products and Colouring Matters. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Fr. Pat. 521281; from *Chem. Zentr.*, 1921, iv, 1271—1272).—Monoacyl derivatives are prepared from diaminodiarylsulphones, obtained from *m*-phenylenediamine, by treatment with acylating agents. *Monoacetyl-2:5-diaminophenyl-1-p-tolylsulphone* is obtained from 2:5-diaminophenyl-*p*-tolylsulphone (D.R.-P. 282214) and acetic anhydride, ethyl acetate, or acetic acid; it forms crystals, m. p. 182—183°. Other derivatives are prepared similarly. *Mono-benzoyl-2:5-diaminophenyl-p-tolylsulphone* has m. p. 186°. *Monophthaloyl-2:5-diaminophenyl-p-tolylsulphone* is transformed by recrystallisation from acetic acid into the *anil*, m. p. 232°. *Monoacetyl-2:5-diaminophenyl-p-chlorophenylsulphone* has m.p. 198—199°. *Monophthaloyl-2:5-diaminophenyl-p-chlorophenylsulphone* gives an *anil*, m. p. 233°. *Monoacetyl-1:4-naphthylenediamine-2-p-toluene-6(7)-sulphonic acid* gives a colourless sodium salt. Colouring matters are obtained from their diazo-compounds and 2-naphthylamine or its derivatives, such as 2-amino-3-hydroxynaphthalene-6-sulphonic acid, 2-naphthylamine-6-sulphonic acid, etc.

G. W. R.

Preparation of Ethers of *p*-Hydroxyphenylcarbamide. J. D. RIEDEL, AKT.-GES. (D.R.-P. 339101; from *Chem. Zentr.*, 1921, iv, 1324).—The carbamides of *p*-aminophenol are converted into hydroxyalkyl ethers by the usual methods for the preparation of phenolic ethers. For example, *p-hydroxyphenyl-hydroxyethylcarbamide* is prepared from *p*-hydroxyphenylcarbamide, ethylene chlorohydrin, and sodium methoxide solution at 100°; *p-hydroxyphenyldihydroxyethylcarbamide* (spherical aggregates, m. p. 155—156°), from *p*-hydroxyphenylcarbamide, glycerol- α -monochlorohydrin, and sodium methoxide solution at 100—110°.

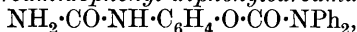
G. W. R.

Changes in the Sweetness of Dulcin (*p*-Phenetolecarbamide) caused by Chemical Alterations of the Molecule and the Sweetening Power of Derivatives of *p*-Hydroxyphenylcarbamide. CARL SPECKAN (*Ber. deut. pharm. Ges.*, 1922, 32, 83—107).—Replacement or substitution of the ethyl group of *p*-phenetolecarbamide led to the complete suppression of the sweet taste of this substance in every case investigated with the exception of β -bromo-*p*-phenetolecarbamide, which was also very sweet, and benzoyl-*p*-hydroxyphenylcarbamide which had a faintly sweet after-taste. Aromatic amino-derivatives prepared from the above bromo-dulcin, having the constitution



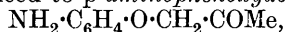
were quite tasteless, whilst the complete replacement of the ethyl

group by such groups as $-\text{CO}_2\text{Et}$, $-\text{CO}\cdot\text{NPh}_2$, etc., as also replacement of the end methyl group by acetyl or phenyl, likewise gave substances in which the sweet taste of dulcin was entirely suppressed. The preparation of the following substances is described. β -Bromo-*p*-phenetolecarbamide, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Br}$, from *p*-hydroxyphenylcarbamide and ethylene dibromide, white needles, m. p. 162—164°. Ethylene dicarbamidophenyl ether, $\text{C}_2\text{H}_4(\text{O}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CONH}_2)_2$, a by-product of the above preparation, forms pale red needles, m. p. 342°. β -Anilino-*p*-phenetolecarbamide, from the β -bromo-derivative and aniline, forms fine, white needles, m. p. 230°. β -*p*-Phenetidino-*p*-phenetolecarbamide, has m. p. 215°. β -*p*-Toluidino-*p*-phenetolecarbamide, has m. p. 180°. β -*o*-Toluidino-*p*-phenetolecarbamide, has m. p. 228—230°. β -*m*-Toluidino-*p*-phenetolecarbamide, has m. p. 215°. β -*m*-Xylidino-*p*-phenetolecarbamide, has m. p. 255°. *p*-Carbamidophenyl ethyl carbonate, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CO}\cdot\text{OEt}$, from *p*-hydroxyphenylcarbamide, sodium ethoxide and ethyl chloroformate, forms white needles, m. p. 158°. *p*-Carbamidophenyl diphenylcarbamate,

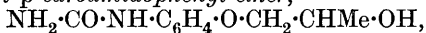


forms white crystals, m. p. 240°. Ethyl α -*p*-carbamidophenoxybutyrate, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CHEt}\cdot\text{CO}_2\text{Et}$, from *p*-hydroxyphenylcarbamide and ethyl α -bromobutyrate in presence of potassium hydrogen carbonate, forms white crystals, m. p. 90°. *p*-Carbamidophenylglycide ether, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2 \\ \diagup \\ \text{O} \end{smallmatrix}$, from

p-hydroxyphenylcarbamide and epichlorohydrin in presence of sodium ethoxide, has m. p. 235°. Benzoyl-*p*-hydroxyphenylcarbamide and benzoyl-*p*-hydroxyphenylbenzoylcarbamide were both obtained by the action of benzoyl chloride on hydroxyphenylcarbamide, and have m. p. 148° and 226—228°, respectively. *p*-Carbamidophenoxyacetophenone, formed by the action of ω -bromoacetophenone on hydroxyphenylcarbamide and sodium ethoxide, has m. p. 140°. *p*-Nitrophenoxyacetone, prepared by the action of chloroacetone on *p*-nitrophenol in presence of sodium amyloxide, has m. p. 82°, and gives a semicarbazone, m. p. 225°, a phenylhydrazone, m. p. 155°, and an oxime, m. p. 105°. On catalytic hydrogenation, it was reduced to *p*-aminophenoxyacetone,



white leaflets, m. p. 236°, and this, on treatment with hydrochloric acid and potassium cyanate, gave *p*-carbamidophenoxyacetone, m. p. 172°, yielding a semicarbazone, m. p. 190°, and a phenylhydrazone, m. p. 145°, and on reduction the corresponding secondary alcohol, *p*-hydroxypropyl *p*-carbamidophenyl ether,



which forms colourless crystals, m. p. 176°, having a faintly sweet after-taste.

G. F. M.

Constitution of Picrorocellin, a Diketopiperazine Derivative from *Rocella fuciformis*. MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE (T., 1922, 121, 816—827).

New Syntheses of Pyrimidines. E. CHERBULIEZ and K. N. STAVRITCH (*Helv. Chim. Acta*, 1922, 5, 267—284).—5-Bromo-6-hydroxypyrimidine-4-carboxylic acid, $\text{NH} \begin{smallmatrix} \text{CO} \cdot \text{CBr} \\ \text{CH} = \text{N} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{H}$, needles, m. p. 206—207°, with evolution of carbon dioxide (copper salt, $[\text{C}_5\text{H}_2\text{O}_3\text{N}_2\text{Br}]_2\text{Cu} \cdot 2\text{H}_2\text{O}$; ethyl ester, $\text{C}_7\text{H}_7\text{O}_3\text{N}_2\text{Br}$, needles, m. p. 155—156°) results from the action of sodium hypobromite on methyleneasparagine. 5-Bromo-6-hydroxypyrimidine, $\text{C}_4\text{H}_3\text{ON}_2\text{Br}$, m. p. 197° (picrate, $\text{C}_{10}\text{H}_6\text{O}_8\text{N}_5\text{Br}$, yellow prisms, m. p. 150—151°; hydrochloride, m. p. 206—207°), obtained by fusion of the carboxylic acid, is converted by the action of phosphoryl chloride into 6-chloro-5-bromopyrimidine, $\text{C}_4\text{H}_2\text{N}_2\text{ClBr}$, b. p. 95·5°/26 mm. (picrate, sparingly soluble in ether), and by reduction with zinc dust into 6-hydroxypyrimidine (Wheeler, A., 1907, i, 879). The last compound also results from the distillation of 6-hydroxypyrimidine-4-carboxylic acid, $\text{C}_5\text{H}_4\text{O}_3\text{N}_2 \cdot \text{H}_2\text{O}$, prisms, m. p. 268—270° (decomp.), which is itself prepared either by oxidation of methyleneasparagine with alkaline permanganate, or from the above bromo-acid and zinc dust.

Similar series of compounds may be prepared from the alkylidene- and arylidene-asparagines, and the reactions have a special interest in view of the natural occurrence of asparagine and of pyrimidine derivatives.

Ethylideneasparagine, $\text{C}_6\text{H}_{10}\text{O}_3\text{N}_2 \cdot \text{H}_2\text{O}$, needles, m. p. 230—231°, must be prepared by condensation of acetaldehyde with sodium asparaginate. 5-Bromo-6-hydroxy-2-methylpyrimidine-4-carboxylic acid, $\text{C}_6\text{H}_5\text{O}_3\text{N}_2\text{Br}$, prisms, m. p. 209—210° (decomp.), copper salt, $(\text{C}_6\text{H}_4\text{O}_3\text{N}_2\text{Br})_2\text{Cu} \cdot 2\text{H}_2\text{O}$. 5-Bromo-6-hydroxy-2-methylpyrimidine, $\text{C}_5\text{H}_5\text{ON}_2\text{Br}$, prisms, m. p. 231—232° (hydrochloride, m. p. 229—230°; acetate, m. p. 234°; picrate, $\text{C}_{11}\text{H}_8\text{O}_8\text{N}_5\text{Br}$, m. p. 163—164°; silver salt soluble in hot water; copper salt, a green, flocculent precipitate). 6-Chloro-5-bromo-2-methylpyrimidine, $\text{C}_5\text{H}_4\text{N}_2\text{ClBr}$, b. p. 107·5°/27 mm. 6-Hydroxy-2-methylpyrimidine-4-carboxylic acid, $\text{C}_6\text{H}_6\text{O}_3\text{N}_2 \cdot 2\text{H}_2\text{O}$, m. p. 261° (decomp.), basic copper salt, $\text{C}_6\text{H}_5\text{O}_3\text{N}_2 \cdot \text{CuOH}$. 6-Hydroxy-2-methylpyrimidine, $\text{C}_5\text{H}_6\text{ON}_2$. 5-Bromo-6-hydroxy-2-phenylpyrimidine-4-carboxylic acid, $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2\text{Br}$, needles, m. p. 250—252°. 5-Bromo-6-hydroxy-2-phenylpyrimidine, $\text{C}_{10}\text{H}_7\text{ON}_2\text{Br}$, prisms, m. p. 252°; 6-chloro-5-bromo-2-phenylpyrimidine, $\text{C}_{10}\text{H}_6\text{N}_2\text{ClBr}$, b. p. 193·5°/24 mm., m. p. 130—131°; 2-phenylpyrimidine, $\text{C}_{10}\text{H}_8\text{N}_2$, b. p. 157·5°/25 mm., m. p. 128° (picrate, $\text{C}_{16}\text{H}_{11}\text{O}_7\text{N}_5$, m. p. 108°). 6-Hydroxy-2-phenylpyrimidine-4-carboxylic acid, $\text{C}_{11}\text{H}_8\text{O}_3\text{N}_2$, m. p. 247° (decomp.), copper salt, $(\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2)_2\text{Cu} \cdot 2\text{H}_2\text{O}$, ethyl ester, $\text{C}_{13}\text{H}_{12}\text{O}_3\text{N}_2$, needles, m. p. 84—85°; 5-bromo-6-hydroxy-2-phenylpyrimidine-4-carboxylic acid, $\text{C}_{11}\text{H}_7\text{O}_3\text{N}_2\text{Br}$, m. p. 252°, from the preceding compound and sodium hypobromite, decomposes on fusion into 5-bromo-6-hydroxy-2-phenylpyrimidine; 6-hydroxy-2-phenylpyrimidine (Pinner, A., 1890, 69; Ruhemann and Hemmy, A., 1897, i, 488) yields a picrate, $\text{C}_{16}\text{H}_{11}\text{O}_8\text{N}_5$, yellow needles, m. p. 151°.

J. K.

Preparation of a New Diethylbarbituric Acid Compound.

CHEMISCHE FABRIK AUF AKTIEN VORM. E. SCHERING (Brit. Pat. 158558).—A new compound of diethylbarbituric acid and 4-dimethylamino-1-phenyl-2:3-dimethyl-5-pyrazolone is obtained by melting the two substances together in the proportion of 1 mol. of the former to 2 mols. of the latter, and purifying the product in the usual manner. The new compound is yellow in colour, melts at 95—97°, and has strong analgesic properties, whilst the hypnotic effect is repressed.

G. F. M.

The Nature of Isatoids. GUSTAV HELLER and WALTER BENADE (*Ber.*, 1922, **55**, [B], 1006—1014; cf. Heller, A., 1920, i, 766; 1921, i, 891; Hantzsch, A., 1921, i, 597).—The existence of the alkylisatoids of von Baeyer and Oekonomides has been confirmed by Heller but denied by Hantzsch; their preparation and behaviour has again been examined in detail.

Methylisatoid is obtained when isatin silver is subjected to the action of methyl iodide in the presence of benzene at 100° and the filtrate, after removal of re-formed isatin and silver iodide, is allowed to evaporate spontaneously while exposed to light. The residue is recrystallised from glacial acetic acid and yields thereby β -methylisatoid. The latter passes into the α -form when recrystallised rapidly from benzene, but appears to undergo further change on protracted heating with this solvent. The α - is converted into the β -variety by recrystallisation from glacial acetic acid. Ethylisatoid, prepared in a similar manner, forms red rhombohedra, m. p. 218—219° (decomp.) after darkening at 211—212°. Contrary to the statement of Hantzsch, the melting points of the methyl and ethyl compounds are quite distinct from one another. Curiously, a mixture of equal amounts of the two substances has a slightly higher melting point. *n*-Propyl iodide and isatin silver give *n*-propylisatoid, quadratic prisms, m. p. 187° (decomp.) after darkening at 180°; attempts to convert it into a desmotropic form resulted in the production of a yellow, flocculent precipitate, m. p. about 177° (decomp.). *iso*Butyl iodide and isatin silver yield a substance, m. p. 147—148°, which by reason of the small amount available could not be further investigated.

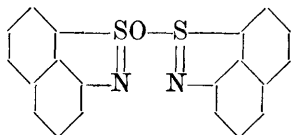
The alkyl group of the alkylisatoids can be removed by treatment with glacial acetic acid and hydrogen bromide, but, unexpectedly, the substance obtained after addition of sodium acetate to the solution is found to be *anhydroindoxyl- α -anthranilide*, $\text{CO}-\text{CH}\cdot\text{NH}$
 $\text{C}_6\text{H}_4\cdot\text{N}---\text{CO} > \text{C}_6\text{H}_4$, brownish-red plates, m. p. 217—218° (decomp.); the mechanism of the addition of the two atoms of hydrogen during the hydrolysis has not been established. The substance is smoothly oxidised by chromic acid to anhydro- α -isatinanthranilide (Friedländer and Roschdestwensky, A., 1916, i, 80). It thus appears to be established that the union of the isatin molecules in the isatoids is accomplished by means of the indole nuclei.

H. W.

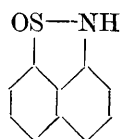
Benzbisthiazoles. STEPHEN RATHBONE HOLDEN EDGE (T., 1922, 121, 772—775).

A New Class of Vat Dyes containing Sulphur and Nitrogen.

ARNOLD REISSERT (*Ber.*, 1922, 55, [B], 858—873).—Erdmann and Süvern have observed that a clear, pale yellow solution is obtained when a salt of 8-nitronaphthalene-1-sulphinic acid dissolved in water is boiled with zinc dust and potassium sulphite; the liquid becomes colourless when acidified with dilute hydrochloric acid and subsequently deposits a blue dye when heated. The latter has now been isolated in the homogeneous condition; it has the empirical formula, $C_{20}H_{12}ON_2S_2$, and the annexed constitution is suggested for it, without, however, being established definitely. It is designated "naphthathiam-blue."



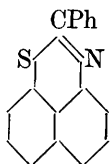
The nitration of naphthalene- α -sulphonyl chloride is carried out in accordance with the directions of Erdmann and Süvern, but an improved method of separating the 1:8- and 1:5-nitronaphthalenesulphonyl chlorides from one another is described in detail. 8-Nitronaphthalene-1-sulphinic acid forms colourless crystals which become brown when exposed to light, decomp. 110° . 5-Nitronaphthalene-1-sulphinic acid has m. p. 140° , and is considerably more stable than the 1:8-isomeride; the sodium and calcium salts are described. 8-Aminonaphthalene-1-sulphinic acid, small, pale-grey, sandy crystals, m. p. 143° (decomp.), is obtained conveniently by the action of sodium hydroxide and ferrous sulphate on the solution obtained by warming 8-nitronaphthalene-1-sulphonyl chloride with sodium sulphite and sodium hydrogen carbonate (the corresponding benzoyl derivative crystallises in colourless, lustrous needles [$+1H_2O$], m. p. $126-127^\circ$ to a dark liquid). It is readily converted into the blue dye when heated in aqueous solution or in the presence of acids. If, however, the solution is treated with so much hydrochloric acid that it just turns Congo paper blue and is allowed to remain at the atmospheric temperature for a day, the dehydration can be arrested at an intermediate stage with the production of naphthathiam (annexed formula), almost colourless needles, which become converted into the blue dye at $153-155^\circ$ [the corresponding nitroso-compound forms orange-yellow, glistening crystals, m. p. 180° (decomp.)]. The aqueous solution of naphthathiam or of 8-aminonaphthalene-1-sulphinic acid is transformed by warm hydrochloric acid into naphthathiam-blue, which in appearance and solubility exhibits a very close resemblance to indigotin. It gives dull, violet-blue shades on wool and somewhat purer tones on cotton, but has little affinity for the latter. Attempts to elucidate the constitution of the dye by oxidative degradation with nitric or chromic acid were unsuccessful, since only dark-coloured, amorphous products were obtained.



The preparation of derivatives of the dye has also been inves-

tigated in the hope of obtaining further confirmation of its structure. Thus, 8-acetylaminonaphthalene-1-sulphonyl chloride is converted by a mixture of concentrated sulphuric and nitric acids (*d* 1.52) into 4-nitro-1-acetylaminonaphthalene-5-sulphonyl chloride which, on account of its instability, was not isolated in the pure condition; the crude chloride is converted by sodium sulphite into 4-nitro-1-acetylaminonaphthalene-5-sulphinic acid, pale yellow, microscopic crystals (+H₂O), decomp. 130°, which is transformed in the manner described for the parent dye into *diaminonaphthathiam-blue*, C₂₀H₁₀ON₂S₂(NH₂)₂. A similar series of reactions when applied to naphthionic acid yielded only a trace of dye.

It is shown in the following manner that the presence of the oxygen atom in the dye is not essential to the development of tinctorial properties. 8-Aminonaphthalene-1-sulphinic acid is reduced by stannous chloride and hydrochloric acid to 8-thiol- α -naphthylamine, which is converted readily by atmospheric oxygen into 1:1'-diaminodinaphthyl 8:8'-disulphide, small, yellow needles, m. p. 118°; either of these compounds is readily oxidised by air in alcoholic alkaline solution to a blue dye which very closely resembles naphthathiam-blue; it appears to have the composition C₂₀H₁₂N₂S₂, but could not be purified satisfactorily. 8-Thiol- α -naphthylamine yields a *dibenzoyl* derivative, colourless needles, m. p. 202°, which is transformed by boiling alcoholic sodium hydroxide solution into 2-phenylperithiazine (annexed formula), golden-yellow needles, m. p. 102–103°.



Initial difficulties encountered in preparing the amino-mercaptan by the method outlined above have led the author to reduce 8-nitronaphthalene-1-sulphinic acid with hydrogen bromide and glacial acetic acid (cf. Fries and Schürmann, A., 1914, i, 676) to 8:8'-dinitrodinaphthyl 1:1'-disulphide, m. p. 214°; the sparing solubility of this compound renders the reduction of the nitro-groups in an acid medium very difficult. Attempts to convert it into the nitrothiol by means of alkali and dextrose led unexpectedly to naphthsultam, C₁₀H₆ $\begin{smallmatrix} \text{NH} \\ \text{SO}_2 \end{smallmatrix}$, in consequence of a remarkable migration of the oxygen atoms from nitrogen to sulphur.

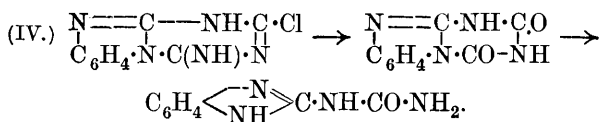
The following compounds have been incidentally prepared: 5-acetylaminonaphthalene-1-sulphinic acid, colourless crystals, incipient decomp. 145°; 4:4'-dinitro-1:1'-diacetylaminodinaphthyl 5:5'-disulphide, decomp. above 300°; 5-chloronaphthalene-1-sulphinic acid, colourless leaflets, incipient decomp. 220°; 5:5'-dichlorodinaphthyl 1:1'-disulphide, pale yellow crystals, m. p. 169–170°.

H. W.

The Quindolines. E. GRANDMOUGIN (*Compt. rend.*, 1922, 174, 1175–1177).—Indigotindianilide (cf. A., 1909, i, 968; 1910, i, 73), when warmed with mineral acids, undergoes isomerisation, giving a substance which is apparently an anilide of 5-indoquindolone. It cannot be oxidised to an isatin and on energetic hydrolysis it loses aniline, giving a new compound, C₂₂H₁₅ON₃, which gives

When boiled with hydrochloric acid, the latter gives phenylene-melanuric acid, $\text{N}=\text{C}(\text{C}_6\text{H}_4\cdot\text{N}\cdot\text{C}(\text{OH})\cdot\text{N})\text{---N}\cdot\text{C}\cdot\text{OH}$, which is also obtained by the action of nitrous acid on phenyleneammeline.

When heated with alkali hydroxide, *o*-phenyleneammetyl chloride loses ammonia and yields the phenyleneguanylcarbamide already obtained from β -cyanophenyleneguanidine and hydrochloric acid (A., 1919, i, 134). Since the same product is formed also from phenylenemelanuric acid, the latter evidently represents an intermediate stage in the reaction :



It is probable that another intermediate product is formed at a still earlier stage by replacement of the chlorine atom alone by a hydroxyl group; such a product would be a phenyleneammeline isomeric with that already described, and may possibly result from gentle hydrolysis of *o*-phenyleneammetyl chloride by means of sodium carbonate, this hydrolysis giving a chlorine-free compound which contains the expected proportion of nitrogen but is amorphous and difficult to purify.

The phenyleneguanylcarbamide obtained by hydrolysis of β -cyanophenyleneguanidine by means of hydrochloric acid (*loc. cit.*) crystallises from water in anhydrous, lustrous scales which undergo no change in contact with the water; that obtained according to scheme (IV) and formed in an alkaline medium from which it is precipitated by either acetic or carbonic acid, crystallises from water in long, lustrous, anhydrous needles, but the latter become opaque and take up 2 mols. of water if left in contact with the solvent. A hot aqueous solution of the hydrated crystals deposits the long, lustrous crystals on cooling. These two forms, which behave alike in other respects, are regarded as desmotropic forms of the structures $\text{C}_6\text{H}_4\langle\text{N}\rangle\text{C}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ and

$\text{C}_6\text{H}_4\langle\text{N}\rangle\text{C}\cdot\text{NH}\cdot\text{C}(\text{OH})\cdot\text{NH}$, the former probably representing the scales obtained in an acid medium and the latter the needles separating in alkaline solution.

o-Phenyleneammetyl chloride, $\text{C}_9\text{H}_6\text{N}_5\text{Cl}$, separates in microscopic crystals, does not melt but turns yellow at about 220° , and possesses slight acidic and basic functions.

o-Phenylenemelanuric acid, $\text{C}_9\text{H}_6\text{O}_2\text{N}_4$, crystallises in small needles and decomposes, without melting, at 300° . This compound also appears to exist in two desmotropic forms. T. H. P.

Catalytic Preparation of Azobenzene and Aniline. C. O. HENKE and O. W. BROWN (*J. Physical Chem.*, 1922, 26, 324—348; cf. this vol., i, 445, 535).—The action of lead and bismuth as

catalysts on the reduction of nitrobenzene by hydrogen has been investigated with catalysts of various origins and at various temperatures. In the presence of lead as catalyst, nitrobenzene is reduced by hydrogen to azoxybenzene, azobenzene, and aniline. It is shown that lead prepared by reducing yellow litharge is the best catalyst for the production of azobenzene, and that the action is best carried out in an iron tube at 290° . The best catalyst for aniline in an iron tube is lead prepared by the reduction of red lead from white lead. In this case, the efficiency is greatest above 308° . A catalyst when used in a glass tube gives a higher yield of azobenzene and a lower yield of aniline than when used in an iron tube, but the activity of the catalyst decreases much more rapidly in glass than in iron. In a glass tube, the catalyst from white lead is best for producing aniline, and the one from red lead made from white lead is best for producing azobenzene. The addition of sodium hydroxide and magnesia to the lead catalyst in an iron tube does not increase its activity and a larger amount of sodium hydroxide decreases it. The addition of 0.5% of ferric oxide to a lead catalyst from a heavy litharge increases the yield of both azobenzene and aniline, whilst 5% of ferric oxide increased the yield of aniline at the expense of the azobenzene. The addition of 5% of cupric oxide to the same catalyst was detrimental to its activity. Within the limits of the present experiments, it is found that the more finely divided the red lead from which the catalyst is prepared the more active the catalyst. The best yield of azobenzene was obtained when lead from yellow litharge was heated in an iron tube at 290° and nitrobenzene passed over at the rate of 4 grams per hour and hydrogen at the rate of 17 litres per hour. In this case the material yield was 55.4% of azobenzene and 26.0% of aniline. Using sublimed litharge to produce the catalyst the yield is 61.1% of aniline and 34.4% of azobenzene at 310° , whilst when lead from white lead is used at 303° , the yield is 74.9% of aniline and 21.0% of azobenzene, all other conditions being the same as stated above.

Nitrobenzene is reduced to azoxybenzene, azobenzene, hydrazobenzene, and aniline by hydrogen with bismuth as catalyst. Using equal volumes of catalyst, that prepared from heavy bismuth oxide is more active than one prepared from the light oxide. The activity of the bismuth does not decrease so rapidly when used in an iron tube as when used in a glass tube. A good temperature to use the bismuth catalyst is between 280° and 300° . When the tube is fed with nitrobenzene at the rate of 4.2 grams per hour and hydrogen at 17 litres per hour the following optimum yields are obtained: with bismuth from the heavy oxide in an iron tube at 230° , a yield of 92% of azobenzene and 4.4% of aniline, whilst under the same conditions at 300° the yield is 73.9% of aniline and 19.3% of azobenzene.

J. F. S.

Facts and Theories in the Constitution of the Hydroxyazo-compounds. E. PUXEDDU and MARCELLA GENNARI (*Gazzetta*, 1922, 52, i, 216—229).—The authors discuss more particularly

the literature dealing with the reduction of the hydroxyazo-compounds and their acyl derivatives, the action of phenyl cyanate on hydroxyazo-compounds, the action of carbon disulphide at a high temperature on *o*-hydroxyazo-compounds, preparation of *m*-hydroxyazobenzene and its signification, isomerisation of the quinonic compounds, and physico-chemical investigations on the hydroxyazo-compounds.

All the results obtained support the view that the hydroxyazo-compounds of the ortho-series are to be differentiated from those of the meta- and para-series. The insolubility of most of the *o*-hydroxyazo-compounds in the calculated proportion or even in considerable excess of alkali hydroxide presents a serious objection to the classification of these compounds as phenolic; that some do dissolve is merely an indication of the instability of the quinonoid structure and of its tendency to become azophenolic.

The behaviour of the acyl derivatives during reduction furnishes a certain proof of the azophenolic constitution of the para- and the hydrazone constitution of the ortho-compounds, notwithstanding the fact that it has been shown that in an aromatic nucleus acyl groups in the ortho-position to a chain containing aminic or iminic hydrogen may pass from the oxygen to the nitrogen during reduction. Such migration during the reduction of acyl-*o*-hydroxyazo-compounds would demonstrate undoubtedly their azophenolic structure, but no such proof exists, and the behaviour of acetyl-*p*-chlorobenzeneazo-*p*-cresol is an exception to the general rule expressing the difference in behaviour of the ortho-compounds from their meta- and para-isomerides. On the other hand, assumption of azophenolic constitutions for *o*-hydroxyazo-compounds on the basis of migration of the acyl group would necessitate the hypothesis that the acyl exchanges position, not with the hydrogen immediately adjacent to it, but with the second hydrogen of the hydrazo-group.

The proofs advanced of the instability of the quinonoid nuclei in the acyl derivatives of *o*-hydroxyazo-compounds require a greater abundance and more uniformity of experimental results before the latter may be regarded as justifying the azophenolic constitution of these ortho-compounds.

The behaviour towards phenylcarbimide scarcely differentiates clearly between the ortho- and para-compounds since the former react, after some weeks, in the same way as the latter, but it shows that the carbimide exerts a double action on ortho-compounds, first converting them into azophenolic compounds and then combining with these.

The conclusions drawn are that both free hydroxyazo-compounds and their acyl derivatives behave as tautomeric substances; that free *p*- and *m*-hydroxyazo-compounds and their acyl derivatives are always phenolic in type; that *o*-hydroxyazo-compounds, both in the free condition and as acyl derivatives, must be regarded as of quinono-hydrazone configuration, with a pronounced tendency to pass into the more stable azophenolic form; and that the meso-hydric formula of Oddo and Puxeddu (A., 1906, i, 991; 1907, ii, 15),

giving a representation of the phenomenon of desmotropy, provides a very simple scheme applicable to all analogous phenomena.

T. H. P.

Degree of Hydrolysis of Alkali Salts of Hydroxyazo-compounds. E. PUXEDDU (*Gazzetta*, 1922, **52**, i, 235—238; cf. A., 1921, i, 366, 623).—The ordinary methods of determining the degree of hydrolysis are inapplicable to the alkali salts of the hydroxyazo-compounds, since the results are affected by the presence of the sparingly soluble free hydroxyazo-compound, which separates as the hydrolysis proceeds.

The author has carried out conductivity measurements on alkaline solutions of sodium and potassium derivatives of various *p*-hydroxyazo-compounds after different intervals of time, vessels filled with the solutions being kept tightly closed in the dark at constant temperature. It is found that the conductivity of such a solution varies markedly with the time, the equilibrium $\text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{ONa} + \text{H}_2\text{O} \rightleftharpoons \text{NPh}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{OH} + \text{NaOH}$ undergoing displacement owing to the separation of increasing proportions of the free hydroxyazo-compound.

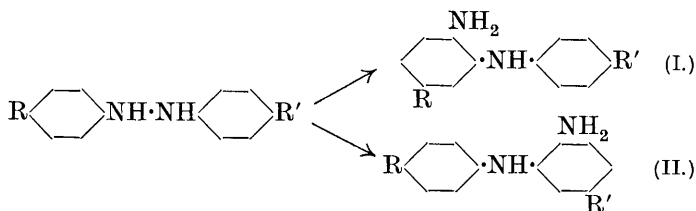
The degree of hydrolysis may, however, be determined by extracting the hydrolysed compound by means of ether. The hydroxyazo-compound is dissolved in the required quantity of sodium hydroxide solution of known titre and the solution made up to a definite dilution and immediately shaken energetically for a few seconds with ether; the ethereal layer is separated, washed and dried with sodium sulphate, and evaporated in a platinum dish, the residue being weighed. This method gives concordant results, provided that the extraction with ether is carried out with the necessary rapidity; it is applicable also when the product of the hydrolysis remains completely dissolved in the aqueous solution, provided that the alkali salt is insoluble, and the above product readily soluble, in ether. The sodium derivatives of benzeneazo-*p*-phenol, *o*-tolueneazophenol, and benzeneazo-*o*-cresol have been examined in this way.

T. H. P.

The Isomeric Changes of Hydrazo-compounds. PAUL JACOBSEN (*Annalen*, 1922, **427**, 142—221).—The paper is in four parts.

(A) *Isomeric Changes of Doubly Para-substituted Hydrazo-compounds* [with D. R. BOYD, M. FREUND, H. L. FULDA, F. HEUBACH, H. JOST, G. LOCKEMANN, A. LOEB, J. PELZER, W. SACHS, H. TIGGES, and K. ZAAR].—Hydrazo-compounds of this class cannot pass into *p*-semidines without loss of one of the para-substituents, but they are capable of yielding *o*-semidines if the necessary ortho-positions are free. In seven out of the eight cases investigated an *o*-semidine was isolated and identified; in the eighth it was detected by qualitative reactions.

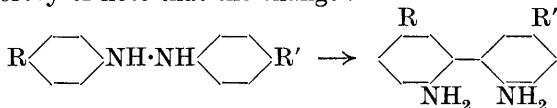
When the groups in the two para-positions are different, the formation of an *o*-semidine can take place in two ways:



so that the relative directing powers of the groups R and R' can be determined. If the semidine I were the main product, the conclusion would be that the group R had a greater directing power than R'. It is remarkable that in none of the cases examined was more than one *o*-semidine isolated, but this does not by any means prove that these conversions take place only in one direction, because a secondary product would be quite likely to escape detection. The groups R and R' were of the following: Br, I, OEt, OAc, NMe₂, Me. An examination of the data shows that of all these the ethoxyl group has the strongest directing power, the methyl group being next in order.

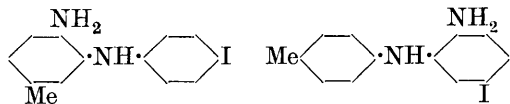
Hydrazo-compounds in which one of the para-substituents was an acetoxyl group gave *p*-semidines, the acetoxyl group being eliminated.

It is worthy of note that the change :



was not realised, and it is to be presumed that there is a strong resistance to the formation of this grouping by the isomeric change of hydrazo-compounds of the benzene series (see below).

(i) *Isomerisation of 4'-Iodo-4-methylhydrazobenzene*.—The *o*-semidine obtained from this substance has the first of the following formulæ :



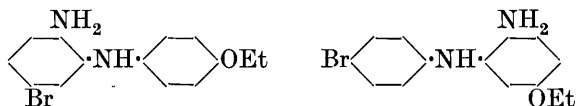
The isomeric substance was synthesised by condensing 4-iodo-1:2-dinitrobenzene with *p*-toluidine and reducing the product.

4'-Iodo-4-methylazobenzene is obtained as golden-red leaflets, m. p. 165—166°, when 4'-amino-4-methylazobenzene is diazotised and treated with potassium iodide. On reduction by means of ammonium sulphide it gives *4'-iodo-4-methylhydrazobenzene*, colourless needles, m. p. 134°, whilst with alcoholic stannous chloride it yields, besides *p*-iodoaniline and *p*-toluidine, *4'-iodo-2-amino-5-methyldiphenylamine*, m. p. 116—117°, which gives the usual reactions of an *o*-semidine with nitrous acid, with benzil (the *stilbazonium* base forms yellowish-green, microscopic needles, m. p. 166—168°), with salicylaldehyde (the *anhydro*-derivative

forms yellow needles, m. p. 132—134°) and with carbon disulphide. The product of the last reaction, 2-mercapto-1-*p*-iodophenyl-6-methylbenziminazole, forms fine, colourless needles, m. p. 284—285°, yields a mercury salt on treatment with mercuric oxide, and a *S*-methyl ether, m. p. 139—140°, with methyl iodide. 5-Iodo-2-nitro-4'-methylidiphenylamine forms red needles, m. p. 104°. 5-Iodo-2-amino-4'-methylidiphenylamine, forms colourless leaflets, m. p. 86—87°; its anhydro-base with salicylaldehyde forms yellow needles, m. p. 148°.

(ii) *Isomerisation of 4'-Ethoxy-4-methylhydrazobenzene*.—The conversion of this substance into an *o*-semidine has previously been described (A., 1896, i, 24). The semidine is now further characterised by its anhydro-base with salicylaldehyde, m. p. 121—124°, and its constitution proved by synthesis from the condensation product of *p*-toluidine with 4-chloro-1:2-dinitrobenzene. This substance on treatment with sodium ethoxide yields 2-nitro-5-ethoxy-4'-methylidiphenylamine, bright brown needles, m. p. 104°; this, on reduction by means of ammonium sulphide at 130°, gives 2-amino-5-ethoxy-4-methylidiphenylamine, identical with the substance obtained from the hydrazobenzene.

(iii) *Isomerisation of 4-Bromo-4'-ethoxyhydrazobenzene*.—This substance could yield the following semidines :

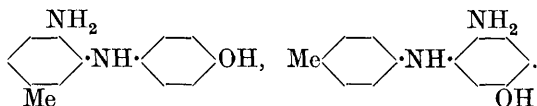


The substance actually isolated was different from the first of these compounds, which was synthesised from 4-bromo-1:2-dinitrobenzene and *p*-phenetidine in the manner previously illustrated.

4-Bromo-4'-ethoxyazobenzene, yellow leaflets, m. p. 135—136°, is formed by ethylating *p*-bromobenzeneazophenol. 4-Bromo-4'-ethoxyhydrazobenzene, which is obtained in good yield by reduction of the azo-compound with zinc dust and alcoholic sodium hydroxide, crystallises in small, colourless needles, m. p. 81—83°. 4'-Bromo-2-amino-5-ethoxydiphenylamine (the semidine obtained from the hydrazo-compound) forms colourless needles, m. p. 67—68°; it gives the nitrous acid reaction and forms a stilbazonium base ($C_{14}H_{15}ON_2Br$) with benzil. On treatment with amyl nitrite, it gives 1-*p*-bromophenyl-6-ethoxybenzotriazole, leaflets, m. p. 145—146°, and with formic acid, 1-*p*-bromophenyl-6-ethoxybenziminazole, needles, m. p. 120°, which on hydrolysis with acids yields 1-*p*-bromophenyl-6-hydroxybenziminazole, pale violet needles, m. p. 295°. With carbon disulphide, the semidine yields 1-*p*-bromophenyl-2-mercapto-6-ethoxybenziminazole, needles, m. p. 255°, and with salicylaldehyde an anhydro-base ($C_{21}H_{19}O_2N_2Br$), m. p. 151°. 5-Bromo-2-nitro-4'-ethoxydiphenylamine, obtained by condensing 4-bromo-1:2-dinitrobenzene with *p*-phenetidine, forms deep red needles, m. p. 115°. The reduction product, 5-bromo-2-amino-4'-ethoxydiphenylamine, is difficult to obtain in a crystalline condition,

but is characterised by the formation of 6-bromo-1-p-ethoxyphenylbenztriazole, m. p. 129°, and by the *salicylidene* derivative, m. p. 146—147°.

(iv) *Isomerisation of 4'-Acetoxy-4-methylhydrazobenzene*.—The isomeric change of this substance was investigated by reducing the corresponding azo-compound with an acid reagent. Elimination of the acetyl group occurred during the formation of the *o*-semidine, which must have one of the following formulæ :

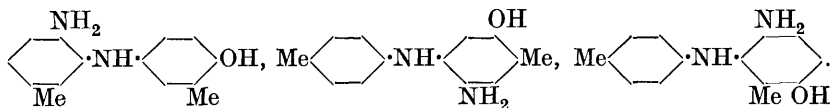


On converting the *o*-semidine into the triazole and then ethylating the hydroxyl group, a product is obtained which is isomeric with the triazole derived from the semidine described in section (ii). If the second of the above formulæ were correct, the substances should be identical. The first formula is thus indicated and its correctness is confirmed by the fission of the substance to quinol and 3 : 4-tolylene diamine.

Along with the *o*-semidine a *p*-semidine, 4'-amino-4-methyldiphenylamine, is produced with the elimination of the acetoxy group.

2-Amino-4'-hydroxy-5-methyldiphenylamine forms colourless needles, m. p. 137°, but turns red in contact with air. The *stillbazonium* base was not obtained in a pure condition. The triazole (1-p-hydroxyphenyl-6-methylbenztriazole), however, forms yellow leaflets, m. p. 187·5—189·5°, and on ethylation with ethyl iodide and sodium ethoxide gives 1-p-ethoxyphenyl-6-methylbenztriazole, m. p. 91°.

(v) *Isomerisation of 4'-Acetoxy-3' : 4-dimethylhydrazobenzene*. This *o*-semidine conversion also is accompanied by the elimination of the acetyl group. The product may have any of the following formulæ :



The third of these is improbable on general grounds, and the second can be proved to be incorrect by ethylating the hydroxyl group of the corresponding iminazole. If the second formula were correct, the product should be the iminazole corresponding with a known semidine, which it is not. The first formula remains, and it is supported by the analogy with the lower homologue (section iv).

In this case also a *p*-semidine is formed with elimination of the acetoxy group.

4'-Acetoxy-3' : 4-dimethylazobenzene is prepared by heating *p*-tolueneazo-*o*-cresol with sodium acetate and acetic anhydride. It forms thick leaflets or nodular aggregates of fine needles, m. p. 65—66°. On reduction under the usual conditions it is converted

into fission products and the semidines. 2-Amino-4'-hydroxy-3':5-dimethyldiphenylamine is difficult to purify, but on heating with formic acid it gives 1:6-hydroxy-m-tolyl-6-methylbenziminazole, glistening leaflets, m. p. 196—197° (nitrate sparingly soluble, hydrochloride forms white leaflets). On ethylation, this substance gives 1:6-ethoxy-m-tolyl-6-methylbenziminazole, which forms a well-defined hydrochloride (needles) and a picrate (prisms, m. p. 186—187°). The isomeric compound, 6-ethoxy-5-methyl-1-p-tolylbenziminazole, prepared from 2-amino-5-ethoxy-4:4'-dimethyldiphenylamine, crystallises with extraordinary ease in fine needles, m. p. 102.5°. Its hydrochloride and nitrate are difficultly soluble and the picrate forms needles, m. p. 228°. 4-Amino-2:4'-dimethyldiphenylamine forms glistening needles, m. p. 78.5°, and behaves as a *p*-semidine towards ferric chloride and nitrous acid. The salicylaldehyde derivative, $C_6H_4Me \cdot NH \cdot C_6H_3Me \cdot N : CH \cdot C_6H_4 \cdot OH$, forms needles, m. p. 116.5°.

(vi) *Isomerisation of 4-Bromo-4'-acetoxyhydrazobenzene*.—The main product of this isomeric change (which was examined by reducing the azo-compound) is the *p*-semidine, the formation of which involves the extrusion of the acetoxyl group. An *o*-semidine was not isolated, but its presence was proved by the formation of a stilbazonium base.

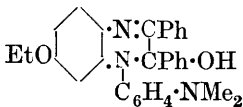
4-Bromo-4'-aminodiphenylamine (the *p*-semidine) forms colourless needles, m. p. 93.5°, and gives a sparingly soluble *hydrochloride* and *sulphate*. It gives colorations with nitrous acid and ferric chloride, and on oxidation by means of chromic acid yields quinone. Its *salicylidene* derivative, $\text{C}_6\text{H}_4\text{Br}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, forms yellow leaflets, m. p. 172°.

(vii) *Isomerisation of 4'-Dimethylamino-4-methylhydrazobenzene*.—The chief product is the *o*-semidine formed under the directive influence of the methyl group (cf. Boyd, T., 1894, **65**, 879).

(viii) *Isomerisation of 4'-Dimethylamino-4-ethoxyhydrazobenzene.*—The structure of the *o*-semidine produced by the isomeric change of this hydrazo-compound was proved by synthesis. The product of condensation of *as*-dimethyl-*p*-phenylenediamine with 4-chloro-1:2-dinitrobenzene was ethoxylated and the ethoxy-compound reduced.

4'-Dimethylamino-4-ethoxyazobenzene is obtained in good yield by coupling diazotised *p*-phenetidine with dimethylaniline. It forms brown, oblique, four-sided tablets, m. p. 149—150°. 2-Amino-4'-dimethylamino-5-ethoxydiphenylamine is produced along with the usual fission products when the azo-compound is reduced with stannous chloride. It cannot be crystallised, and must be characterised by derivatives. 1-*p*-Dimethylaminophenyl-6-ethoxybenziminazole, obtained with the aid of formic acid, forms small needles, m. p. 141—143°. The stilbazonium base, annexed formula, prepared by condensation with benzil, forms canary-yellow needles, m. p. 187—190°. The salicylaldehyde derivative, C₂₃H₂₅O₂N₃, forms golden-yellow leaflets having a green metallic reflex, m. p. 141.5—142.5°.

$$\text{EtO}-\text{C}_6\text{H}_4-\text{N}^+\text{:CPh} \cdot \text{N}^-\text{:CPh-OH} \cdot \text{C}_6\text{H}_4-\text{NMe}_2$$



and 6-ethoxy-1-*p*-dimethylaminophenyl-2-*o*-hydroxyphenyl-6-benz-*imidazole*, the condensation product with salicylic acid, forms white, glistening needles, m. p. 182—183°. 5-Chloro-2-nitro-4'-dimethylaminodiphenylamine is prepared from *as*-dimethyl-*p*-phenylenediamine and 4-chloro-1:2-dinitrobenzene. It forms small, reddish-brown needles, m. p. 181°, and with sodium ethoxide gives 2-nitro-4'-dimethylamino-5-ethoxydiphenylamine, small, deep brown crystals, m. p. 122—123°, which on reduction gives the above semidine.

(ix) Semidines are not obtained on reduction of 4-amino-4'-dimethylaminoazobenzene, 4-acetylamino-4'-dimethylaminoazobenzene, or 4:4'-bis-dimethylaminoazobenzene.

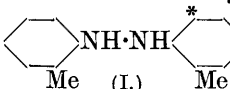
(x) The observations of Meisenheimer and Witte (A., 1904, i, 193) on the conversion of $\beta\beta'$ -azonaphthalene into 2:2'-diamino-1:1'-dinaphthyl are confirmed. This reaction has very few analogies in the benzene series (cf., however, Boyd, Diss., Heidelberg, 1896).

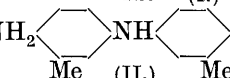
2:2'-Bis-*p*-methoxybenzylideneamino-1:1'-dinaphthyl, prepared from 2:2'-diamino-1:1'-dinaphthyl and anisaldehyde, is a yellow, crystalline powder, m. p. 194—195°.

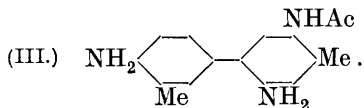
(B) *Isomeric Changes of Singly Para-substituted Hydrazo-compounds* [with M. JAENICKE and G. LOCKEMANN]; cf. A., 1909, i, 852).—

(i) The extension of a meta-substituent during semidine formation has not previously been observed. 4-Methoxyazobenzene-3-carboxylic acid on reduction by means of tin and hydrochloric acid yields 2-amino-5-methoxydiphenylamine together with fission products.

(ii) A remarkable instance of the directive effect of a group in the meta-position is provided by the isomerisation of 4-acetylamino-

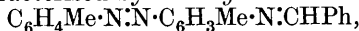
2':3-dimethylhydrazobenzene (I),  (I),

The yield of *p*-semidine (II),  (II), is very small, the main product being a diphenyl base (III),



The isomerisation of *p*-acetylaminohydrazobenzene gives rise only to the *p*-semidine, and the formation of the diphenyl base from the dimethyl homologue must be considered as due to para-direction (that is, to the position marked *) from the methyl group.

4-Amino-2':3-dimethylazobenzene, the acetyl derivative of which on reduction by means of stannous chloride gives the products mentioned, is characterised by a *benzylidene* derivative,



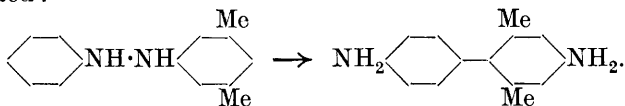
deep red prisms, m. p. 96—97°, and a *salicylidene* derivative, $\text{C}_6\text{H}_4\text{Me}\cdot\text{N}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, orange-yellow needles or

leaflets, m. p. 111—112°. 4-Amino-4'-acetylamino-3:3'-dimethyldiphenylamine forms small, white crystals, m. p. 174—175°, and gives a *salicylidene* derivative,

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NH}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{NHAc}$, which crystallises in small, yellow needles, m. p. 185—186°. 2:4'-Diamino-5-acetylamino-3':4-dimethyldiphenyl is difficult to purify, but it forms a crystalline *dibenzylidene* derivative, $\text{CHPh}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{C}_6\text{H}_2\text{Me}(\text{NHAc})\cdot\text{N}\cdot\text{CHPh}$, m. p. 204—205°, a *salicylidene* derivative,

$\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{N}\cdot\text{C}_6\text{H}_3\text{Me}\cdot\text{C}_6\text{H}_2\text{Me}(\text{NHAc})\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, m. p. 239—240°, and an acetyl derivative, 2:4':5-triacetyltri-amino-3':4-dimethyldiphenyl, m. p. 360°.

(C) *The Isomerisation of Hydrazo-compounds which are not Para-substituted* [with F. HÖNIGSBERGER and L. HUBER].—The example studied was 3:5-dimethylhydrazobenzene. A *p*-semidine was not isolated, but the product contained a large amount of a diphenyl base, which, from the fact that it yielded 2:6-dimethyldiphenyl on elimination of the amino-groups, must have the structure indicated:

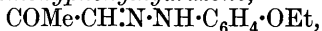


3:5-Dimethylazobenzene is prepared by condensing nitrosobenzene with *m*-xylidine. It is a deep red oil, b. p. 197·5°/17—19 mm., d_{20}^{20} 1·060. On reduction by means of zinc dust and alkali, it gives 3:5-dimethylhydrazobenzene, which crystallises in long, slender, colourless needles, m. p. 78—79°. 4:4'-Diamino-2:6-dimethyldiphenyl, the main product of isomerisation, forms colourless needles, m. p. 124°, and gives a benzaldehyde derivative, 4:4'-dibenzylidinediamino-2:6-dimethyldiphenyl, which forms pale yellow, hair-like needles, m. p. 199—200°. On eliminating the amino-groups by reducing the diazonium salt with hypophosphorous acid, 2:6-dimethyldiphenyl is obtained, which boils at 260—265°, and is characterised by a *trinitro*-derivative, m. p. 257—258°, and a *tetranitro*-derivative, m. p. 227—229°. The same hydrocarbon was prepared from *v-m*-xylidine (2-amino-1:3-xylene) by treating its dry hydrochloride with ethyl alcoholic amyl nitrite and allowing the diazonium chloride so produced to react with benzene in the presence of aluminium chloride. The isomeric hydrocarbon, 2:4-dimethyldiphenyl, prepared in a similar way from *as*-xylidine is an oil, b. p. 270—276°, and forms a *tetranitro*-derivative, m. p. 154·5—155°.

(D) *An Attempt to Generalise the Isomeric Change of Hydrazo-compounds* [with H. JOST, ST. PINKUS, and P. SCHMIDT].—Three types of hydrazo-compounds (or the desmotropic hydrazones) have been examined. (a) Compounds, $\text{R}\cdot\text{NH}\cdot\text{NH}\cdot\text{R}'$, in which R is aromatic and R' purely aliphatic, (b) compounds in which R is aromatic and R' is a residue such as benzyl in which an aromatic nucleus is joined indirectly to the hydrazo-group, (c) compounds

in which both R and R' are residues of this kind. Changes analogous to the semidine and benzidine conversions have not been observed in these cases.

Pyruvaldehyde p-ethoxyphenylhydrazone,



orange-yellow leaflets, m. p. 144.5° , is formed by condensing acetoacetic acid with diazotised *p*-phenetidine; *di-p-ethoxyphenylformazyl methyl ketone*, $\text{COMe} \cdot \text{C}(\text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}) : \text{N} \cdot \text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{OEt}$, small, deep red needles, m. p. 143° , is also formed. *Pyruvic acid p-ethoxyphenylhydrazone*, canary-yellow needles, m. p. $120-122^\circ$, is obtained by condensing ethyl methylacetoacetate with diazotised *p*-phenetidine and hydrolysing the product (m. p. 110°). On reduction by means of sodium amalgam, it yields α -*p-ethoxyphenylhydrazinopropionic acid*, pale yellow needles, m. p. $128-138^\circ$.

C. K. I.

Summary of Results on the Isomeric Changes of Hydrazo-compounds, and Considerations relating to the Possibilities of their Explanation. PAUL JACOBSEN (*Annalen*, 1922, 428, 76—121).—An ordered summary of all previous work on the subject of this isomeric change, and a discussion of the principal views which have been expressed.

C. K. I.

The Action of Amines on Semicarbazones. I. Preparation of an Optically Active Semicarbazide. FORSYTH JAMES WILSON, ISAAC VANCE HOPPER, and ARCHIBALD BARCLAY CRAWFORD (*T.*, 1922, 121, 866—870).

Reactions of Thiosemicarbazones. I. Action of Halogen Compounds. FORSYTH JAMES WILSON and ROBERT BURNS (*T.*, 1922, 121, 870—876).

Is the Heat-coagulation of Protein a Hydrolysis? MARGIT HIRSCH-POGANY (*Biochem. Z.*, 1922, 128, 396—401).—The author has attempted to determine whether the heat-coagulation of egg-white is due to hydrolysis by determining the increase in weight and the increased content of hydrogen and oxygen by analysis. The changes found were too small to indicate hydrolysis with any certainty.

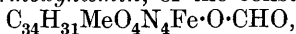
H. K.

Fibrinolysis. II. MAX ROSENMANN (*Biochem. Z.*, 1922, 128, 372—381).—The fibrinolytic agent for which the authors adopt the name *thrombolysin* is precipitable by alcohol, ammonium sulphate, and zinc chloride. It exhibits maximum activity at 37° and in neutral solution. It is inactivated at $46-48^\circ$. Fibrin heated at $57-62^\circ$ is no longer acted on by thrombolysin. The best solution for preserving the active material is 25% alcohol. Human and horse fibrin behave similarly towards thrombolysin.

H. K.

The Prosthetic Group of Blood Pigment. Formoxy-hæmin. WILLIAM KÜSTER and ADOLF GERLACH (*Z. physiol. Chem.*, 1922, 119, 98—116).—The hæmatin-like substance obtained by Partos (*A.*, 1920, i, 773) by the action of methyl alcohol con-

taining formic acid on blood-coagulum is found to be an *inner* salt of *monomethylformoxyhæmin*, of the constitution



fine, slender needles, insoluble in water and all organic solvents, including aniline and pyridine, and in 5% sodium carbonate solution at the ordinary temperature, whilst it dissolves slowly in 5% sodium carbonate solution on heating, and in cold 1% sodium hydroxide solution. On digestion with methyl alcohol containing sulphuric acid, it slowly dissolves, and from the solution by the addition of hydrogen chloride, a β -*dimethylchlorohæmin*, $\text{C}_{36}\text{H}_{36}\text{O}_4\text{N}_4\text{FeCl}$, small deformed needles, can be isolated.

Attempts to prepare α - and β -formoxyhæmins have not resulted in obtaining chlorine-free compounds.

Acetyloxyhæmin, a microcrystalline black powder, of the formula $\text{C}_{36}\text{H}_{35}\text{O}_6\text{N}_4\text{Fe}$, is obtained by the action of ethyl alcohol and acetic acid on oxyhæmoglobin powder.

W. O. K.

The Hæmochrome of Herzfeld and Klinger. S. PARTOS (*Biochem. Z.*, 1922, 129, 89—100).—An extensive comparison of Herzfeld and Klinger's hæmochrome (A., 1920, i, 781) and hæmatin establishes their identity.

H. K.

Physical Characteristics of Gelatin Solutions. CLARKE E. DAVIS and EARLE T. OAKES (*J. Amer. Chem. Soc.*, 1922, 44, 464—479; cf. this vol., i, 63).—In the present paper, the variation of the density of gelatin solutions with temperature between 0° and 60°, the variation of density with concentration at 40°, the transition point of gel to sol, the variation of viscosity with concentration at 40°, the variation of viscosity with temperature from 25° to 60°, and the variation of viscosity with the hydrogen-ion concentration at 40° have been determined. It is shown that the density of a gelatin solution, expressed in grams per c.c., at any temperature and any concentration, is equal to the density of water at that temperature plus 0.00290 multiplied by the percentage concentration of the gelatin by weight. The viscosities of gelatin solutions of various concentrations at 40° conform with Arrhenius's viscosity formula. The viscosity-temperature curve of gelatin solutions shows a sharp deflexion at the transition point of gelatin. There are two maxima in the viscosity-hydrogen-ion concentration curve for gelatin solutions at 40°. These maxima are equidistant from the neutral point of water, and the effect of the isoelectric point, $P_H=4.7$, is not noticeable on the curve. The transition point of gelatin sol form A \rightleftharpoons gel form B is a temperature of 38.03°.

J. F. S.

Protein Enzymes. RUDOLF EHRENBURG (*Biochem. Z.*, 1922, 128, 431—449).—The author revives a hypothesis of enzyme action similar to that of Liebig. The enzyme is not a resting definable entity, but is a process into which the substrate may be induced to pass under certain conditions. The hypothesis is illustrated at length by reference to experiments on trypsin and pepsin.

H. K.

Rôle of Acids in Peptic Digestion. WO. OSTWALD and A. KUHN (*Kolloid Z.*, 1922, **30**, 234—243).—The swelling of gelatin and egg-albumin by solutions of sulphosalicylic acid has been investigated at various temperatures between 13·7° and 20·2°. It is shown that sulphosalicylic acid brings about the swelling of gelatin in exactly the same way as other acids, that is, it accelerates it in small concentrations, but retards it when present in greater concentrations. In the case of egg-albumin the sol swelling is furthered by small concentrations of sulphosalicylic acid and a precipitation is brought about by larger concentrations. In earlier papers, it has been shown that the swelling of the substrate plays an important part in peptic digestion, inasmuch as a furtherance of the swelling by acids also brings about a furtherance of the fermentation process. In opposition to this rule, Gyemant (A., 1920, i, 783), and Michaelis (A., 1921, i, 74) have shown that the sulphosalicylic acid which precipitates albumin makes peptic digestion possible. The present work shows that this case does not present an exception to the above-mentioned rule, for sulphosalicylic acid exerts a swelling action in concentrations of the same order as those at which Michaelis and Gyemant found the maximum peptic digestion. J. F. S.

Invertase. II. RICHARD WILLSTÄTTER and FRITZ RACKE (*Annalen*, 1922, **427**, 111—141; cf. A., 1921, i, 823).—An investigation of the nature of the enzymatic process by means of which invertase may be set free from the yeast-cell, and of the condition in which invertase occurs in the cell. The general conclusion is that the invertase occurs as such, and not as a complicated carbohydrate molecule or higher polyose, but that it is protected and prevented from diffusing by the membranes of the cell-structure. The function of the liberating enzymes is to destroy these membranes so that the invertase can diffuse away.

The liberating enzyme is somewhat unstable, and the process which results in the dissolution of the invertase is dependent therefore on the manner in which the yeast is killed. If it is killed, for instance, by water at 50°, by 2% acetic acid, by 50% alcohol, or by cold ethyl acetate, the invertase content is quite unaffected, but its dissolution is hindered owing to the destruction of the liberating enzyme. Invertase itself is not appreciably decomposed by water below 55°.

The following experiment shows the liberating enzyme to be a polysaccharase rather than a proteolytic enzyme. If the yeast is killed by means of warm ethyl acetate (which destroys the enzyme), and either pepsin or trypsin is added, a large part of the yeast (the proteins) passes into solution, but the whole of the original invertase remains in the insoluble portion. If now this is treated with a polysaccharase such as tannase or malt-diastrase, the whole of the invertase is liberated.

There are four ways in which invertase might be supposed to occur in the yeast-cell: (a) as a complex carbohydrate molecule, (b) as a polyose, (c) as adsorbed invertase, (d) as invertase con-

served between the membranes of the cell. If, however, the yeast is ground with an abrasive material for a long period at a temperature too low for any enzymatic process to occur, the whole of the invertase becomes soluble. Moreover, the substance present in this solution evidently does not belong to a more complex molecular species than the invertase obtained by enzymatic action, as can readily be shown by examining its behaviour with various adsorbents. Evidently, therefore, the invertase must exist as such enclosed in protecting membranes, which must be broken before it can diffuse. The destruction of the membranes can be effected by mechanically reducing the cell, but the same result is obtained much more quickly by allowing a polysaccharase to attack the membranes.

The solutions of invertase obtained by subjecting yeast killed by means of warm ethyl acetate, first to proteolysis, and then to diastatic decomposition (fractional enzymatic extraction), are considerably richer than those formed by the action of the enzyme present in the yeast (autolysis). The invertase obtained by either process may be purified by adsorption and isolated as described in the previous paper (*loc. cit.*). The preparations of invertase obtained by fractional enzymatic extraction are comparable in strength with those obtained from solutions formed by autolysis, but whilst the latter are free from carbohydrates and contain proteins, the former are free from proteins and contain carbohydrates. Other impurities which may be present are (a) foreign matter, including mineral substances derived from the adsorbents, (b) decomposed invertase, (c) and other carbohydrate-hydrolysing enzymes, such as raffinase and stachyase.

C. K. I.

The Temperature Coefficients in the Degradation of Starch and the Thermostability of Malt Diastase and Ptyalin.

ERF. ERNSTROM (*Z. physiol. Chem.*, 1922, **119**, 190—263).—The optimal zone of reaction for malt diastase is P_H 4—6, that of ptyalin is P_H 6·5. Malt diastase is not influenced by the presence of sodium chloride in low concentrations; higher concentrations, however, have an inhibiting action. Ptyalin is inactive in the absence of sodium chloride. Ptyalin and malt diastase retain their activity at 0°. The temperature coefficient of these two enzymes falls with the rising temperature. The constant A of Arrhenius's formula for various ranges of temperature and under various conditions was worked out. The highest stability of malt diastase lies at P_H 5·9, that of ptyalin at P_H 6·0—6·1. The presence of sodium chloride (optimum concentration $N/10$) greatly enhances the stability of ptyalin; the stability of malt diastase is not affected by the presence of sodium chloride. The inactivation temperature of ptyalin under optimal conditions is 57·5°, in the absence of sodium chloride it is 51·5—52°. Malt diastase is entirely inactivated when heated for one hour at 60°. The rate of inactivation of malt diastase and of ptyalin is not in accordance with that for a unimolecular reaction, but, as in the case of saccharase, it falls off more quickly than is required by the formula

$$k_e = 1/t \log k_a/k_i.$$

The rate of inactivation in low concentrations increases with the decrease in the concentration of the enzyme. The heated enzymes could not be regenerated. S. S. Z.

The Influence of Hydrogen-ion Concentration on the Action of Pancreatic Amylase. J. TEMMINCK GROLL (*Arch. Néerland. physiol.*, 1922, 6, 445—449).—The optimum range of hydrogen-ion concentration for pancreatic amylase extends from $P_{H4.6}$ to $P_{H6.8}$. On either the acid or alkaline side of this range the activity falls off with great rapidity. C. R. H.

σ -Emulsin (Oxynitrilase), δ -Emulsin (Oxynitrilase), and Carboligase. L. ROSENTHALER (*Biochem. Z.*, 1922, 128, 606—607).—Polemical against Nordefeldt (this vol., i, 66) and Neuberg and co-workers (*A.*, 1921, i, 480; this vol., i, 305). H. K.

Classification of Carboligase. C. NEUBERG and J. HIRSCH (*Biochem. Z.*, 1922, 128, 608—609).—Polemical against Rosenthaler (preceding abstract). H. K.

Succinodehydrogenase. ERIK P. WIDMARK (*Skand. Arch. Physiol.*, 1921, 41, 200—220; from *Chem. Zentr.*, 1921, iii, 1362—1363; cf. Battelli and Stern, *A.*, 1911, ii, 132, and Thunberg, *A.*, 1918, i, 140).—The enzyme found in the muscles of horses and cattle, called "succinicoxydone" (Battelli and Stern) or "succinodehydrogenase" (Thunberg) changes succinic acid into fumaric acid with elimination of hydrogen. The course of the reaction may be followed by using methylene-blue as hydrogen acceptor, it being thereby changed into the leuco-base. Directions are given for the preparation of the enzyme, from horse or cattle muscle. The time required for the decoloration of a 0.25% solution of methylene-blue was used as a measure of the reaction of the enzyme with succinic acid. With constant concentration of succinate the decolorising power was proportional to the concentration of the enzyme. With constant enzyme concentration, the decolorising power rose at first quickly with the succinate concentration, but then approached a limiting value. G. W. R.

Aliphatic Arsinic Acids, and Aliphatic-aromatic Arsenious Acids. A. J. QUICK and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, 44, 805—816).—Alkylarsinic acids may readily be prepared by heating together an aqueous solution of sodium arsenite and the requisite alkyl bromide or chloride. The method has been applied to the preparation of several alkylarsinic acids as well for allyl- and benzyl-arsinic acids. For the preparation of dialkylarsinic acids, the necessary alkylchloroarsine is dissolved in sufficient 10*N*-sodium hydroxide to produce the disodium alkyl arsenite and then the alkyl bromide is added and the mixture is heated under a reflux condenser. In this way, diethylarsinic acid, *propylbutylarsinic acid*, m. p. 127—128°, and *dibutylarsinic acid*, m. p. 137—138°, giving a light blue copper salt, have been obtained. For the aliphatic-aromatic arsinic acids the dichloroarsine is dissolved in alkali as described above and the alkyl or aryl haloid added at the ordinary temper-

ature, the reaction taking place rapidly. In this way a number of compounds having the general formula $\text{NHR} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{AsRO}_2\text{H}$ have been obtained, where R is a phenyl, *p*-aminophenyl, or *p*-acetylaminophenyl group, and R' is a phenyl or substituted phenyl group. The compounds described are: *Phenylarsinoacetic acid*, m. p. 141—142° (decomp.); *phenylchloroarsineacetic acid* $\text{AsPhCl} \cdot \text{CH}_2 \cdot \text{CO}_2\text{Et}$, m. p. 102—103°; *phenylbromoarsineacetic acid*, m. p. 113—114°; *phenylarsinoacetanilide*, m. p. 182—183° (decomp.); *phenylbromoarsineacetanilide*, m. p. 108—110°; *phenylarsinoacetophenetidine*, m. p. 175° (decomp.); *phenylarsinoacetoarsanilic acid*; *phenylarsino-o-acetylaminobenzoic acid*, m. p. 198—200° (decomp.); *phenoxyethylphenylarsinous acid*, m. p. 122—123°; *ethylenediphenyldiarsinous acid*, m. p. 209—211°; *p*-aminophenyldichloroarsine hydrochloride; *p*-aminophenylarsinoacetanilide, m. p. 181—182° (decomp.); *p*-acetylaminophenylarsinoacetanilide, m. p. 205—206° (decomp.); *p*-glycylaminophenylarsinoacetanilide, m. p. 199° (decomp.); *p*-aminophenylarsinoacetophenetidine, m. p. 211·5—212·5°; *p*-acetylaminophenylarsinoacetophenetidine, m. p. 214—215° (decomp.); *p*-aminophenylarsinoacetoarsanilic acid; *p*-acetylaminophenylarsinoacetoarsanilic acid; *p*-aminophenylarsino-*p*-acetylaminobenzoic acid, m. p. 217° (decomp.).

Butyldichloroarsine, b. p. 192—194°, is obtained by the action of sulphur dioxide on butylarsinic acid in hydrochloric acid solution in the presence of a little potassium iodide. *p*-Chloroacetylaminobenzoic acid, m. p. 239°, is obtained by the action of chloroacetyl chloride on *p*-aminobenzoic acid.

The arsenic derivatives described above dissolve readily in aqueous alkalis, giving solutions which have relatively low toxicity but at the same time only a slight trypanocidal action. W. G.

The Sulphur Content of Arsphenamine (Salvarsan) and its Relation to the Mode of Synthesis and the Toxicity. I. WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1922, **44**, 847—854; cf. this vol., i, 186; Fargher and Pyman, T., 1920, **117**, 370).—The total sulphur content of salvarsan was found to vary from 0·4% up to 3%, according to the method of preparation, and those preparations which contained the highest percentage of sulphur were the most toxic. There was no direct relationship, however, between these two factors. Only the sulphur in excess of that introduced when 3-nitro-4-hydroxyphenylarsinic acid is reduced by hyposulphite under the most favourable conditions has any great effect on the toxicity. The sulphonc acid of salvarsan, described by King (T., 1921, **120**, 1107, 1414), could only be isolated from salvarsan preparations made from the nitro-acid under the least favourable conditions. The presence of this sulphonc acid cannot account for the whole of the high toxicity which is obtainable.

W. G.

The Sulphur Content of Arsphenamine (Salvarsan) and its Relation to the Mode of Synthesis and the Toxicity. II. WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1922, **44**, 854—859; cf. preceding abstract).—Highly toxic salvarsan preparations

with high sulphur content prepared by the hyposulphite reduction of 3-nitro-4-hydroxyphenylarsinic acid differ from those obtained from known mixtures of 3-amino-4-hydroxyphenylarsinic acid and its 5-sulphonic acid (cf. King, T., 1921, **120**, 1107, 1414) in several points, such as the rate at which the sulphonic acid separates from the alcohol solution, the effect of temperature on the formation of the precipitate, the ease of separation of the precipitate from the mother-liquor, and the rate of death of rats when the preparations are injected intravenously. These differences, it is suggested, may be due to heating causing a rearrangement of some unstable substance or to an alteration in colloidal properties. W. G.

Lead Triaryl, a Parallel to Triphenylmethyl. III. Lead Triphenyl, Tri-*p*-tolyl and Tri-*o*-tolyl and Dark Red Lead Diaryls. ERICH KRAUSE and G. G. REISSAUS (*Ber.*, 1922, **55**, [B], 888—902).—In continuation of the work on lead tri-*p*-xylyl (Krause and Schmitz, A., 1920, i, 197) and lead tricyclohexyl (Krause, A., 1921, i, 825), the lower homologues are now described; it has also been found possible to isolate certain intermediately formed lead diaryls in the homogeneous condition. The latter are intensely coloured, dark red, apparently amorphous powders which give blood-red solutions in benzene or ether from which they are precipitated unchanged by alcohol. In freezing benzene they have the simple molecular weight, and hence are shown definitely to be derivatives of bivalent lead. They are highly unsaturated. In the solid state or in solution, they readily absorb atmospheric oxygen, becoming decolorised and transformed into derivatives of quadrivalent lead. They combine instantly with iodine and reduce silver nitrate to metallic silver. On the other hand, when isolated they are comparatively stable and retain their red colour for weeks if carefully shielded from light and air. They are very analogous to the tin diaryls (Krause and Becker, A., 1920, i, 340) but are considerably less stable than these substances. When heated alone or in solution, they undergo complex decomposition, whereas in the presence of an excess of magnesium aryl bromide they are converted smoothly and readily into lead triaryls.

Lead triphenyl is remarkable for its close resemblance to hexaphenyldistannan (Krause and Becker, *loc. cit.*); in the solid condition it is probably bimolecular, but the designation "hexaphenyldiplumban" does not appear to be appropriate, since it has the simpler molecular weight in dilute solution. This is also true of the tri-*p*-tolyl, tri-*o*-tolyl, and tri-*p*-xylyl compounds. The lead triaryls show remarkable differences in the ease with which they pass into tetra-aryls; this occurs very readily with the phenyl compounds, more difficultly with the *p*-tolyl derivative, whereas it is not possible with the *o*-tolyl or *p*-xylyl compounds.

The following individual substances have been prepared by the action of the requisite magnesium aryl haloid on lead chloride in the presence of ether or benzene. It is remarkable that the yields appear to depend to a not inconsiderable extent on the origin of

the lead chloride. The success of the experiments is governed greatly by exact adherence to experimental conditions, which are described fully in the original. *Lead diphenyl*, a blood-red, amorphous powder which is decolorised and decomposed at about 100° , becomes yellow at 120° and melts above 200° , without, however, blackening below 260° . *Lead di-p-tolyl*. *Lead triphenyl*, almost colourless, lustrous rhombohedra ($+C_6H_6$) from benzene, pale yellow, rhombic platelets from chloroform, incipient decomp. 155° and m. p. 225° (m. p. of lead tetraphenyl); it is converted into lead tetraphenyl when heated alone (see above), in benzene solution at 100° , or in pyridine solution at $60-65^{\circ}$; its solution in benzene is converted by an aqueous alcoholic solution of iodine into lead triphenyl iodide and by a dilute solution of iodine in benzene into lead iodide, together with a little lead diphenyl diiodide. *Lead tri-p-tolyl*, hexagonal platelets or rhombohedra, decomp. 193° and subsequent m. p. 240° (m. p. of lead tetra-*p*-tolyl); in contrast to lead tri-*p*-xylyl and lead tricyclohexyl, it is converted by bromine in freezing pyridine into lead bromide and lead tetra-*p*-tolyl, thus pointing to the possible existence in pyridine solution of the equilibrium $2Pb(C_7H_7)_3 \rightleftharpoons Pb(C_7H_7)_4 + Pb(C_7H_7)_2$; with iodine in the presence of water, it gives *lead tri-p-tolyl iodide*, m. p. 115° , decomp. about 195° . *Lead tri-o-tolyl*, microscopic rhombohedra which deposit lead at about 240° and melt to a black liquid at about 250° . *Lead tri-p-xylyl chloride* crystallises in silvery, rectangular plates, m. p. 167.5° , decomp. about 195° .

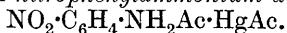
H. W.

The Nitroanilines. MORRIS S. KHARASCH, FREDERICK W. M. LOMMEN and ISADORE M. JACOBSON (*J. Amer. Chem. Soc.*, 1922, **44**, 793—805).—Evidence is adduced in support of the nitronic structure of *o*- and *p*-nitroanilines, and it is considered that in alcoholic solution they exist in two or more tautomeric forms (cf. Baly, Edwards, and Stewart, T., 1906, **89**, 517). In alcoholic solution they give with mercuric acetate intensely coloured mercury salts, whereas with *m*-nitroaniline the reaction is only slow and the product is almost white. Using nascent mercuric oxide, Jackson and Peakes (A., 1908, i, 523) obtained highly coloured compounds with all three isomerides, but it is shown that their compound obtained from the meta-isomeride is only an additive compound, as, on extraction with acetone, the whole of the nitroaniline is removed and only the mercuric oxide is left. The *o*- and *p*-salts, when similarly extracted, remain unchanged. The authors suggest a formula for *p*-nitrodimethylaniline, in which its nitronic structure is retained, which should overrule Baly's objections (cf. T., 1910, **97**, 581). The mechanism of mercurisation is discussed and three possible ways in which *o*- and *p*-nitroanilines might be mercurised are suggested. The positions taken by the entering mercury in the nitroanilines has been established as ortho or para or ortho-para to the amino-group. This has been shown by acetylation and subsequent replacement of the mercury by bromine.

o-Acetoxymercuri-*p*-nitroaniline is best obtained by the interaction of mercuric acetate and *p*-nitroaniline in alcoholic solution. With hydrochloric acid it yields *o*-chloromercuri-*p*-nitroaniline, and with sodium thiosulphate it gives *o*:*o*'-mercury-bis-*p*-nitroaniline. With dilute sodium hydroxide or carbonate, the acetoxy- or chloro-derivatives give *quinone-1-imide-aci-4-nitro-2-mercury*. If, in the preparation of the acetoxy-derivative, an excess of mercuric acetate is used *o*:*o*'-diacetoxymercuri-*p*-nitroaniline is obtained. On acetylation the acetoxy-derivative yields *o*-acetoxymercuri-*p*-nitroacetanilide, which on bromination gave *p*-nitro-*o*-bromoacetanilide.

Similar derivatives were prepared from *o*-nitroaniline as follows: *p*-acetoxymercuri-*o*-nitroaniline; *p*-chloromercuri-*o*-nitroaniline; *quinone-1-imide-aci-2-nitro-4-mercury*; *p*-acetoxymercuri-*o*-nitrodiacetanilide; *p*-acetoxymercuri-*o*-nitroacetanilide.

m-Nitroaniline reacts with mercuric acetate in alcohol to give *N*-isomercuriacetate-*m*-nitrophenylammonium acetate,



By varying the conditions and the quantities of the reacting substances *o*:*p*-diacetoxymercuri-*m*-nitroaniline and *p*-acetoxymercuri-*m*-nitroaniline are obtained, the latter yielding *p*-acetoxymercuri-*m*-nitroacetanilide on acetylation.

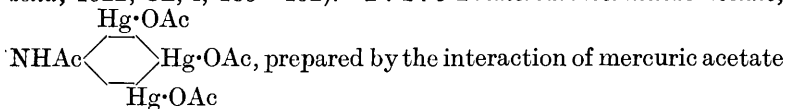
W. G.

Organic Nitro-compounds containing Mercury. GEORGE W. RAIZISS and A. PROSKOURIAKOFF (*J. Amer. Chem. Soc.*, 1922, **44**, 787—793).—In the case of nitrophenol and nitrosalicylic acid, the introduction of mercury into the nucleus is effected by warming the compound with either mercuric acetate or oxide in water for several hours. A mixture of mono- and di-mercurated products usually results. The corresponding chloromercuri-compounds may be obtained by the action of hydrochloric acid. The authors obtained such a mixture from *o*-nitrophenol, their results thus disagreeing with those of Hantsch and Auld (cf. *A.*, 1906, i, 471). With 5-nitrosalicylic acid, the dimercury derivative is obtained almost exclusively, even although allowed to react with only equimolecular quantities of mercuric oxide or acetate. The biological properties of these compounds have been examined, and of the entire number sodium hydroxymercuri-*o*-nitrophenoxide was found to be far superior to the others. The following compounds are described: 4-chloromercuri-2-nitrophenol; sodium hydroxymercuri-*o*-nitrophenoxide (mercurophen) (cf. *J. Infect. Diseases*, 1919, **24**, 547); 2-chloromercuri-4-nitrophenol; 4-acetoxymercuri-2-nitroresorcinol; 4-chloromercuri-2-nitroresorcinol; 3-chloromercuri-5-nitrosalicylic acid, m. p. 238° (decomp.); diacetoxymercuri-5-nitrosalicylic acid. The mercurisation of 3-bromo-5-nitrosalicylic acid and of 3:5-dinitrosalicylic acid gave mixtures of mono- and di-mercury compounds from which it was not possible to separate pure substances. None of the compounds described above were affected by ammonium sulphide at room temperature within thirty minutes (cf. *A.*, 1920, i, 196).

Modifications in the preparation of 5-nitro- and 3:5-dinitrosalicylic acids are described.

W. G.

Colloidal Trimercuriacetanilide Acetate. G. ROSSI (*Gazzetta*, 1922, **52**, i, 189—192).—2 : 4 : 5-Trimercuriacetanilide acetate,



and acetanilide at 140°, forms a friable, vitreous mass and softens and decomposes at above 180°. It dissolves slowly but abundantly in water, yielding colloidal solutions which froth when shaken, coagulate when heated, and are incapable of dialysis; in these properties, the compound resembles the corresponding tetra- and penta-mercuriacetanilide acetates (cf. Raffi and Rossi, A., 1912, i, 931; 1914, i, 610). With these three acetates, the colloidal properties become more clearly marked as the molecular weight increases. Treatment of trimercuriacetanilide acetate in aqueous solution with excess of bromine dissolved in potassium bromide solution results in the formation of 2 : 4 : 5-tribromoacetanilide. T. H. P.

Preparation of Esters of Complex Mercuridicarboxylic Acids and their Products of Hydrolysis. WALTER SCHOELLER and WALTHER SCHRAUTH (D.R.-P. 339494; from *Chem. Zentr.*, 1921, iv, 1224).—Esters of sulphido-mercuricarboxylic acids are heated, whereby mercuric sulphide is split off; the resulting esters may be hydrolysed (cf. Schoeller, Schrauth, and Hueter, A., 1920, i, 455—456). Methyl sulphido-dimercuri-*o*-acetylamidobenzoate, prepared by the action of freshly prepared alcoholic hydrogen sulphide on methyl acetoxy-mercuriacetylanthranilate, is heated at 80—100° until 1 molecule of mercuric sulphide is split off. The resulting methyl mercuridiacetylamidobenzoate is separated by solution in acetone and filtration from the mercuric sulphide. It has a light yellow colour and m. p. about 200° with previous discoloration. Ethyl mercuridisalicylate is similarly prepared; it is a crystallisable oil. Methyl mercuridibenzoate, prepared by way of the sulphidomercuribenzoate, is a white, microcrystalline compound. By hydrolysis, it gives an amorphous substance, containing 45·07% of mercury, identical with the mercuridibenzoic acid of Pesci (A., 1901, i, 624). Ethyl sulphido-mercurimethoxybutyrate, from ethyl acetoxymercurimethoxybutyrate (itself obtained from the action of mercuric acetate on ethyl crotonate) gives on heating ethyl α -mercuridi- β -methoxybutyrate obtained as microcrystalline needles by recrystallisation. α -Mercuridi- β -methoxybutyric acid is obtained by hydrolysis as a white, amorphous powder. G. W. R.

Physiological Chemistry.

Estimation of the Relative Numbers of Red Blood-corpuscles of Differing Resistance (Osmotic Resistance Curves) by means of Sodium Sulphate. H. J. HAMBURGER (*Biochem. Z.*, 1922, 129, 163—182).—Corpuscles washed with isotonic sodium sulphate solution lose their adsorbed lecithin layer and when exposed to solutions of sodium sulphate of increasing concentration show a curve of resistance to hæmolysis different from that of unwashed corpuscles. Washed corpuscles are more resistant than unwashed. It is shown that regeneration of blood after anæmia due to blood-letting in rabbits is most rapid if lecithin and fatty foods be consumed.
H. K.

The Dextrose Content of the Red Blood-corpuscles of Man and their Behaviour in Isotonic Sugar Solutions. M. BÖNNIGER (*Biochem. Z.*, 1922, 128, 482—486).—The red blood-corpuscles of man, when kept in isotonic dextrose solution at 0°, 15°, or 37°, show a considerable increase in volume after one hour, especially at the higher temperatures. When kept longer, those at 0° decrease in volume, whilst those at 15° and 37° continue to increase and finally those at 37° show hæmolysis. The corpuscles of sheep and guinea pigs always diminish in volume independently of the temperature.
H. K.

The Importance of Potassium and Calcium Ions for the Production of Artificial Œdema and for the Width of the Blood Vessels. RUDOLF J. HAMBURGER (*Biochem. Z.*, 1922, 129, 153—162).—Potassium can be omitted from a perfusion fluid for a frog's limb without production of œdema if the solution contain 0.6% NaCl and 0.007% $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$. Addition of 0.01% KCl or a fall of concentration of the calcium chloride to 0.006% produced œdema. Higher concentrations of calcium chloride, for instance, 0.01% constrict the blood-vessels so that no fluid will pass, but on addition of a little potassium chloride the flow recommences. The action is reversible. The action of the calcium ion is to constrict the capillaries and to cause a thickening of their walls, a property also possessed by solutions saturated with oxygen.
H. K.

The Sterilisation of the Intestine during Fasting. STEFAN DOMBROWSKI and (the late) STANISLAS KOZŁOWSKI (*Bull. Soc. Chim. Biol.*, 1922, 4, 71—79).—Fasting, accompanied by daily washings with tepid water to eliminate fæces remaining from the period preceding the fast, produces an advanced sterilisation of the intestine. From the fourth day, the excretion of conjugated sulphuric acid and of indican in the urine is at a minimum, whilst bilirubin and cholesterol undergo no change in the intestine, but are excreted as such in the fæces.
E. S.

The Rôle of Ketonic Compounds in Intermediate Exchanges and in the Formation of Sugar from Fat. H. CHR. GEELMUYDEN (*Skand. Arch. Physiol.*, 1921, **40**, 211—225; from *Chem. Zentr.*, 1921, iii, 1508—1509).—Oil was injected into the stomach of rabbits poisoned with phloridzin. The elimination of sugar rose at once and remained high for several days. The increase in sugar was not, however, in excess of that to be expected from the amount of oil administered. Phloridzin-diabetic dogs excrete "extra sugar" after subcutaneous injection of sodium acetate and sodium butyrate, but not in the case of sodium *n*-hexoate. Strongly diabetic men show, after administration of "ketogenous" amino-acids (*isovaleric acid*, tyrosine, phenylalanine, *d*-leucine, and butyric acid), increased excretion of sugars and ketonic compounds. Ketonic compounds and sugar may be formed on the one hand from fats and their derivatives and on the other from the amino-acids of proteins. Ketonuria must be considered as a sign of defective or incomplete sugar synthesis. G. W. R.

Physical Chemistry of Colour Vision. FRITZ WEIGERT (*Z. physikal. Chem.*, 1922, **100**, 537—565).—A theoretical paper in which the physical chemistry of the mechanism of colour vision is discussed. J. F. S.

Odour and Chemical Structure. H. ZWAARDEMAKER (*Arch. Neerland. physiol.*, 1922, **6**, 336—354).—The intensity of the odour of a substance is an additive property, depending on such physical properties as volatility and solubility in lipoids; the quality of the odour is a constitutive property, depending on the presence in the molecule of certain specified groupings, designated "odoriphores," and on the magnitude and number of the groupings in the molecule and their intra-molecular arrangement. Thus attention is directed to the regular transition in the type of odour observed in ascending certain homologous series of compounds.

With reference to the theory that odour is due to intra-molecular movements, it is pointed out that these movements are themselves determined by the above-mentioned factors. C. R. H.

The Rôle of Vitamins in the Chemistry of the Cell. EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1922, **119**, 117—120).—The author points out that he had published conclusions similar to Hess (this vol., i, 399) on the relation of the antineuritic vitamin to cell oxidation processes. W. O. K.

Chemical Conditions for the Maintenance of Normal Cell Structure. IV. Difference in Nitrogen and Water Content of Muscle treated with Sodium and Calcium Chloride. ERIK M. P. WIDMARK and GUNNAR LINDAHL (*Skand. Arch. Physiol.*, 1921, **41**, 221—226; from *Chem. Zentr.*, 1921, iii, 1367—1368; cf. Widmark, A., 1911, ii, 56).—The extraction of rabbit muscle by solutions of sodium chloride, and sodium chloride together with calcium chloride, respectively, was studied. The nitrogenous substances extracted amounted to 15—20% of the weight of tissue used. There was no marked difference between the amount

extracted by the two solutions. In the case of the solution containing calcium chloride, however, the water content of the tissue was lowered, probably owing to dehydration of tissue colloids. The effect of calcium ions on muscle is attributed to this rather than to extraction of proteins.

G. W. R.

Chemical and Physical Properties of Muscle and Muscle Extracts. VI. Muscle Extract of Octopus. G. QUAGLIARIELLO (*Arch. internat. Physiol.*, **16**, 228—238; from *Chem. Zentr.*, 1921, iii, 1368; cf. A., 1921, i, 831).—Muscle extract from octopus has d_{18}^{20} 1.051; it is slightly acid in reaction and shows under the ultramicroscope, particularly on dilution with 3.5% sodium chloride solution, great numbers of myosin granules in energetic Brownian motion. The relative viscosity is 5.09; relative conductivity at 18°, 0.0233 reciprocal ohm; surface tension (by stalagmometer), 0.68. The opalescence increases above 38°, and at 54—55° coagulation takes place. The extract contains 85.8% of water, 3.02% of ash, 1.626% of total nitrogen, and 0.374% of residual nitrogen.

G. W. R.

Calcium Fixation by Animal Tissues. VII and VIII. E. FREUDENBERG and P. GYÖRGY (*Biochem. Z.*, 1922, **129**, 134—137; 138—143).—VII.—The ultra-filtration of calcium from a serum solution is accelerated by addition of potassium chloride more than by nitrate, acetate, phosphate, or hydrogen carbonate. Anions also influence the swelling of cartilage, the imbibition being greater for calcium chloride than nitrate or acetate. Fixation of calcium is inhibited by creatine or ethylamine.

VIII.—Formaldehyde and dextrose inhibit fixation of calcium by cartilage, but ethyl alcohol and acetone in decinormal solution are without action. Calcium fixation is accelerated by rise of temperature.

H. K.

Dyeing of Deaminated Wool. W. W. PADDON (*J. Physical Chem.*, 1922, **26**, 384—389).—Ordinary white wool, and the same material which had been deaminated by treating with nitrous acid at 4° and subsequently boiling, has been dyed by orange II and lake scarlet-R and the amount of dye removed from the bath determined. The change in the P_H value at the end of the operation was also determined. The P_H values have been plotted against the quantity of dye removed, and curves very similar in shape and position obtained; the differences between the two curves could well be attributed to experimental errors. The results show that the amino-groups in wool play no part whatever in the dyeing of that fibre by acid dyes.

J. F. S.

Toxin of the Fish, *Plotosus anguillaris*. I. KABESHIMA (*Nippon Biseibutsugakki Zasshi*, 1918, **6**, 45—270; *Jap. Med. Literature*, 1920, **5**, 23—24).—Plototoxin, a poison occurring in the fish, *Plotosus anguillaris*, consists of two active substances, *plotospasmin* and *plotohæmolysin*, which may be separated by

adsorption methods. The experimental work is concerned with the physiological behaviour of these two substances, and with the effect of heat, light, and shaking on their potency.

CHEMICAL ABSTRACTS.

Fatty Matters in the Sea Urchin. KATSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1922, **43**, 243—257).—Analysis of the sea urchin gave: water 45·31%, dry substance 54·69%, total nitrogen 2·43%, crude fat 12·91%, crude ash 13·22%, and phosphorus 0·41%. The crude fatty matter contained lecithin 19·628%, kephalin 1·736%, cholesterol 5·585%, and fat 73·051%. The fat gave 19·181% of saturated acids (mainly palmitic acid, with small quantities of stearic or myristic acid) and 53·870% of unsaturated acids which gave four bromides containing 66·26%, 61·20%, 55·25%, and 43·57% of bromine, respectively. The properties and composition of the lecithin and kephalin were in good agreement with those from the hen's egg.

K. K.

Presence of Aromatic Hydroxy-acids in Urines. G. DE SANCTIS and Q. FIORI (*Boll. Chim. Farm.*, 1922, **61**, 97—102).—The authors discuss this subject and describe the isolation of hydroparacoumaric or β -*p*-hydroxyphenylpropionic acid from the urine of a patient to whom no aromatic medicaments had been administered by ingestion. The acid is derived from the tyrosine of food under the influence of intestinal putrefaction. T. H. P.

Hæmatoporphyrin in the Urine in Cases of Lead Poisoning. O. SCHUMM (*Z. physiol. Chem.*, 1922, **119**, 139—149).—On examining several samples of urine from patients suffering from lead poisoning, it was found that a hæmatoporphyrin identical with the hæmatoporphyrin from fæces, or one resembling it very much, was present either alone or in preponderance in the urine.

S. S. Z.

Estimation of Urinary Colloids by the Gold Number. B. OTTENSTEIN (*Biochem. Z.*, 1922, **128**, 382—390).—The author has determined the gold number of dialysed urine containing colloids both of normal persons and of pathological cases. In normal urine, the gold number varies between 7 and 3·5, and is independent of the reaction of the urine. In pathological cases, there is considerable variation.

H. K.

The Proteolytic Enzymes in Albuminous Urines. S. G. HEDIN (*Z. physiol. Chem.*, 1922, **119**, 264—279).—Strongly albuminous urine, when previously kept acid, digests its protein or added casein in alkaline solution more readily than when it is previously kept in weakly alkaline solution. It is suggested that the urine contains an inhibitory substance which is decomposed by acid. The action of trypsin on casein and peptone is inhibited to a greater extent by the addition of urine previously kept alkaline than by that of urine previously kept acid.

S. S. Z.

Chromic Acid Nephritis. R. H. MAJOR (*Bull. Johns Hopkins Hosp.*, 1922, **33**, 56—61).—A fatal case of nephritis, consequent on the cauterisation of a wound with chromic acid, is described. The maximum concentrations in the blood, expressed as mg. per 100 c.c., were: non-protein nitrogen, 373; urea nitrogen, 340; creatinine, 17; creatine, 19; uric acid, 9; sugar, 220. The plasma carbon dioxide capacity fell to 31%, and the plasma chlorine remained low, about 400 mg. per 100 c.c.

CHEMICAL ABSTRACTS.

Physiological Action of Proteinogenic Amines. V. J. ABELIN (*Biochem. Z.*, 1922, **129**, 1—49).—Experiments on rats show that substances such as tyramine, phenylethylamine, adrenaline, choline, pilocarpine, and atropine, which stimulate the vegetative nervous system, influence the metabolic processes. There is increased gaseous metabolism, mobilisation of glycogen, hyperglycemia and glycosuria, and increased excretion of urine. Tyramine and phenylethylamine reinforce the action of each other, and, in conjunction with small quantities of thyroid preparations which in themselves are inactive, produce a strong increase in the gaseous metabolism. Histamine has no influence on the gaseous metabolism, whilst acetylcholine depresses it.

H. K.

The Cinchona Alkaloids. H. W. ACTON (*Lancet*, 1922, i, 124—128; from *Physiol. Abstr.*, 1922, **7**, 58).—The “cinchonine series”—cinchonine, cupreidine, and quinidine—which are dextro-rotatory are more powerful in their physiological action than their lævorotatory isomerides of the “cinchonidine series”—cinchonidine, cupreine, and quinine. The hydroalkaloids are more stable and in many respects more active than the natural alkaloids. Of the alkyl-hydroalkaloids, the higher members are more toxic than the lower members to mammals, protozoa, and bacteria.

W. O. K.

Surface Activity and Toxic Action of Saponins. LUDWIG KOFLER (*Biochem. Z.*, 1922, **129**, 64—72).—The author has measured the hæmolytic index, the drop number, and the fish index (the concentration of substance which kills a young roach, 0.1—0.5 gram in one hour) of eight saponins. There is no parallelism in these properties. The order of the drop numbers may even change with change in the concentrations studied. It is considered essential that in order to trace the relation between the surface activity and the physiological action, the concentration used in the surface tension measurements should be that used in the physiological experiment.

H. K.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Arsenious Acid on Bacterial Growth. R. COBET and V. VAN DER REIS (*Biochem. Z.*, 1922, **129**, 73—88).—No evidence was found that arsenious acid could stimulate the growth of bacteria. H. K.

Influence of Lactic Acid on Lactic Acid Fermentation. B. J. HOLWERDA (*Biochem. Z.*, 1922, **128**, 465—481).—As the result of conductivity measurements and colorimetric measurements on lactic acid and of potentiometric measurements on mixtures of lactic acid and sodium or calcium lactate, the dissociation constant of lactic acid is found to be 1.5×10^{-4} at 25°. Bredig's diazoacetic ester method gives values for the dissociation constants of organic acids which are 8 to 10% too low. Lactic acid fermentation in a whey containing peptone is inhibited by undissociated lactic acid. H. K.

Zymase Formation in Yeast. I. F. HAYDUCK and H. HAEHN (*Biochem. Z.*, 1922, **128**, 568—605).—The distribution of zymase in bottom beer-yeast and in distillery yeast is different. Bottom beer-yeast contains free zymase and zymase combined with protoplasm, the former zymase alone being active after treatment of such yeast by Lebedev's process or in yeast fixed by acetone, even in the presence of toluene. Distillery yeast, which gives no active press juice or active zymase after acetone fixation, contains only combined zymase, its activity being inhibited by toluene owing to formation of impermeable emulsions with the lipid membranes of the cells. Experiments on a torula yeast poor in zymase showed that cultivation in a wort with a weak air supply caused an increased content of zymase and parallel with this an increased nucleic acid metabolism. The differences observed in the two first-named yeasts is attributed to differences in their mode of living. H. K.

A New Acid Fermentation produced by *Sterigmatocystis nigra*. MARIN MOLLIARD (*Compt. rend.*, 1922, **174**, 881—883).—When *Sterigmatocystis nigra* [*Aspergillus niger*] is grown on a medium very poor in nitrogen and mineral salts the main, and in some cases the only acid produced is *d*-glucosic acid. If only the nitrogen is low in the medium then citric acid predominates in the products, but if phosphorus is the nutrient which is lacking there is marked acidity produced, due in this case to a mixture of citric and oxalic acids. If, on the other hand, potassium is the missing nutrient, then there is an accumulation of oxalic acid. On a properly balanced medium only traces of free acid are produced. W. G.

A New Antiseptic with High Iodine Content. (Diethylene Disulphide Tetraiodide.) C. BACHEM (*Biochem. Z.*, 1922, **129**, 190—193).—The properties of diethylene disulphide tetraiodide,

$\text{SI}_2 \langle \begin{smallmatrix} \text{CH}_2 \cdot \text{CH}_2 \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \rangle \text{SI}_2$, containing 81% of iodine have been examined with a view to its use as a wound antiseptic. Its most striking action is its powerful inhibitory action on bacterial growth. It is not decomposed by proteins, is relatively non-toxic to rabbits, but has a disagreeable odour. The iodine is liberated slowly by water and completely by ether. H. K.

Relationships between Antiseptic Action and Chemical Constitution, with Special Reference to Compounds of the Pyridine, Quinoline, Acridine, and Phenazine Series. C. H. BROWNING, J. B. COHEN, R. GAUNT, and R. GULBRANSEN (*Proc. Roy. Soc.*, 1922, [B], **93**, 329—366).—The bactericidal action of derivatives of pyridine, quinoline, acridine, and phenazine on *Staphylococcus aureus* and on *Bacillus coli* has been investigated. In the pyridine, quinoline, and phenazine series no compound has been found possessing an activity equalling that of certain diaminoacridine derivatives, particularly in presence of serum which inhibits their efficiency. In the acridine group, the introduction of amino-groups enhances the antiseptic potency, and this effect is in general weakened again by alkylation or acetylation, or replacement by hydroxyl. The methochloride is equal to or better than the hydrochloride of the same base. Substitution of the methyl group by another radicle is without much effect. The carboxyl group seems to depress the antiseptic property. The comparative efficiencies for *S. aureus* and *B. coli* do not invariably run parallel.

The following new compounds have been prepared. α -Dimethylaminopyridine methiodide, fine, colourless needles which turn yellow in the air; dinitro- β -naphthaquinoline, m. p. 245—247°; diamino- β -naphthaquinoline, pale yellow plates, m. p. 250°; 2:7-diacetyl-diaminoacridine chloroacetate, yellow crystals; 2:7-diaminoacridine-chloroacetate, red crystals; 2:7-diaminoacridine chloroacetanilide, brown crystals; 2-amino-9-phenyl-3-methylnaphthacridine, yellow needles, m. p. 269—271°; 7-amino-2-dimethylamino-6-methylphenazine methochloride, microcrystalline powder with dark green lustre; 2-dimethylamino-6-methylphenazine methiodide, brownish-black plates; N-methyltetrahydroquinoline-2-aminophenazine methochloride, green, iridescent mass (zinc salt). W. O. K.

The Relation between Chemical Constitution and Antiseptic Action in the Coal Tar Dyes. THOMAS H. FAIRBROTHER and ARNOLD RENSHAW (*J. Soc. Chem. Ind.*, 1922, **41**, 134—144).—The action of numerous dyes on cultures of paramoecia and of various bacteria was examined.

It was found that efficient antiseptic action was dependent on the presence in the molecule of free amino-groups, but that the effect of these was neutralised by the presence of sulphonic, carboxyl, nitro-, and naphthylamino-groups. The most actively antiseptic dyes were those of the triphenylmethane series and the oxazines. The triphenylmethane dyes were especially active in the simple salt form and in the form of a double salt with a metallic

salt of the same acid as the dye (for example, crystal-violet zinc chloride). Some of the dyes possessed a selective action; thus the oxazines in general killed gram-positive organisms and left the gram-negative ones unaffected.

Antiseptic activity is associated with the possibility of tautomeric change in the molecule, and with the existence of the substance in the molecular dispersoid form. It does not vary with intensity of colour or with molecular weight.

C. R. H.

Influence of Selenium and Radium on the Germination of Seeds. J. STOKLASA (*Compt. rend.*, 1922, 174, 1075—1077).—Both selenites and selenates exert a markedly injurious influence on the germination of seeds. Selenates are much less toxic than selenites, and at great dilution even exert a favourable influence. This injurious action of selenium compounds is to a large extent neutralised by the radioactivity of the medium. In the absence of selenium compounds, the germinative energy of seeds is considerably increased by water charged with radioactive emanation.

W. G.

Studies on Photosynthesis. IV. Carbon Dioxide Assimilation by Leguminosæ. S. KOSTYTSCHEV (*Ber. Deut. bot. Ges.*, 1922, 40, 112—119; cf. this vol., i, 307, 308).—In gasometric experiments with the concentration of carbon dioxide above that in the atmosphere, carbon dioxide assimilation by Leguminosæ is markedly greater than by other plants. The presence of nitrates in the soil increases the assimilation; the effect is, however, not shown in short period experiments. Alder species although possessing nodules on their roots do not resemble the Leguminosæ in their energy of carbon dioxide assimilation.

G. W. R.

Aluminium Salts and Acids at Varying Hydrogen-ion Concentrations, in Relation to Plant Growth in Water Cultures. S. D. CONNER and O. H. SEARS (*Soil Sci.*, 1922, 13, 23—41).—The results of the investigation showed that the toxicity of aluminium salts is due to the aluminium-ion more than it is to the hydrogen-ion in the case of such plants as barley and that this toxicity is reduced when much phosphate is present in the nutrient medium. Acid soils are toxic to many plants mainly because they contain readily soluble aluminium salts.

W. P. S.

The Part Played by Lipoids in the Metabolism of Plant Cells. II. FRIEDRICH BOAS (*Biochem. Z.*, 1922, 129, 144—152).—The action of solanine, bile acids, urethane, quinine, and cocaine has been examined on the fermenting capacity of yeast-cells. Saponaceous substances like solanine and the bile acids, in presence of neutral salts, have an inhibitory action attributed to a change of the lipid structure of the cell, causing increased permeability. Quinine and cocaine were found to promote fermentation.

H. K.

Influence of Selenium on Plant Evolution in the Presence or Absence of Radioactivity. J. STOKLASA (*Compt. rend.*, 1922, **174**, 1256—1258).—Sodium selenate at a concentration of 5×10^{-6} up to 10^{-5} gram-atoms of selenium per litre produces a stimulating effect on the growth of maize, but at higher concentrations it is toxic. Selenites are more toxic than selenates. This injurious action of selenium compounds is almost completely neutralised by the presence of radium emanation to the extent of 0.0000056 mg. per plant. Selenium dioxide is much more toxic than sulphur dioxide towards plants.

W. G.

Absorption of Ions by the Roots of Living Plants. I. Absorption of the Ions of Calcium Chloride by Pea and Maize. GLADYS M. REDFERN (*Ann. Bot.*, 1922, **36**, 167—174).—Seedlings of pea and maize grown in culture solutions were transferred to solutions of calcium chloride of varying concentration. The percentage absorption of calcium is in every case greater than the percentage absorption of chlorine, the difference being less in the most dilute solutions used (0.001N). The P_H remains approximately constant, potassium and magnesium diffusing from the roots and presumably replacing the calcium absorbed. Equilibrium is reached in the intake of this salt within the first twenty-four hours in the case of peas and within the first forty-eight hours in the case of maize. No trustworthy evidence of periodicity in absorption was obtained.

G. W. R.

The Genesis of Amylase and Maltase in Plants. W. PALLADIN and HELENE POPOV (*Biochem. Z.*, 1922, **128**, 487—494).—In green and etiolated leaves of various plants, some diastase remains fixed by the protoplasts even after protracted autolysis and thorough percolation in water, and some passes into solution. More diastase is found fixed in young leaves than in old leaves and none is found in dead leaves.

H. K.

The Hydrocyanic Acid Question. K. SIEGFRIED (*Schweiz. Apoth. Ztg.*, 1921, **59**, 325; cf. *Schweiz. Wochschr.*, **47**, 541; Rosenthaler, A., 1921, i, 484; Wester, *Pharm. Weekblad*, 1914, **51**, 207).—Old cherry-laurel leaves yield low percentages of hydrocyanic acid. Recent estimations in fresh leaves showed 0.253%, and in older leaves on the same branches 0.185%, both high results.

CHEMICAL ABSTRACTS.

The Hydrocyanic Acid Question. VIII.—Plants containing Hydrocyanic Acid and Saponin. IX.—Hydrocyanic Acid Content of Cherry-laurel Leaves Infected by Fungi. X.—Influence of Lesions on the Hydrocyanic Acid Content of Cherry-laurel Leaves. L. ROSENTHALER (*Schweiz. Apoth. Ztg.*, 1921, **59**, 466—469; 641—643, 643—647; cf. A., 1921, i, 484).—VIII.—Of one hundred Argentinian plants examined, fourteen yield hydrocyanic acid but do not contain saponin, eighty-five contain saponin but do not yield hydrocyanic acid, whilst only one (*Manihot tweedienus*) contains saponin and also yields hydrocyanic acid.

IX.—Normal leaves had an average of 0.23 and 0.21% of hydrogen cyanide in two series; infected leaves had only 0.13 and 0.165%. In normal young sprouts, the content of hydrogen cyanide decreases with distance from the centre of growth; infected sprouts show irregular amounts.

X.—Cuts were made into half of the leaf-blade, both halves being separately examined later. Lesions made in August and September showed no increase in hydrogen cyanide content.

CHEMICAL ABSTRACTS.

Comparative Plant Chemistry. II. The Berry Fruit of some Caprifoliaceæ. GISELA NOWAK and JULIUS ZELLNER (*Monatsh.*, 1921, **42**, 293–310).—The fruit (flesh and seeds together) of the following species of Caprifoliaceæ was submitted to qualitative and quantitative chemical examination: *Lonicera xylosteum*; *L. nigra*; *Viburnum opulus*; *V. lantana*; *Sambucus nigra*; *S. racemosa*; and *Symphoricarpus racemosa*. There was found a marked general similarity among the different species which can be expressed in the following average results, calculated on the dry materials: water-soluble, 50%; invert-sugar, mainly dextrose, 25%; pectin, 3%; free acid, 3%; water-soluble inorganic salts, 3%; total ash, 4%; proteins, 7%; 1.5% waxy substances, small quantities of tannin. There are several fairly wide variations from the mean, for example *Symphoricarpus racemosa* has about 55% invert-sugar and *Sambucus racemosa* gave about 30% of fatty oil, which in this case only is contained in the flesh of the fruit as well as in the seeds. The presence of a crystalline substance xylostein, m. p. 124°, in *L. xylosteum* was confirmed; it is probably the poisonous principle of the berry; and isovaleric acid was found in *V. opulus*. The oils from the different species had the following constants: *L. xylosteum*, saponification number (*S*), 184.85; iodine number (*I*), 132.8; unsaponifiable (*U*), 4.9%; oxygen taken up during drying (*O*), 12%; *L. nigra* (*S*), 156.53; (*I*), 101.4; (*U*), 21.6%; (*O*), 8.2%; n_{23}^{23} 1.494; *V. opulus* (*S*), 192.3; (*I*), 108.0, (*U*), 2.3%; (*O*), 7.1%; n_{23}^{23} 1.484, d_{15}^{15} 0.9252; *V. lantana*, (*S*), 192.5; (*I*), 121.0; (*O*), 7.3%; n_{23}^{23} 1.486; *Sambucus nigra* (*S*), 190.0; (*I*), 157.8; (*U*), 4.5%; (*O*), 15.1%; n_{23}^{23} 1.485; d_{15}^{15} 0.9407; *S. racemosa* (*S*), 190.8; (*I*), 162.0; (*U*), 0.6%; (*O*), 16.0%; n_{23}^{23} 1.485; d_{15}^{15} 0.934; *Symphoricarpus racemosa* (*I*), 131.8. E. H. R.

The Structure of the Cotton Hair and its Botanical Aspects.

HUMPHREY JOHN DENHAM (*Trans. Text. Inst.*, 1922, **13**, 99–112).—A critical and historical review is given of the microscopy and development of the cotton hair, and the facts are discussed in the light of modern theories, especially of the nature of cell-walls in general. It is suggested that as there are so few real botanical abnormalities about cotton, it offers a promising field for the study of cell-walls, including the biochemistry of polysaccharide deposition.

J. C. W.

The Chemical Constituents of Raw Cotton. ROBERT GEORGE FARGHER and JOHN CHARLES WITHERS (*Trans. Text. Inst.*, 1922, **13**, 1–16).—An exhaustive review of the present state

of knowledge of the ash, wax, protein, pigments, and cellulose in raw cotton, with a short account of the behaviour of the minor constituents in technical operations. More than one hundred references to the literature are cited.

J. C. W.

The Chemical Constituents of Green Plants. XVIII. The Acids from the Berry of the Mountain Ash (*Pyrus aucuparia*) which are precipitated by Lead Acetate. HARTWIG FRANZEN and RUDOLF OSTERTAG (*Z. physiol. Chem.*, 1922, **119**, 150—165).—On precipitating the acids of the berry of the mountain ash and extracting the fraction with ether, malic acid is mainly obtained. Traces of citric and succinic acids may also be present. Liebig's statement that this berry contains considerable quantities of tartaric and citric acids cannot be confirmed.

S. S. Z.

Tyramine (*p*-Hydroxyphenylethylamine) as the Active Principle of the Drug *Semina cardui* Mariæ. ALFRED ULLMANN (*Biochem. Z.*, 1922, **128**, 402—406).—An aqueous extract of the powdered drug was precipitated with phosphotungstic acid and the bases were fractionated by Kossel and Kutscher's process. The final filtrate had a strong pressor action, due to the presence of tyramine which was isolated by extraction with amyl alcohol and identified by its benzoyl derivative and colour reactions.

H. K.

Classification of Soil Moisture. F. W. PARKER (*Soil Sci.*, 1922, **13**, 43—54).—It is shown that the dilatometer method (A., 1917, i, 510) does not measure different forms of water in soils and that soils do not contain a considerable quantity of inactive or unfree water. Investigations on the rate of evaporation of water from soils, the vapour pressure at different moisture contents, the equilibrium relations with seeds, and depression of the freezing point due to solid material yielded results which did not indicate the presence of different forms of water in soils. Although the old classification of soil moisture into hygroscopic, capillary, and gravitational water has certain objections it seems to be the best yet offered.

W. P. S.

Relation of the Phosphoric Acid of the Soil to Pot Experiments. G. S. FRAPS (*Texas Agr. Exp. Stat. Bull.*, 1920, **267**).—Soils which contain more than the average amount of total nitrogen tend to give higher yields of phosphate to crops than soils containing the same quantities of active phosphate, but the average amounts of total phosphate and nitrogen. Soils containing the same amounts of active phosphate tend to withdraw larger amounts of phosphate when these soils have a higher nitrogen content and a higher total phosphate content. When the soils are arranged in groups according to the amounts of phosphate withdrawn by the crops in the pot experiments, there is a relationship between the amount of phosphate removed from the soil and the active phosphate in the soil, the correlation coefficient for the active phosphate being 0.57, and for total phosphate 0.45. The presence of lime introduces a complication.

CHEMICAL ABSTRACTS.

Organic Chemistry.

Migration of a Double Linking. JOSÉ PUYAL (*Anal. Fis. Quím.*, 1922, 20, 80—83).—*iso*Amyl alcohol (γ -methylbutanol) was dehydrated at 400° , using, as a catalyst, a preparation of infusorial earth. The amino-alcohol prepared from the resulting hydrocarbon by way of the bromohydrin was identical with the base of stovaine, namely, methylethyldimethylaminomethyl carbinol. This alcohol and the corresponding bromohydrin are ordinarily derived from β -methyl- Δ^α -butylene, $\text{CH}_3\cdot\text{CMe}\cdot\text{CH}_2\text{Me}$. The dehydration of the alcohol used must thus have produced this hydrocarbon and not the expected β -methyl- Δ^β -butylene. It is supposed that γ -methyl- Δ^α -butylene, $\text{CHMe}_2\cdot\text{CH}\cdot\text{CH}_2$, is first formed, and that the β -methyl- Δ^α -butylene results from a rearrangement at the temperature of the reaction by means of a series of alternate hydrations and dehydrations. G. W. R.

Conversion of Allyl Alcohol into Glyceryl Chloro- and Bromo-hydrins. JOHN READ and ERIC HURST (*T.*, 1922, 121, 989—999).

The Action of Acetylene on the Sodium Derivatives of Ketones and the Preparation of Dialkylethinylcarbinols. R. LOCQUIN and SUNG WOUSENG (*Compt. rend.*, 1922, 174, 1427—1429).—When acetylene is passed into a solution of a methyl ketone in an inert solvent containing sodium ethoxide or sodamide, an acetylenic tertiary alcohol is obtained, but with very poor yield (cf. Ruzicka and Fornasir, A., 1919, i, 193). The yield is much improved if the sodium derivative of the ketone is first prepared by means of sodamide and then into this material in ether or benzene the acetylene is passed under pressure. In addition to the required tertiary alcohol, a small amount of a hydrocarbon and some bi-tertiary acetylenic γ -glycol of the type $\text{OH}\cdot\text{CRR}'\cdot\text{C}:\text{C}\cdot\text{CRR}'\cdot\text{OH}$, is obtained. Thus from methyl isohexyl ketone, *methylisohexylethinylcarbinol*, b. p. $83\text{--}85^\circ/10$ mm. and $187\text{--}188^\circ/760$ mm., giving an *allophanate*, m. p. $114\text{--}115^\circ$, is obtained, together with some *methylethylisohexylcarbinol*, b. p. $92\text{--}93^\circ/15$ mm., and its *allophanate*, m. p. $110\text{--}111^\circ$, and the two stereoisomeric forms of a bi-tertiary acetylenic γ -glycol, b. p. $183\text{--}184^\circ/12$ mm., of which the *a*-form has m. p. $66\text{--}68^\circ$, and the *b*-form has m. p. 35° . From methyl nonyl ketone the products are *methylnonylcarbinol*, b. p. $127\text{--}128^\circ/11$ mm., its *allophanate*, *methylethyl-nonylcarbinol*, b. p. $131\text{--}134^\circ/14$ mm., and the *a*- and *b*-forms of the γ -glycol, b. p. $237\text{--}238^\circ/10$ mm., and having m. p. $91\text{--}92^\circ$ and $70\text{--}71^\circ$, respectively. Dipropyl ketone yields *dipropylethinylcarbinol*, b. p. $69\text{--}71^\circ/12$ mm., d_4^{25} 0.8691, n_D^{25} 1.4443, and its *allophanate*, m. p. 143° , *dipropylethylcarbinol*, b. p. $78\text{--}79^\circ/16$ mm., and its *allophanate*, m. p. 124° , and the γ -glycol [$\delta\eta$ -*dipropyl- Δ -decinene*].

$\delta\eta$ -diol], b. p. $174^{\circ}/18$ mm., m. p. 118 — 119° . Methyl *tert.*-butyl ketone gives *methyltert.butylethynylcarbinol*, b. p. 142 — 144° , d_4 0.8806 , n_D 1.4441 , and its *allophanate*, m. p. 156° , *methyltert.butylethylcarbinol*, b. p. 152° , and its *allophanate*, m. p. 134 — 135° , and the γ -glycol, b. p. 148 — $150^{\circ}/14$ mm., of which the α -form has m. p. 88 — 89° and the β -form m. p. 78° . W. G.

The Unsaturated Reduction Products of Sugars and their Transformations. IV. A Glucoside-like Derivative of a Simple Hydroxyketone, δ -Acetyl-*n*-butyl Alcohol. The Constitution of Fructose. MAX BERGMANN and ARTHUR MIEKELEY (*Ber.*, 1922, **55**, [B], 1390—1403).—In a previous communication (this vol., i, 227), it has been shown in the cases of α - and β -methylglucosides and α - and β -methylglucosides that substances of similar constitution may possess very varying degrees of stability and that conclusions with respect to the finer structure of substances which are based on their comparative stability are particularly liable to error. The point appears to be of particular importance for the chemistry of the sugars, and is to be elaborated in a series of papers, of which this is the first.

The relationships of δ -acetyl-*n*-butyl alcohol and its semi-acetal have been investigated. The parent substance is characterised by the extreme readiness with which it reacts with methyl alcohol in the presence of acids, which in concentration even as low as $N/2000$ bring about quantitative acetalisation at the atmospheric temperature in a short time. In this respect, δ -acetyl-*n*-butyl alcohol is more reactive than any aldehydic or ketonic alcohol which has been investigated. As is to be expected, the hydrolysis of the semi-acetal is effected with unusual ease by dilute aqueous acids (the same is true of γ -acetylpropyl alcohol). The observations have considerable interest with reference to the structure of sucrose, in which the 1 : 2-oxide structure has been postulated (cf. Haworth and Law, T., 1916, **109**, 1344), as a result of the comparison of sucrose and its hydrolytic products with ethylene oxide and similar unstable systems. The properties of acetylbutyl alcohol semi-acetal show that the ready hydrolysis observed with sucrose is not by any means necessarily dependent on the presence of the ethylene oxide ring, and that further investigation of the structure of the fructose residue is necessary.

δ -Acetyl-*n*-butyl alcohol, $\text{COMe}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, or $\text{OH}\cdot\text{COMe}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{O}-\text{CH}_2\end{smallmatrix}\rangle\text{CH}_2$, has d_4^{21} 1.0072 , n_D^{21} 1.4438 . It is transformed by methyl-alcoholic hydrogen chloride into the corresponding *semi-acetal*, $\text{OMe}\cdot\text{COMe}\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{O}-\text{CH}_2\end{smallmatrix}\rangle\text{CH}_2$, a mobile, very volatile liquid, with a marked odour of camphor, b. p. $76^{\circ}/99$ mm., $d_4^{19.5}$ 0.94702 , d_4^{20} 0.94642 , $d_4^{21.5}$ 0.94445 , $n_D^{19.5}$ 1.4275 , n_D^{20} 1.4272 , $n_D^{21.5}$ 1.4264 , which can also be prepared in a similar manner from the anhydride of δ -acetyl-*n*-butyl alcohol, $\text{CMe}\langle\begin{smallmatrix}\text{CH}\cdot\text{CH}_2 \\ \text{O}-\text{CH}_2\end{smallmatrix}\rangle\text{CH}_2$. The velocity of the former reaction is measured by determining the amount of

unchanged alcohol after given intervals, this being effected by treatment with a known quantity of acetic anhydride dissolved in pyridine, and final estimation of unused acetic acid. The rate of the latter reaction is measured by treating a known amount of the solution of the anhydride in methyl alcoholic hydrogen chloride with an excess of aqueous hydrogen carbonate solution, oxidising the unchanged anhydride with an excess of an ethereal solution of perbenzoic acid, and estimating the excess of the latter by titration of the iodine liberated after addition of potassium iodide.

The velocity of hydrolysis of the *cycloacetal* in water and aqueous hydrochloric acid has also been examined. The method adopted consists in making the experimental solutions alkaline with potassium carbonate after given intervals of time and extracting them thoroughly with ether. After removal of the latter, the residue is acetylated with acetic anhydride in the presence of pyridine. The excess of acid anhydride is destroyed by water, the solution is exactly neutralised by sodium hydroxide, and the amount of acetyl present estimated by hydrolysis.

The $\alpha\delta$ -structure of the oxygen bridge in glucal has been largely adopted on account of its sensitiveness towards acids and the coloration it gives with a pine shaving. Since it is found that these reactions are also shared by γ -acetyl-*n*-butyl alcohol and γ -acetyl-*n*-propyl alcohol, the furoid structure can no longer be regarded as established, and further examination of the ring system of glucal and the related glucosides and polysaccharides is necessary.

H. W.

The Autoxidation of Ethyl Ether. A. M. CLOVER (*J. Amer. Chem. Soc.*, 1922, **44**, 1107—1118).—Ethyl ether absorbs oxygen from the air very slowly at first with the formation of a peroxide by direct addition. The rate of peroxidation becomes much greater in time owing to the catalytic influence of acetaldehyde, which is formed by the spontaneous decomposition of the peroxide. To this peroxide the author assigns the constitution $\text{OEt}\cdot\text{CHMe}\cdot\text{O}\cdot\text{OH}$, which is most in accord with the properties of the compound. The active oxygen content of the pure peroxide is approximately that required for a substance formed by the addition of one molecule of oxygen to one molecule of ether, half the added oxygen being active. The peroxide is formed directly by the action of oxygen on ether. It is volatile and decomposes, especially under the influence of light, with the formation of carbon dioxide, methane, acetaldehyde, and alcohol. With acidified water, it reacts yielding hydrogen peroxide quantitatively. The peroxide is acidic in character. It is shown that hydrogen peroxide is not a primary product of the oxidation of the ether.

W. G.

Action of Dichloroethyl Ether, $\text{CH}_2\text{Cl}\cdot\text{CHCl}\cdot\text{OEt}$, on the Mixed Magnesium Derivative of Allyl Bromide. R. LESPIEAU (*Bull. Soc. chim.*, 1922, [iv], **31**, 412—414).—By the action of dichloroethyl ether on magnesium allyl bromide in ethereal solution, ϵ -chloro- δ -ethoxy- Δ^4 -pentene, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{OEt})\cdot\text{CH}_2\cdot\text{CH}:\text{CH}_2$, b. p. 158—158.5°, d^{17}_4 0.967, n^{17}_D 1.44, is obtained amongst other products,

the yield being small. On bromination it gives α -chloro- δ -dibromo- β -ethoxypentane, b. p. 143—144°/16 mm., d^{25}_D 1.630, n^{25}_D 1.5115.

W. G.

Hydrate of Ethylene Oxide. A. MAZZUCHELLI and R. ARMENANTE (*Gazzetta*, 1922, **52**, i, 338—346).—Investigation of the freezing-point diagram of the system water-ethylene oxide shows that this oxide forms only one hydrate, $C_2H_4O \cdot 7H_2O$, m. p. $12.8 \pm 0.1^\circ$. The hydrate forms large, transparent, tabular crystals or aggregates of radiating needles, apparently of the triclinic system, and exhibits a marked tendency to give supersaturated aqueous solutions. Its formation is accompanied by considerable contraction and if, as is usually assumed, the molecules of ordinary ice are dimeric and those of ice formed under pressures exceeding 2000 atmospheres monomeric, the water in ethylene oxide hydrate exists as simple molecules.

T. H. P.

Organic Derivatives of Selenic Acid. JULIUS MEYER and WALTER WAGNER (*Ber.*, 1922, **55**, [B], 1216—1222).—In continuation of their work on the similarity of selenic and sulphuric acids (cf. Meyer and Wagner, this vol., ii, 372), the behaviour of selenic acid towards organic substances has been examined. Close analogies are again found, but the organic derivatives of selenic acid are distinguished by a much greater liability to internal oxidation, whilst, also, selenic acid appears in some instances to exert a powerful condensing action.

Methyl selenate, Me_2SeO_4 , is prepared as a yellow liquid, d^{25}_D 1.652, n 1.4316, by the action of methyl iodide on silver selenate. It could neither be caused to crystallise nor distilled without decomposition. It deposits selenium at the atmospheric temperature. It is hydrolysed readily by aqueous acids or alkalis. It can be used as a methylating agent in the same manner as methyl sulphate. *Ethyl selenate* is prepared similarly; it has d^{25}_D 1.501, n 1.4445. Propyl selenate could not be obtained by the action of propyl iodide on silver selenate.

Methyl hydrogen selenate is an exceedingly unstable substance the lead and potassium salts of which are described; they decompose very readily. Ethyl hydrogen selenate and its lead, strontium, and potassium salts are too unstable to be analysed. Similar observations are recorded with *n*-propyl hydrogen selenate and its lead, strontium, calcium, and potassium salts.

Potassium phenyl selenate, $KO \cdot SeO_2 \cdot OPh$, colourless leaflets which are moderately stable toward air, is prepared by the action of potassium pyroselenate on a concentrated aqueous solution of potassium phenoxide; it is decomposed by hydrochloric acid into phenol and selenic acid.

The action of selenic acid on phenol is very energetic and proceeds differently from that of sulphuric acid. It was not found possible to isolate a phenolselenonic acid from the products of the change, which appear to consist of complex substances of unknown constitution.

Concentrated selenic acid oxidises aniline with explosive violence;

by mixing the substances in the presence of ether, aniline selenate is obtained as a very unstable, colourless salt. H. W.

The Auto-oxidation of Organic Sulphur Compounds. MARCEL DELÉPINE (*Compt. rend.*, 1922, **174**, 1291—1293).—A few further experiments on the auto-oxidation of organic sulphur compounds are described (cf. A., 1910, i, 295, 545, 612; 1911, ii, 1061; 1912, ii, 509) in which it is shown that only a very small amount of the organic vapour is oxidised and the action ceases long before either the oxygen or the organic compound present is used up. It is suggested that these organic sulphur compounds act as their own anti-oxygens (cf. Moureu and Dufraisse, this vol., i, 250). W. G.

The Chlorinated Dialkyl Sulphides. WILLIAM JACKSON POPE and JAMES LEONARD BRIERLEY SMITH (T., 1922, **121**, 1166—1170).

The Sulphilimines, a New Class of Organic Compounds containing Quadrivalent Sulphur. FREDERICK GEORGE MANN and WILLIAM JACKSON POPE (T., 1922, **121**, 1052—1055).

Bromination of Acids in the α -Position. CHARLES FREDERICK WARD (T., 1922, **121**, 1161—1165).

Studies of the Constitution of Soap Solutions. Sodium Behenate and Sodium Nonoate. ORIEL JOYCE FLECKER and MILLICENT TAYLOR (T., 1922, **121**, 1101—1109).

The Effect of High Concentration of Salt on the Viscosity of a Soap Solution. ANNIE MILLICENT KING (*J. Soc. Chem. Ind.*, 1922, **41**, 147—148).—The addition of increasing quantities of salt to a solution of sodium palmitate containing 0.5 gram-mol. in 1 kilo. of water was accompanied by a rapid increase in the viscosity, which, however, reached a very decided maximum of 10.5—10.6 C.G.S. units with a concentration of sodium chloride of 0.5N. On further addition of sodium chloride, the viscosity progressively declined to a value of 1.95 at a salt concentration of 0.88N, at which point the liquid commenced to form two heterogeneous layers preliminary to the formation of curd. The progressive addition of potassium chloride to potassium oleate solution caused a similar transition from a clear, mobile liquid to a stiff, transparent jelly, a clear, viscous liquid, and finally two liquid layers and curd separation. It is evident that this behaviour is general for soap solutions. G. F. M.

The Co-ordination Forms of Glycerides. AD. GRÜN (*Oesterr. Chem. Ztg.*, 1922, **25**, 73—74; cf. this vol., i, 420).—A further reply to Klimont (this vol., i, 517). H. W.

The Unsaturated Fatty Acids of Egg Lecithin. P. A. LEVENE and IDA P. ROLF (*J. Biol. Chem.*, 1922, **51**, 507—513).—In view of the results obtained with liver lecithin (cf. this vol., i, 424), egg lecithin has now been investigated. On hydrolysis,

this yields three unsaturated acids, namely, oleic, linolic, and arachidonic. Egg lecithin differs from liver lecithin in containing only a small proportion of highly unsaturated fatty acids.

E. S.

C₁₈ Fatty Acids. IV. A Rearrangement of the Benzilic Acid Type in the Aliphatic Series. BEN H. NICOLET and ALFRED E. JURIST (*J. Amer. Chem. Soc.*, 1922, **44**, 1136—1141).—When *θ*-diketostearic acid, obtained by the oxidation of *θ*-dihydroxystearic acid with chromic acid, is fused with potassium hydroxide at 160° *θ*-dihydroxystearic acid and α -hydroxy- α -octylsebacic acid are obtained. This is taken as evidence that *θ*-diketostearic acid is an intermediate product in the formation of α -hydroxy- α -octylsebacic acid from *θ*-dihydroxystearic acid by fusion with potassium hydroxide (cf. Le Sueur, T., 1901, **79**, 1313). This is probably the first recognised benzilic acid rearrangement of a compound of the type $R\cdot CH_2\cdot CO\cdot CO\cdot CH_2R'$. In the fusion of the diketo-acid with potassium hydroxide as described above pelargonic and azelaic acids are also formed by a modified Cannizzaro reaction.

Methyl θ-diketostearate, m. p. 55°, and *ethyl θ-diketostearate*, m. p. 50°, are described.

W. G.

The Esterification of Ethyl Hydrogen Diethylmalonate and of Diethylmalonic Acid. PHILIPPE DUMESNIL (*Bull. Soc. chim.*, 1922, [iv], **31**, 419—420).—In the esterification of ethyl hydrogen diethylmalonate by boiling alcoholic hydrochloric acid, a certain amount of ethyl α -ethylbutyrate is obtained along with the ethyl diethylmalonate. In the esterification of diethylmalonic acid under similar conditions, only a small amount of the ethyl ester is obtained, the main product being ethyl hydrogen diethylmalonate with a trace of ethyl α -ethylbutyrate.

W. G.

The Formation of Malic Acid. JOHN MORRIS WEISS and CHARLES R. DOWNS (*J. Amer. Chem. Soc.*, 1922, **44**, 1118—1125).—A preliminary study of the equilibrium between maleic, fumaric, and malic acids in aqueous solutions over the temperature range 140—200°. At the lower temperature, in aqueous solution, an equilibrium exists among the three acids, but at the higher temperature maleic acid substantially disappears and the equilibrium is between fumaric acid and *i*-malic acid. Further, at the higher temperature approximately the same end-point is reached whether starting with maleic, fumaric, *i*-malic, or *l*-malic acid. Malic acid does not appear to be necessarily an intermediate product in the transformation of maleic acid to fumaric acid. By simple boiling at atmospheric pressure, malic acid solutions are practically unchanged.

For the detection of small amounts of maleic acid in mixtures with fumaric and malic acids, the solution is saturated with respect to fumaric acid at 25°, and then the maleic acid is converted into fumaric acid by the addition of bromine and under the influence of the light from a mercury vapour quartz lamp. The solution

is again brought to 25° and well stirred, and the amount of fumaric acid separating is estimated. W. G.

The Configuration of the Simple α -Hydroxy-acids. KARL FREUDENBERG and FRITZ BRAUNS (*Ber.*, 1922, **55**, [B], 1339—1352).—It has been shown by Freudenberg (A., 1914, i, 924) that *l*-malic acid is configurationally related to *d*-glyceric and *d*-lactic acids in the grouping $-\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$. Since, further, the relationship of tartaric acid to dextrose has been established, it is only necessary to effect a definite transformation of tartaric acid to malic acid in order to complete the steric series of α -hydroxy-acids. The reduction of *d*-tartaric acid to *d*-malic acid has been effected previously, but the yields are minimal and the conditions are such that a Walden inversion might readily occur. The relationship of the two acids is, however, placed beyond doubt in the following manner.

Methyl *d*-tartrate is converted by a slight excess of acetyl chloride in the presence of methyl acetate into *methyl acetyl-d-tartrate*, m. p. 83—84°, $[\alpha]_D^{25} + 7.40^\circ$ in aqueous solution. The latter is transformed by thionyl chloride in the presence of dry chloroform and anhydrous pyridine into methyl acetyl chloromaleate, $[\alpha]_D^{25} + 3.1^\circ$, which is probably stereochemically not quite uniform by reason of a partial inversion at the halogenated carbon atom. The ester is hydrolysed at the atmospheric temperature by a saturated solution of hydrogen chloride in methyl alcohol (96%) and subsequently by aqueous hydrochloric acid (*d* 1.19), after which the aqueous solution of the acid is allowed to remain in contact with a zinc rod wrapped with a platinum wire until combined chlorine can no longer be detected. After purification through the lead salt, crystalline *d*-malic acid is obtained in 80% yield. It has $[\alpha]_D^{17} \text{ yellow} + 2.18^\circ$ in water (8.1%) — 1.84° in water (54.5%), + 5.90° in acetone and + 30.60° in pyridine, these values being in close harmony with those of *l*-malic acid quoted in the literature for the sodium *D*-line. The acid is identified further by conversion into the bisphenylhydrazide and amide.

The communication also contains a theoretical discussion of the regularities in steric series, the configuration systems of the simple hydroxy-acids and the monoses, and their mutual relationships, for details of which the original must be consulted.

H. W.

Sativic Acid. ERICH REINGER (*Ber. deut. Pharm. Ges.*, 1922, **32**, 124—131).—The progressive elimination of hydroxyl groups from sativic acid (tetrahydroxystearic acid) prepared by the oxidation of linoleic acid, was carried out by heating the acid with 60% sulphuric acid whereby 1 mol. of water was eliminated, and the unsaturated acid produced was converted by hydrogenation into trihydroxystearic acid. By repeating the operation with this acid, a dihydroxy-unsaturated acid and finally dihydroxystearic acid were obtained, from which a monohydroxy-unsaturated

acid and monohydroxystearic acid were prepared. The constitution of each of the unsaturated acids was determined by an examination of their oxidation products, and that assigned by Eckert (A., 1917, i, 317) to sativic acid, based on the products obtained from it by the action of an oxidising alkali fusion, was confirmed, namely

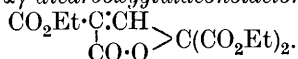
$\text{CH}_3 \cdot [\text{CH}_2]_4 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{CH}(\text{OH}) \cdot [\text{CH}_2]_7 \cdot \text{CO}_2\text{H}$.
The position of the double bonds in linoleic acid follows accordingly. The preparation and properties of the following substances are described: Trihydroxy-unsaturated acid, $\text{C}_{18}\text{H}_{34}\text{O}_5$, prepared by the elimination of 1 mol. of water from sativic acid, a thick, dark yellow oil of unpleasant odour which is converted by oxidation into the lactone of a trihydroxydecoic acid and by hydrogenation into $\lambda\mu$ -trihydroxystearic acid, a solid, white substance, m. p. 134—135°; from which the dihydroxy-unsaturated acid, $\text{C}_{18}\text{H}_{34}\text{O}_4$, was obtained as a reddish-yellow oil. On oxidation, this substance gave azelaic acid as one of its degradation products, and on hydrogenation it was converted into $\lambda\mu$ -dihydroxystearic acid, identical with that obtained by Hartley from liver and heart fat (*J. Physiol.*, 1909, 38, 353). The further elimination of water from this dihydroxystearic acid was achieved by heating with sulphuric-acetic acid, and the hydrogenation of the product gave the already known λ -hydroxystearic acid, m. p. 80°. G. F. M.

A Property of Ethyl Tartrate. THOMAS STEWART PATTERSON (T., 1922, 121, 1042—1044).

Racemic Acid in Solution. STUART WORTLEY PENNYCUICK (*J. Amer. Chem. Soc.*, 1922, 44, 1133—1136).—The author has measured the interfacial tensions between aqueous solutions of (a) *d*-tartaric acid, (b) *l*-tartaric acid, and (c) racemic acid and the following inert liquids: toluene, paraffin, and a solution of camphor in benzene. The results show that there is no measurable difference in interfacial tension against the several inert liquids between the *d*- and the *l*-acid, but the curve for the racemic acid shows a marked divergence from that of the active acids. These results point to the existence in solution of the racemic acid molecule. As the dilution increases, the curves indicate an increasing dissociation of the racemic acid into the *d*- and *l*-forms. W. G.

Some Transformations of Ethyl γ -Bromo- $\alpha\gamma$ -dicarboxyglutaconate. FRANZ FALTIS and CARLA RUIZ DE ROXAS (*Monatsh.*, 1921, 42, 459—470).—It was hoped that, by removing hydrogen bromide from the γ -bromo- $\alpha\gamma$ -dicarboxyglutaconic ester prepared by Guthzeit and Hartmann (A., 1910, i, 386) it would be possible to obtain ethyl allenetetracarboxylate, $\text{C}(\text{CO}_2\text{Et})_2 \cdot \text{C} \cdot \text{C}(\text{CO}_2\text{Et})_2$. This hope was not realised, but a number of new products were obtained. The bromo-compound was prepared by brominating the copper salt of ethyl dicarboxyglutaconate in chloroform solution. The bromodicarboxyglutaconic ester decomposes slowly when heated on the water-bath. Attempts to remove hydrogen bromide by heating the compound with diethyl-

aniline (method of Crossley and Le Sueur) were unsuccessful. When distilled in a vacuum, bromodicarboxyglutaconic ester decomposed into ethyl bromide and a lactonic compound which was proved to be *triethyl γ-hydroxy-α-γ-dicarboxyglutaconolactone*,



It distils at 212—216°/16 mm. as a green, fluorescent oil, crystallising in star-shaped crystals, m. p. 28—30°. In its intense fluorescence it resembles the structurally similar methylamino-citraconic methylimide and ethyl aminocyanofurancarboxylate, the only other known fluorescent aliphatic compounds. When the lactone is treated with alcoholic potassium hydroxide or potassium ethoxide, the lactone ring is not ruptured, but a carbethoxyl group is split off with a molecule of carbon dioxide and the enol potassium salt of *diethyl γ-hydroxy-α-carboxyglutaconolactone*, $\text{CO} \cdot \text{C}(\text{CO}_2\text{Et}) > \text{CH}$, is obtained. It forms a copper salt, lustrous, orange needles, losing water of crystallisation at 105°, m. p. 195° (decomp.). When ethyl bromodicarboxyglutaconate is treated with potassium ethoxide, it appears to behave in a similar manner to the above lactonic ester, losing a carbethoxy-group and carbon dioxide and leaving a product which gives an intense bluish-violet coloration with ferric chloride, and forms a green copper salt containing bromine.

E. H. R.

Steric Transformations with α-Sulphonedialiphatic Acids.

R. AHLBERG (*Ber.*, 1922, **55**, [B], 1279—1281).—A preliminary communication due to the recent publication by Fitger (this vol., i, 107, 108).

The same α-sulphonedibutyric acid, $\text{SO}_2(\text{CHEt} \cdot \text{CO}_2\text{H})_2$, m. p. 152°, is obtained by the oxidation of *meso*-, *r*-, or optically active α-thiodibutyric acids with potassium permanganate. The experiments with *l*-α-thiodibutyric acid, however, prove that a certain amount of optically active α-sulphonedibutyric acid exists in the freshly oxidised solution which becomes inactive in the course of a few hours. Preliminary experiments show that the α-sulphonedibutyric acid, m. p. 152° (which is thus proved to be the racemic form), can be resolved into its optical components by brucine in aqueous solution; the *l*-acid undergoes auto-racemisation when dissolved in water, the undissociated acid being affected more slowly than its ions.

Similar results are obtained with α-sulphonediiisovaleric acid, which, however, is rather more stable optically than its lower homologue.

H. W.

Preparation of Formaldehyde or its Polymerides from Mixtures of Carbon Monoxide and Hydrogen.

ERNEST JOSEPH LUSH (*Brit. Pat.* 180016).—When mixtures of carbon monoxide and hydrogen in suitable proportions such as may be obtained by the purification of "suction gas" or water gas, are passed rapidly over catalysts prepared, preferably, from a mixture

of 4 parts of nickel, 1 part of copper, and 5 parts of alumina, large quantities of formaldehyde or its polymerisation products are formed, and the residual gas consists mainly of methane and hydrogen. The gas is preferably forced through the catalyst at an initial temperature of 300—400°, under 10 atmos. pressure, at such a velocity as to ensure that the temperature does not fall below 160—180° on leaving the catalyst. To promote rapid cooling thereafter, the high-pressure gas is allowed to issue from a small constriction and is then led into water scrubbers to remove the formaldehyde. In order to restore the activity of the catalyst, steam is blown through periodically, or, alternatively, it may be mixed with the compressed gases.

G. F. M.

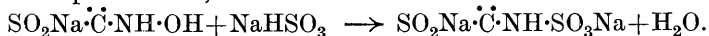
Conversion of Active Glyceraldehyde into Active Glyceric Acid. A. WOHL and R. SCHELLENBERG (*Ber.*, 1922, **55**, [B], 1404—1408).—*d*-Glyceraldehydedimethylacetal, $[\alpha]_D^{25} + 21.2^\circ$ in aqueous solution, is hydrolysed by aqueous *N*/10-sulphuric acid and the solution is oxidised with yellow precipitated mercuric oxide in the presence of barium hydroxide. A dextrorotatory barium glycerate, having $[\alpha]_D^{25} + 8.45^\circ$ in aqueous solution is thereby obtained. Since the active glyceric acids rotate in the opposite sense to their salts it follows that *d*-glyceraldehyde is genetically related to *l*-glyceric acid.

H. W.

Bisulphite Compounds of Oximinoketones and Glyoximes.

C. GASTALDI and G. BRAUNIZER (*Gazzetta*, 1922, **52**, i, 307—316).—The action of sodium hydrogen sulphite on chloroximinoacetone yields: (1) a compound, $C_3H_5O_5NCISNa$, which loses the SO_3Na group quantitatively as sulphurous acid when heated with dilute hydrochloric acid. This behaviour is that of bisulphite compounds having the SO_3Na group united to a carbon atom, so that the formula of the above compound is probably $SO_2Na \cdot O \cdot CMe(OH) \cdot CCl : NOH$; (2) a compound which results from further action of the sodium hydrogen sulphite and subsequent decomposition, crystallises in cubes, and is free from nitrogen and chlorine. This compound has not been obtained pure, but when treated with phenylhydrazine in dilute acetic acid, it yields a compound, $C_9H_9O_2N_3$, which is reduced by sodium amalgam to phenylhydrazineacetic acid, ammonia, and aniline, and hence appears to be 2-phenyl-1:3-dihydro-1:2:3-triazole-4-carboxylic acid; under similar conditions, 2-phenyl-1:2:3-triazole-4-carboxylic acid (cf. Pechmann, A., 1891, 1112) yields phenylhydrazineacetic and hydrocyanic acids.

Thus, the action of sodium hydrogen sulphite on oximinoketones (cf. A., 1921, i, 602) is exerted principally on the group $:C: \dot{N}OH$, transforming this into the group $SO_2Na \cdot \dot{C} \cdot NH \cdot OH$, and hence yielding a derivative of hydroxylamine. In a further stage of the action, another molecule of sodium hydrogen sulphite reacts, with formation of compounds derivable from either ammonia or aminosulphonic acid,



An analogous reaction occurs with carbonyl compounds and with

certain unsaturated compounds having a double linking between two carbon atoms. It may be that the same reaction applies to compounds with a double linking between oxygen and nitrogen and that the interaction of nitrous acid and sodium hydrogen sulphite may be explained by assuming that the $\cdot\text{N}:\text{O}$ group of the acid behaves similarly to the $:\text{C}:\text{O}$ of carbonyl compounds, the $:\text{C}:\text{N}\cdot$ of oximinoketones, and the $:\text{C}:\text{C}:$ of some unsaturated compounds, so that the initial product is hydroxylaminohydroxysulphonic acid, $\text{SO}_3\text{Na}\cdot\text{N}(\text{OH})_2$; from the latter, by further action of one or two molecules of sodium hydrogen sulphite, hydroxylamine-disulphonic and the so-called nitrilosulphonic acids would result. An analogous interpretation may be given to the formation of the compound $\text{K}_2\text{SO}_3\cdot 2\text{NO}$, to which Raschig ascribes the structure $\text{KO}\cdot\text{N}(\text{NO})\cdot\text{SO}_3\text{K}$.

The compound $\text{SO}_2\text{Na}\cdot\text{O}\cdot\text{CMe}(\text{OH})\cdot\text{CCl}:\text{NOH}$ forms small, colourless rhombohedra and decomposes when either dissolved in water or exposed to the air.

The acid $\text{C}_9\text{H}_9\text{O}_2\text{N}_3$ (see above) is obtained in colourless needles containing benzene of crystallisation, and when freed from benzene has m. p. $178-179^\circ$ (evolution of carbon dioxide).

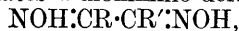
The analogous acid, $\text{C}_9\text{H}_8\text{O}_2\text{N}_3\text{Br}$, obtained when *p*-bromophenylhydrazine is used in place of phenylhydrazine, forms pale yellow, lustrous laminae, m. p. 185° (evolution of carbon dioxide).

The compound $\text{SO}_2\text{Na}\cdot\text{O}\cdot\text{CMe}(\text{CH}:\text{NOH})\cdot\text{NH}\cdot\text{SO}_3\text{Na}$, and the corresponding potassium compound, obtained when methylglyoxime is treated with sodium (potassium) hydrogen sulphite solution saturated with sulphur dioxide, form colourless needles containing water of crystallisation, give yellow solutions in dilute alkali hydroxide solutions, and do not yield insoluble compounds with nickel salts. When treated with phenylhydrazine, they give methylglyoxal phenylosazone, and when heated with 10% sulphuric acid solution, small proportions of oximinoacetone.

When the sodium hydrogen sulphite compounds of oximino-ketones and of methylglyoxime are hydrolysed by means of 10% hydrochloric acid, the SO_3Na group united to carbon is eliminated as sulphurous acid, and that united to nitrogen as sulphuric acid. Since these reactions are almost quantitative, the proportions of the SO_3Na group combined in the two ways may be estimated.

T. H. P.

Dioximes. II. G. PONZIO and G. RUGGERI (*Gazzetta*, 1922, 52, i, 289—301; cf. this vol., i, 17).—If, in accordance with the Hantzsch-Werner hypothesis, the isomerism of the α -dioximes is attributed to the different relative positions occupied in space by the two hydroxyl groups, the properties of methylacetylglyoxime (dimethyltriketone α -dioxime) not only indicate no choice between the four possible configurations, but fail also to explain the behaviour of this compound towards nitrogen tetroxide. Indeed, whereas the latter dehydrogenates α -dioximino-derivatives,



giving the corresponding peroxides (furoxans), $\text{R}\cdot\text{C}_2\text{N}_2\text{O}_2\cdot\text{R}'$, it

$z^* 2$

converts methylacetylgyoxime into a keto- ψ -nitroleoxime, namely, α -oximino- β - ψ -nitrole- γ -ketopentane, $\text{NOH}:\text{CMe}:\text{CAc}:\text{N}_2\text{O}_3$. Hence the two oximino-groups of methylacetylgyoxime are not equivalent and as a similar phenomenon is encountered with other α -dioximes, but only for one form of them, there can be no question in this case of geometrical isomerism.

Three configurations are possible for α -oximino- β - ψ -nitrole- γ -ketopentane according as the structure of the N_2O_3 group is represented by $:\text{C}(\text{NO})\cdot\text{NO}_2$, $:\text{C}:\text{N}\cdot\text{O}\cdot\text{NO}_2$, or $:\text{C}:\text{NO}\cdot\text{NO}_2$. When this compound is treated with aqueous ammonia, it gives rise to methylaminoglyoxime, which is probably formed as the result of the following reactions: (1) The hydrolysis, $\text{OH}\cdot\text{N}:\text{CMe}:\text{C}(\text{NO})(\text{NO}_2)\cdot\text{CO}\cdot\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{OH}\cdot\text{N}:\text{CMe}:\text{CH}(\text{NO})\cdot\text{NO}_2 + \text{CH}_3\cdot\text{CO}_2\text{H}$; (2) the isomerisation, $\rightarrow \text{OH}\cdot\text{N}:\text{CMe}:\text{C}(\text{NO}_2):\text{N}\cdot\text{OH}$, and (3) substitution of the nitro-group of the methylnitroglyoxime by the amino-group, $\text{NOH}:\text{CMe}:\text{C}(\text{NO}_2):\text{NOH} + \text{NH}_3 \rightarrow \text{NOH}:\text{CMe}:\text{C}(\text{NH}_2):\text{NOH} + \text{HNO}_2$. The first of these reactions has been already observed with the amylnitro- ψ -nitrole, $\text{N}_2\text{O}_3\cdot\text{CEtAc}$, which yields propylnitrolic and acetic acids when treated with potassium hydroxide solution (Ponzio, A., 1899, i, 667). The third stage, replacement of a nitro- by an amino-group by the action of ammonia, is very common with aromatic polynitro-derivatives, and is met also in the conversion of phenylnitroformaldehyde arylhydrazones into the corresponding hydrazidines,

$\text{NO}_2\cdot\text{CPh}:\text{N}\cdot\text{NHA}r + \text{NH}_3 \rightarrow \text{NH}_2\cdot\text{CPh}:\text{N}\cdot\text{NHA}r + \text{HNO}_2$
(Ponzio, A., 1910, i, 443, 699). Further, the compound obtained when α -oximino- β - ψ -nitrole- γ -ketopentane is treated with ammonia is identical with the one formed by replacement of the chlorine atom of chloromethylglyoxime by the amino-group,

$\text{NOH}:\text{CMe}:\text{CCl}:\text{NOH} + \text{NH}_3 \rightarrow \text{NOH}:\text{CMe}:\text{C}(\text{NH}_2):\text{NOH}$,
and is undoubtedly methylaminoglyoxime, which is both an α -dioxime and a primary amine.

Acetylmethylglyoxime forms a diacetyl derivative, an internal anhydride, and a trioxime, and may be regarded as an equilibrated mixture of the tautomeric nitroso-oxime, $\text{NOH}:\text{CMe}:\text{CHAc}:\text{NO}$, and α -dioxime, $\text{NOH}:\text{CMe}:\text{CAc}:\text{NOH}$. The first of these formulæ indicates how the action of nitrogen peroxide may yield α -oximino- β -nitroso- β -nitro- γ -ketopentane, whilst the second explains (1) the acetylation by the action of acetic anhydride in the cold to a compound which, when heated, loses a molecule of water and forms acetylmethylfurazan,

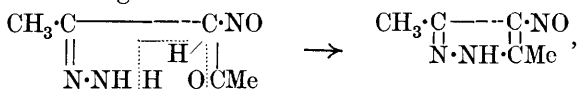
$$\begin{array}{ccc} \text{CH}_3\cdot\text{C} & \text{---} & \text{C}\cdot\text{Ac} \\ | & & | \\ \text{NOH} & & \text{NOH} \end{array} \rightarrow \begin{array}{ccc} \text{CH}_3\cdot\text{C} & \text{---} & \text{C}\cdot\text{Ac} \\ | & & | \\ \text{N}\cdot\text{O} & & \text{N} \end{array} + \text{H}_2\text{O},$$

and (2) the formation, by the action of hydroxylamine, of dimethyltriketonetrioxime, $\text{NOH}:\text{CMe}:\text{C}(\text{NOH})\cdot\text{CMe}:\text{NOH}$, in which, as will be shown later, three oximino-groups undoubtedly exist. Thus, it must be assumed that the hydrogen atom of the β -oximino-group is mobile and may migrate from the oxygen to the carbon with consequent isomerisation of the group $\text{NOH}:\text{C}:\text{C}:\text{NOH}$ into $\text{NOH}:\text{C}:\text{CH}:\text{NO}$.

The β -oximic group of acetylmethylglyoxime is the one which

pre-exists in oximinoacetylacetone (dimethyltriketone β -monoxime), from which the dioxime is formed by the action of hydroxylamine. If it is assumed that the oximic hydrogen of oximinoacetylacetone also is mobile and may migrate from the oxygen to the carbon, $\text{NOH}:\text{CAc}_2 \rightleftharpoons \text{NO}\cdot\text{CHAc}_2$, it is possible easily to explain its conversion into derivatives of 4-nitrosopyrazole, $\text{N} \ll \begin{smallmatrix} \text{CH}\cdot\text{C}\cdot\text{NO} \\ \text{NH}\cdot\text{CH} \end{smallmatrix}$, by

treatment with hydrazine, phenylhydrazine, semicarbazide, etc. (cf. Wolff, Bock, Lorentz, and Trappe, A., 1903, i, 210; Sachs and Alsleben, A., 1907, i, 356). Thus, if oximinoacetylacetone behaves as $\alpha\gamma$ -diketo- β -nitrosopentane, the action of hydrazine should yield the hydrazone, the latter then losing the elements of water according to the scheme :



giving 4-nitroso-3 : 5-dimethylpyrazole.

Acetylmethylglyoxime, best prepared by treating oximinoacetylacetone in the cold with the theoretical proportion of hydroxylamine hydrochloride and with sodium acetate in highly concentrated aqueous solution, forms elongated laminae, often rectangular and sometimes united in pennate aggregates, m. p. 141° (decomp.), and dissolves in concentrated sulphuric acid with an emerald-green coloration and in sodium hydroxide solution without coloration. The low melting point, 128° , given by Wolff is due to the fact that the compound undergoes alteration when heated with water or with an organic solvent containing water. In aqueous solution, it does not attack nickel, cobalt, copper, or iron, or react with salts of these metals. Its *diacetyl* derivative, $\text{C}_9\text{H}_{12}\text{O}_5\text{N}_2$, forms white prisms, m. p. $77\text{--}78^\circ$, and yields methylacetylfulrazan when heated with water.

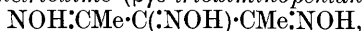
α -Oximino- β - ψ -nitrole- γ -ketopentane, $\text{C}_5\text{H}_7\text{O}_5\text{N}_3$, crystallises in white prisms, m. p. $102\text{--}103^\circ$ (decomp.), and dissolves without coloration in cold concentrated sulphuric acid, giving a solution from which it is precipitated on addition of water. It is stable in the air, but decomposes rapidly, with evolution of nitrous fumes, when kept in a closed vessel. Even weak bases hydrolyse it with rupture of the carbon atom chain between the ψ -nitrolic and carbonyl groups; the first products are acetic acid and methyl-nitroglyoxime, these then undergoing further changes, the nature of which varies with the base used. When treated in aqueous suspension with silver carbonate, it yields carbon dioxide and silver nitrite.

Aminomethylglyoxime, $\text{NOH}:\text{CMe}\cdot\text{C}(\text{NH}_2):\text{NOH}$, prepared by treating the preceding compound with aqueous ammonia and purified by precipitation of its nickel derivative and removal of the nickel from the latter as potassium nickelocyanide, forms white needles or laminae, m. p. $183\text{--}184^\circ$ (partial sublimation), and in aqueous solution attacks nickel, cobalt, iron, and copper, slowly at the ordinary temperature and rapidly at about 100° .

The *nickel* salt, $(C_3H_6O_2N_3)_2Ni \cdot H_2O$, forms orange-red laminæ and becomes anhydrous at 130° . The *dibenzoyl* derivative, $C_{16}H_{15}O_4N_3$, crystallises in white needles, m. p. 206° . The *hydrochloride*, $C_3H_7O_2N_3 \cdot HCl$, forms white prisms, m. p. 170° (evolution of gas).

Acetylmethylfurazan, $C_5H_6O_2N_2$, forms a colourless liquid with a suffocating odour, heavier than water, b. p. $154.5^\circ/742.8$ mm., and yields methylfurazancarboxylic acid when oxidised with permanganate. The *oxime*, $C_5H_7O_2N_3$, crystallises in white laminæ, m. p. 86° , and forms an *acetyl* derivative, $C_5H_6ON_2 \cdot NOAc$, crystallising in long, white needles, m. p. $60-61^\circ$, and a *benzoyl* derivative, $C_{12}H_{11}O_3N_3$, crystallising in white prisms, m. p. $120-121^\circ$. The *hydrazone*, $C_5H_6ON_2 \cdot N \cdot NH_2$, forms white prisms, m. p. 120° , with previous softening, the *phenylhydrazone*, $C_{11}H_{12}ON_4$, straw-coloured needles, m. p. 117° , and the *semicarbazone*, $C_6H_9O_2N_5$, white prisms, m. p. 232° .

Dimethyltriketone trioxime ($\beta\gamma\delta$ -trioximinopentane),



the first compound of its class, purified by means of its nickel compound, forms white prisms, m. p. 175° (decomp.), dissolves in concentrated sulphuric acid and in alkali hydroxide solutions without coloration, and in aqueous solution readily attacks compact nickel, cobalt, copper, and iron. Under the action of acetic anhydride and fused sodium acetate, the β -oximino-group undergoes acetylation, whilst the other two oximino-groups unite with loss of water, the resulting compound being the acetyl derivative of methylacetylfurazanoxime, $\begin{array}{c} N \cdot CMe \\ | \\ O \text{---} N \end{array} \gg C \cdot CMe \cdot NOAc$. The *nickel* salt,

$(C_5H_8O_3N_3)_2Ni$, crystallising in orange-red prisms or needles, turns brown without melting at about 260° , and dissolves in alkali hydroxide or ammonia solution, giving an orange-red solution; it is of the type of compounds considered by Tschugaev (A., 1905, i, 743; 1908, i, 554; T., 1914, **105**, 2187) as characteristic of the so-called syn-forms of the α -dioximes, being derived from two molecules of the trioxime by replacement of two atoms of oximinic hydrogen by an atom of nickel. Other $\alpha\beta\gamma$ -trioximes yield analogous nickel derivatives. The *tribenzoyl* compound, $C_{26}H_{21}O_6N_3$, forms white prisms, m. p. $191-192^\circ$. T. H. P.

Croconic Acid and Leuconic Acid. B. HOMOLKA (Ber., 1922, **55**, [B], 1310-1311).—Leuconic acid is hydrolysed by cold, aqueous sodium carbonate solution to glyoxal and sodium mesoxalate, whereby its constitution, $\begin{array}{c} CO \cdot CO \\ | \\ CO \cdot CO \end{array} > CO$, is established. The position of the two hydroxyl groups in croconic acid remains undecided. H. W.

The Preparation of Pure Galactose. G. MOUGNE (Bull. Soc. Chim. Biol., 1922, **4**, 206-208).—When prepared by Clark's method (A., 1921, i, 647), galactose is probably contaminated with dextrose. In the method described, dextrose is removed from the mixed monosaccharoses obtained by the hydrolysis of lactose

by fermentation with top yeast. The galactose, which is un-
 attacked, is recrystallised from 75% alcohol. E. S.

The Action of Ammonia and of Amino-compounds on Reducing Sugars. I. The Action of Ammonia on Dextrose and Lævulose. ARTHUR R. LING and DINSHAW RATTONJI NANJI (*J. Soc. Chem. Ind.*, 1922, **41**, 151—155t).—Dextrose unites with ammonia at 35° to form an additive compound, *glucose-ammonia*, $C_6H_{12}O_6 \cdot NH_3$, probably $OH \cdot CH_2 \cdot [CH \cdot OH]_4 \cdot CH(OH) \cdot NH_2$, analogous to aldehyde-ammonia, which can be isolated as a pale amber-coloured, friable mass by evaporating the solution in a vacuum at a temperature not exceeding 37—38°. It is extremely hygroscopic, and even in the solid state gives off ammonia. It reduces alkaline copper and silver solutions in the cold with the formation of a mirror. In solution, it is dissociated, for the specific rotatory power is the same as that of the sugar freed from ammonia. An aqueous solution of the sugar was obtained from glucose-ammonia by aspirating air through it. The sugar could not be crystallised, but it reduced potassium permanganate in the cold, which has been shown to be a property of the so-called γ -glucose. Its specific rotatory power $[\alpha]_D +4.4^\circ$, and it was shown to be a mixture of aldose and ketose in equilibrium, the point of equilibrium being changed according to the reaction of the solution, and in *N*/4 hydrochloric acid 100% aldose is present. Lævulose when treated with ammonia is partly converted into aldose and this unites with ammonia, the solution behaving in every way similarly to the product from dextrose. When the ammonia is removed from the solution a similar mixture of aldoses and ketoses in equilibrium is obtained. G. F. M.

Preparation of Complex Iron Compounds of the Phosphoric Esters of Higher Aliphatic Polyhydroxyl Compounds. FARBENFABRIKEN VORM. F. BAYER & Co. (D.R.-P. 338735; from *Chem. Zentr.*, 1921, iv, 1223).—Phosphoric esters of polyhydroxyl compounds are treated with iron compounds in the presence of alkalis. The calcium salt of lævulose diphosphoric acid by reaction with oxalic acid, sodium hydroxide, and ferric chloride gives the *normal iron* salt of the ester, a white powder insoluble in water. By the action of 33% sodium hydroxide solution on the normal salt, a deep reddish-brown solution is obtained, from which, after the addition of 95% ethyl alcohol, the complex *iron* salt separates as a dark brown oil which may be obtained as a dark brown powder by agitation with absolute alcohol. It contains phosphorus 6.26%, sodium 11.48%, and iron 15.12%. The complex *iron* salt of lævulose-monophosphoric acid is a brown powder containing phosphorus 5.27%, sodium 9.87%, and iron 14.11%. The complex *iron* salt of sucrose monophosphoric acid contains phosphorus 4.89%, sodium 4.01%, and iron 12.21%. The complex *iron* salt of mannitol monophosphoric acid contains phosphorus 3.82%, sodium 11.40%, and iron 20.83%. The compounds are slightly soluble in water with alkaline reaction. Phosphorus is in organic combination. The products have therapeutic uses. G. W. R.

Chemistry of Starch. V. Methyl and Acetyl Products of the "Polyamyloses." HANS PRINGSHEIM and WALTER PERSCH (*Ber.*, 1922, 55, [B], 1425—1433).—The conversion of tetra-amylose into octamethyltetra-amylose has been described previously (Pringsheim and Persch, this vol., i, 113); the third hydroxyl group could not, however, be methylated, and it was therefore suggested tentatively that it was concerned in the union of the diamylose complexes in tetra-amylose. This does not appear to be the case, since octamethyltetra-amylose is converted readily by acetic anhydride and pyridine into the corresponding *tetra-acetate*, $(C_6H_7O_5Me_2Ac)_4$, hexagonal rods which darken without melting at 120° , $[\alpha]_D^{20} +118.62^\circ$ in ethyl alcohol. Diamylose resembles tetra-amylose in that it is converted by successive treatment with methyl sulphate and sodium hydroxide and methyl iodide and silver oxide into *tetramethyldiamylose*, hexagonal plates which do not melt below 200° , $[\alpha]_D^{20} +143.74^\circ$ in ethyl alcoholic solution. Attempts to methylate the third hydroxyl group were unsuccessful.

The behaviour of the polyamyloses of the β -series towards methylation is peculiar. With hexa-amylose, reducing action towards Fehling's solution is observed after a single treatment with methyl sulphate and sodium hydroxide, although the solution was not at any time acidic. With triamylose, the phenomenon was first noticeable after the first methylation with silver oxide and methyl iodide and became more marked after a second treatment with the same reagents.

The author's method of acetylation with acetic anhydride and pyridine permits without depolymerisation the conversion of the slimes obtained by the degradation of starch with *Bacillus macerans*, into *hexa-amylose dodeca-acetate*, aggregates of minute needles, which shrinks at 135° , but does not melt definitely below 215° , $[\alpha]_D^{20} +95.77^\circ$, $[\alpha]_D^{22} +95.77^\circ$, when dissolved in glacial acetic acid. It is converted by alcoholic potassium hydroxide solution into the initial material, which is thus characterised as α -hexa-amylose.

H. W.

Chemistry of Starch. VI. Polyamyloses. HANS PRINGSHEIM and DIAMANDI DERNIKOS (*Ber.*, 1922, 55, [B], 1433—1445).—The acetylation of polyamyloses with acetic anhydride and pyridine has been extended to α -tetra-amylose, which, as expected, yields *α -tetra-amylose dodeca-acetate*, $[C_6H_7O_2(OAc)_3]_4$, needles, $[\alpha]_D^{18} +115.8^\circ$ in glacial acetic acid solution, the molecular weight of which has been determined in benzene and bromoform. It is reconverted by alcoholic potassium hydroxide solution into α -tetra-amylose, the identity of which is established by the determination of its molecular weight. The application of this method of acetylation to polyamyloses of the β -series has led to surprising results, since β -hexa-amylose is thereby converted into the same triamylose nona-acetate, $[C_6H_7O_2(OAc)_3]_3$, $[\alpha]_D^{18} +117.9^\circ$ in glacial acetic acid solution, as was obtained previously by acetylation in the presence of zinc chloride; a possible explanation of the unexpected depolymerisation is found in the fact that the experi-

mental conditions, by reason of the sparing solubility of the initial material, were necessarily more drastic than those adopted with the members of the α -series.

Karrer has recently expressed the opinion that β -hexa-amylose is not depolymerised by acetylation in the presence of zinc chloride, in which case Pringsheim's triamylose must be merely de-acetylated β -hexa-amylose (this vol., i, 435). Karrer's arguments are criticised in detail. Reasons are advanced for considering that data obtained from the action of acetyl bromide on polysaccharides are completely unsatisfactory in the quantitative form given to them by Karrer. The compounds of triamylose with the alkali hydroxides have, according to Karrer, the formula $C_{12}H_{20}O_{10}.NaOH$. It is pointed out that a compound prepared in accordance with Karrer's directions by the precipitation of a solution of β -hexa-amylose in aqueous sodium hydroxide (10%) with alcohol had the composition, $(C_6H_{10}O_5)_3.NaOH$, but great value cannot be placed on the results of analyses of these substances, since their alkali content is greatly dependent on the experimental conditions. Hydrolysis of triamylose acetate with sodium ethoxide followed by thorough washing of the precipitate with absolute alcohol gives a substance, $(C_6H_{10}O_5)_3.NaOH$. Contrary to Karrer's observations, β -hexa-amylose invariably contains a higher percentage of water of crystallisation than triamylose. The solubilities of the two substances in water are not identical; as concordant result of two different methods, the solubility of triamylose in water at 20° is 1.3 by weight and 1.34% by volume, the corresponding figures for β -hexa-amylose being 2.4 and 2.65. Contrary to Karrer, the optical activity of triamylose is lower than that of β -hexa-amylose. A revision of the crystalline forms of triamylose and β -hexa-amylose confirms Karrer's observation of their identity. Attempts to determine the molecular weight of triamylose in boiling water were unsuccessful, since a true solution could not be obtained.

Measurements of the crystals of diamylose, triamylose, and β -hexa-amylose, tetra-amylose, and α -hexa-amylose are recorded.

H. W.

Chemistry of Starch. VII. Relationship of the α - and β -Polyamyloses to the Content and Integument Substance of the Starch Granule. HANS PRINGSHEIM and KURT GOLDSTEIN (*Ber.*, 1922, 55, [B], 1446—1449).—It has been shown by Samec and his co-workers that starch can be separated by electrodialysis of its solutions into erythroamyloses and amyloamyloses. The close relationship of these substances to the β - and α -amyloses is illustrated.

The erythroamyloses give a brown and the amyloamyloses a blue coloration with starch; the iodine additive compounds with β -polyamyloses are brownish-red whereas those with α -polyamyloses are green when dry, but become blue when moistened. The erythroamyloses and amyloamyloses have $[\alpha]_D +195$ to 196° and $+189^\circ$, respectively; the β -polyamyloses are more highly

active than the α -compounds, the respective specific rotations being $+152^\circ$ to 158° and $+132^\circ$ to 136° , respectively. The molecular weights of the erythroamyloses and amyloamyloses are approximately 130,000—140,000 and 80,000; the ratio is approximately 3:2, which is the same as for the fundamental tri- and di-amyloses of the β - and α -polyamyloses. Fermentation of the amylopectins and amyloses by *Bacillus macerans* shows that β -polyamyloses are obtained in larger yield from the erythro-, α -poly-amyloses from the amyloamyloses. Iodine unites more readily with amyloamyloses than with erythroamyloses; similarly, the fractional addition of iodine to a solution containing α -tetra-amylose and β -hexa-amylose results in the initial precipitation of green needles of the α -tetra-amylose compound, followed by brownish-red prisms of tri-iodo-hexa-amylose, the yields and separation being highly satisfactory.

The optical activity of glycogen and its behaviour towards *B. macerans* allies it closely to the electrolyte-free amylopectins; an exact determination of its molecular weight (which has been found by methods of little trustworthiness to be 140,000) is, however, necessary before it can be regarded definitely as an erythro-amylose.

H. W.

Constitution of Polysaccharides. IV. Inulin. JAMES COLQUHOUN IRVINE, ETTIE STEWART STEELE, and MARY ISOBEL SHANNON (T., 1922, **121**, 1060—1078).

Inulin. II. Inulin and Glycogen. HANS PRINGSHEIM and MAX LASSMANN (*Ber.*, 1922, **55**, [B], 1409—1414).—Redeterminations of the molecular weight of inulin acetate dissolved in glacial acetic acid by the method of Barger as modified by Rast have confirmed the previous measurements, but the process cannot be applied in the cases of the acetates of glycogen and soluble starch. The method does not appear to be practicable for the determination of molecular weights exceeding 3000.

Glycogen is transformed by acetic anhydride in the presence of pyridine into *glycogen acetate*, $C_{12}H_{16}O_8$, m. p. 165° (indefinite), $[\alpha]_{18}^D +159.6^\circ$ when dissolved in pyridine; when hydrolysed by alcoholic potassium hydroxide, it gives a white, pulverulent glycogen, which is coloured brownish-red by iodine and is hydrolysed in the same manner as the initial glycogen by "fermasol D.S." (a preparation containing diastase).

Starch which had been rendered soluble by being heated at 190° in the presence of glycerol and did not reduce Fehling's solution was converted into its acetate. The product differs from glycogen acetate, whereas the same substance is prepared by the methylation of soluble starch or glycogen (Karrer, this vol., i, 11).

The differing behaviour of starch and glycogen towards iodine has been ascribed by Karrer (*loc. cit.*) to the presence of impurities. This is regarded as improbable since the de-acetylated starch and glycogen acetates retain their characteristic properties towards iodine.

H. W.

Inulin. III. HANS PRINGSHEIM and ALEXANDER ARONOWSKY (*Ber.*, 1922, **55**, [B], 1414—1425).—Inulin, in the solid condition and in its colloidal solution, is a product of the association of a trebly polymerised anhydro-trifructose. In the latter, the fructose residues are not present in the same form as in fructose stable in solution [with butylene oxide oxygen bridge], but exist as the so-called γ -fructose which probably contains an ethylene oxide ring. The ready hydrolysis of inulin, and particularly of tri-fructose, thereby receives an explanation.

In previous communications (Pringsheim and Aronowsky, A., 1921, i, 545; Pringsheim and Lassmann, preceding abstract), it has been shown that inulin triacetate is fundamentally composed of nine fructose residues. The proof of the identity of the inulin regenerated from the acetate with the original inulin was obtained from Röntgen spectrographic observations. Attempts to confirm this identity by fermentative hydrolysis with *Penicillium glaucum* have led to interesting results since the properties of the ferment are found to depend largely on the conditions of its culture. From the same specimen of *Penicillium* three cultures are obtained, the first of which, nourished with sucrose, does not hydrolyse inulin, whereas the second, nourished with natural inulin, hydrolyses the latter, but not de-acetylated inulin acetate, whilst the third, nourished with artificial inulin, hydrolyses both inulins. It is not considered that these observations afford a proof of the different degrees of polymerisation in the two products.

Previous attempts to hydrolyse inulin with ferments or acids have never led to the isolation of a di- or tri-saccharide, and renewed efforts in this direction are now recorded. The action of phenylhydrazine acetate on an aqueous solution of inulin leads mainly to the production of glucosazone, but indications are also obtained that a second osazone which is soluble in hot water is formed; it could not, however, be isolated in quantity sufficient for further experiment.

The acetolytic degradation of inulin cannot be effected with acetic anhydride and sulphuric acid, since the products are too readily carbonised. A suitable acetylating mixture is secured by using glacial acetic acid (2 parts) and acetic anhydride (1 part) for each part of inulin; the inulin acetate thus obtained could not be caused to solidify. When, however, it is dissolved in absolute alcohol and treated with sodium ethoxide, it gives *trifructose sodium*, $(C_6H_{10}O_5)_3NaOH$. The reducing power of the latter towards Fehling's solution is approximately one-third of that of fructose sodium. The corresponding trifructose cannot be precipitated by the addition of alcohol to solutions of trifructose in water which have been neutralised with acetic acid. Attempts to prepare a derivative of it did not meet with success, since phenylbenzylhydrazine gave only fructosephenylbenzylhydrazone.

Inulin sodium has the composition $(C_6H_{10}O_5)_3NaOH$, whether obtained by precipitating a solution of inulin in aqueous sodium hydroxide (10%) with alcohol or by the hydrolysis of inulin acetate with sodium ethoxide. The sparingly soluble barium inulin is

constituted similarly. It is, however, pointed out that the method first mentioned for the isolation of the additive compounds of polysaccharides and sodium hydroxide is untrustworthy; the sodium content of such substances depends entirely on the concentration of the sodium hydroxide solution, from which they are precipitated by alcohol or on the quantity of water with which they are treated for the removal of adherent sodium hydroxide. H. W.

An Alkali-soluble Modification of Cellulose. EMIL KNOEVENAGEL and HEDWIG BUSCH (*Cellulosechemie*, 1922, **3**, 42—60).—When viscose cellulose is subjected to acid hydrolysis under conditions equivalent to those employed for the preparation of Girard's hydrocellulose, it yields a product which is completely soluble in cold 8% sodium hydroxide solution, even after drying, and is reprecipitated practically without loss on neutralisation. This alkali-soluble cellulose may also be prepared at the ordinary temperature by treating viscose cellulose containing from 2 to 11% of moisture with dry hydrogen chloride. The conversion does not take place if the cellulose is completely dried. Alkali-soluble cellulose contains 8.3% of hygroscopic moisture as compared with 11.0% for viscose cellulose, and has the formula $(C_6H_{10}O_5)_3 \cdot H_2O$; it has the unusually high "copper value" of 12.5—14.0, and forms a phenylhydrazone of indefinite properties containing 4.3% of nitrogen. It has no acid reaction (towards phenolphthalein); when heated with dilute alkali hydroxides it gives a yellow coloration; when boiled with calcium hydroxide for eight hours, it loses 50% in the form of soluble products, but, unlike oxy- and hydro-cellulose under similar treatment, it behaves as a uniform substance, in that the "copper value" of the residue is substantially the same of that of the original material. It resembles viscose cellulose in the fact that it is not readily acetylisable by the usual methods, but it yields a benzoate with the greatest of ease; this is completely soluble in chloroform.

The capacity to form alkali-soluble cellulose is determined by the nature of the previous modification of the cellulose and by the residual affinities released thereby. The formation is proportional to the "hydration value" of the modified cellulose before hydrolysis, as determined by Schwalbe's method (difference between the copper values before and after boiling with 5% sulphuric acid for fifteen minutes). Ordinary hydrocellulose and cellulose regenerated by saponification of cellulose acetate will not yield the alkali-soluble product. Viscose cellulose yields it most readily; strongly mercerised cotton or wood cellulose, on subsequent hydrolysis, yields up to 20%, and the yield may be increased by the more severe action of hot concentrated alkali hydroxides. Wood cellulose when heated for several hours at 140° in an indifferent medium, such as xylene or glycerol, gives substantial yields of alkali-soluble cellulose after subsequent hydrolysis, but the presence of a little moisture during the preliminary heating treatment is essential to ensure the desired type of modification [cf. *J. Soc. Chem. Ind.*, 1922, 458A].

J. F. B.

Behaviour of Oxidised Cellulose. EDMUND KNECHT and F. P. THOMPSON (*J. Soc. Dyers and Col.*, 1922, **38**, 132—136).—Oxidation of cotton cellulose with potassium permanganate in the presence of cold dilute sulphuric acid showed that in the initial stages the consumption of oxygen was approximately proportional to the formation of aldehydic or ketonic groups, as measured by the increase in the "copper value" of the oxidised products. After the expenditure of half an atomic equivalent of active oxygen, however, the increase in "copper value" with further oxidation was very small and, since the more highly oxidised products were to a large extent soluble in alkali hydroxide solution, it is inferred that the later stages of oxidation are complicated by formation of carboxylic acid groups. Acetylation of the original and oxidised celluloses under identical conditions indicated that the oxidised cellulose was esterified more slowly than the original and suffered considerable hydrolysis to products soluble in water. On nitration under identical conditions, the oxidised cellulose yielded products containing in all cases less nitrogen than the nitrates from the original cellulose. Hence it would appear that there is a definite suppression of active hydroxyl functions as the result of oxidation, although this loss is not accurately proportional to the quantity of oxygen consumed. [See also *J. Soc. Chem. Ind.*, 1922, July.] J. F. B.

The Spontaneous Oxidation of Lignin, Natural Humus Material and Coal and the Influence of Alkali thereon. HANS SCHRADER (*Brennstoff-Chemie*, 1922, **3**, [ii], 161—167).—It has been shown previously that lignin is almost completely oxidised to humic acids by heating with sodium hydroxide solution to 200° under pressure. In order to obtain evidence more directly bearing on the possibility of the humus fraction of coal being a decomposition product of lignin, this oxidation was investigated at atmospheric temperature and pressure. A weighed quantity of lignin was placed in a flask covered with 5*N*-sodium hydroxide solution, the flask filled with oxygen, tightly corked, and allowed to remain for forty-six hours. It was then opened, water added, and the whole contents filtered. The humic acids were precipitated from the filtrate by acidification and warming, washed, and dried at 105° in a current of carbon dioxide. They amounted to 9·4% of the (pure) lignin used. The acid filtrate on evaporation to dryness and extraction of the residue with ether yielded a crystalline substance. If the flask was filled with nitrogen instead of oxygen, oxidation proceeded much more slowly, and stopped when 2·3% of humic acids had been formed. A repetition of the above oxidation lasting eight months with 375 grams of pure lignin yielded 192·5 grams of undissolved organic material, 103·5 grams of humic acids, 10·3 grams of non-volatile acids soluble in ether (including 1·62 grams of succinic acid, 0·47 gram of oxalic acid, 0·26 gram of isophthalic acid (?), and an indeterminate quantity of higher benzenecarboxylic acids), and 6·1 grams of non-volatile acids soluble in alcohol. The 62·3 grams loss includes acetic acid, formic acid, water, and carbon dioxide.

The comparative rates of absorption of oxygen by lignin, pine wood sawdust, lignite, cellulose (filter-paper), and coal, each of them as a finely divided suspension in 5*N*-sodium hydroxide solution, were next determined, over a period of a thousand hours with regular shaking, the oxygen being measured from a gas burette. The volume absorbed by 1 gram of substance ranged downwards in the order mentioned above from 82 c.c. with lignin to 6.7 c.c. for coal. In no case had absorption ceased after a thousand hours' treatment, and it was further shown that the absolute results obtained varied with the degree of shaking. The methoxyl content of the humic acid produced in this way was much lower than that of the original lignin, a point of similarity to natural humic acid. The part played by the sodium hydroxide in these oxidations may, it is suggested, be filled in nature by lime or ammonia, whilst bacterial action may also be of importance. The analogy is discussed at length.

C. I.

The Colloids Arabic Acid and Arabic Acid plus Gelatin.

F. W. TIEBACKX (*Pharm. Weekblad*, 1922, **59**, 574—589).—The precipitation of gum and gelatin together from a mixture of solutions, in presence of very dilute acids, occurs for values of p_H between the isoelectric points; for gelatin in presence of hydrochloric acid, this point is about 1×10^{-4} HCl (Hardy), for arabic acid in presence of hydrochloric acid, the isoelectric point is found to correspond with about 2×10^{-3} HCl.

Arabic acid, prepared by repeated precipitation with alcohol and long dialysis, containing no calcium or chlorine, and only 0.1% ash (K_2CO_3), has an equivalent weight 1210, agreeing with O'Sullivan's molecular weight 2418. The formula HAAH is suggested, A being the arabic acid anion. The molecule can be imagined, on the hypothesis of Duclaux, to be $(nHA)AH$, where $n=1$; instead, therefore, of being regarded as a typical colloid, gum really approaches the crystalloid.

By Kohlrausch's method, the conductivity at 18° ($K \times 10^{-4}$) was found to be 8.7. From the alteration of the conductivity on neutralisation, the acid appears to act as a moderately strong monobasic acid. The degree of dissociation of the salts has been measured, but it is extremely difficult to remove traces of electrolytes, which interfere with the determinations; there appears to be no true dissociation constant. The dissociation of the potassium and sodium salts decreases with dilution, passing through a minimum value.

S. I. L.

The Solution of Tetramethylammonium Aluminate.

JINDŘICH BŘEZINA (*Chem. Listy*, **16**, [2], 25—26).—Metallic aluminium is dissolved in a solution of tetramethylammonium hydroxide, and the conductivity of the solution with varying amounts of aluminium is measured. From the measurements thus obtained it is deduced that the aluminium hydroxide produced is neutralised in the same way as by an inorganic base, and that it acts as a monobasic acid, since solution of aluminium ceases when there is present 1 mol. of aluminium hydroxide to one of base. The salt

thus formed is highly dissociated in solution. The transport number for the anion of ortho-aluminic acid is 24 at 0°. R. T.

The Preparation and Properties of Organic Stanno- and Stanni-chlorides. IV. Some Diamine Stannichlorides.

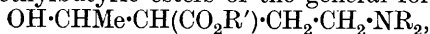
J. G. F. DRUCE (*Chem. News*, 1922, **124**, 310—313).—In continuation of previous work (A., 1919, i, 481), certain diamine stannichlorides have been prepared. *Hydrazine stannichloride* was obtained by mixing stannic chloride and hydrazine hydrochloride in hydrochloric acid. *Methylenediamine stannichloride*, *ethylene-diamine stannichloride*, and *propylenediamine stannichloride* were similarly prepared. Crystallographic data are given for the crystals of propylenediamine stannichloride and for *m*- and *p*-phenylenediamine stannichlorides. All the diamine stannichlorides described are soluble in water with partial hydrolysis and can best be crystallised from hydrochloric acid. W. G.

The Amino-alcohols. Homologues of Novocaine. E.

FOURNEAU and J. PUYAL (*Bull. Soc. chim.*, 1922, [iv], **31**, 424—435).—Propylene, butylene, and amylene were prepared by passing the vapours of the corresponding alcohol over infusorial earth at 400°. Starting with a commercial amyl alcohol boiling at 128—130°, the main product was β -methyl- Δ^2 -butylene. These hydrocarbons were converted into the bromohydrins by the action of bromine water, and these in turn by the action of dimethylamine yielded the dimethylamino-alcohols, from which certain derivatives were prepared. The following compounds are described: Propylenebromohydrin. β -Bromo- γ -hydroxybutane, $\text{CHMeBr}\cdot\text{CHMe}\cdot\text{OH}$, b. p. 63°/16 mm. and 154°, *d* 1.5016. β -Chloro- γ -hydroxybutane, b. p. 138—140°, and the corresponding Δ^2 -butylene oxide, b. p. 56°. α -Bromo- β -methylbutan- β -ol, $\text{CH}_2\text{Br}\cdot\text{CMeEt}\cdot\text{OH}$, b. p. 67°/18 mm., *d* 1.42. α -Dimethylaminopropan- β -ol, b. p. 45°/20 mm. α -Diethylaminopropan- β -ol, b. p. 157°. β -Dimethylaminobutan- γ -ol, b. p. 53°/18 mm. and 145°. β -Diethylaminobutan- γ -ol, b. p. 74°/16 mm. and 167—174°. α -Dimethylamino- β -methylbutan- β -ol, b. p. 53°/18 mm. and 144—146°. From these amino-alcohols certain substituted benzoyl derivatives have been prepared, namely: Nitrobenzoyloxydimethylaminopropane hydrochloride, m. p. 198°. Nitrobenzoyloxydiethylaminopropane hydrochloride, m. p. 187°, and the corresponding aminobenzoyl derivative (methylnovocaine), m. p. 150—152°. Nitrobenzoyloxydiethylaminobutane hydrochloride, m. p. 148°, and the aminobenzoyl derivative, m. p. 172°. The derivatives obtained from dimethylaminomethylbutanol were shown to be identical with known stavaine derivatives. W. G.

Preparation of β -Aracyl- α -dialkylaminoethylbutyric Esters.

FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Brit. Pat. 161539).—Dialkylaminoethyl haloids are caused to react with ethyl sodioacetoacetate, and the resulting ketonic acid esters are reduced, for example, by means of sodium amalgam to β -hydroxy- α -dialkylaminoethylbutyric esters of the general formula,



where R is an alkyl group, and R' an alkyl or aryl group. *Ethyl β -hydroxy- α -diethylaminoethylbutyrate* is a colourless liquid, b. p. 135—136°/10 mm., soluble in water to an alkaline solution. When heated with an aromatic acid chloride, as, for example, benzoyl chloride, the desired aromatic ester is formed, in this case *ethyl β -benzoxy- α -diethylaminoethylbutyrate*, which is a colourless oil forming a crystalline *hydrochloride*, m. p. 130—131°, readily soluble in water, and possessing valuable local anæsthetic properties.

G. F. M.

Explosion of Hydrargyrum Oxycyanatum. E. MERCK (*Pharm. Zentr.-h.*, 1922, **63**, 232—233).—Mercury oxycyanide is liable to explode when ground in a mortar, or rubbed between a glass stopper and the neck of a bottle; explosion has also taken place when the compound has been mixed with indifferent substances by means of a wooden spatula on a wooden board.

W. P. S.

Sulphur Thiocyanate. HANS LECHER and MAX WITTEW (Ber., 1922, **55**, [B], 1481—1482; cf. Lecher and Wittwer, this vol., i, 641).—A solution of thiocyanogen in ether reacts readily with dry hydrogen sulphide with the separation of *sulphur thiocyanate*, $S(SCN)_2$, colourless, pearly leaflets which are decomposed by an excess of the gas. The substance decomposes somewhat readily when preserved at the atmospheric temperature. When heated in an open tube in the water-bath it rapidly darkens and then suddenly decomposes with evolution of orange-coloured vapours. A solution of it in a mixture of ether and benzene does not react with powdered iron, but the violet red colour of ferric thiocyanate is immediately developed when a drop of water is added; the substance and also disulphur dithiocyanate (following abstract) are thus distinguished sharply from free thiocyanogen.

H. W.

Disulphur Dithiocyanate. HANS LECHER and ALFRED GOEBEL (Ber., 1922, **55**, [B], 1483—1495).—Sulphur chloride reacts with metallic thiocyanates with the formation of *disulphur dithiocyanate*, but the course of the change is greatly dependent on the particular thiocyanate and the solvent. Potassium thiocyanate appears to be quite unsuitable and lead thiocyanate is not dependable, the reaction being governed by unknown catalytic influences. The best and most uniform results are obtained with mercuric thiocyanate. If solutions of the compound are desired, chloroform or carbon tetrachloride are conveniently used as solvents, since they do not dissolve the mercury salts; if, however, the compound is to be isolated, carbon disulphide is to be preferred. For its isolation, the solutions prepared in this solvent are cooled in a mixture of solid carbon dioxide and acetone; the mother-liquor is decanted, the residue is dissolved in ether, from which it is frozen out, and the process is repeated as often as necessary. A special form of apparatus which permits the necessary filtration and manipulation at a low temperature and with the minimum exposure to air is described and figured in the text. Disulphur dithiocyanate forms colourless crystals, m. p. -3.3° (corr.), to an

odourless, yellow, viscous liquid. It is somewhat unstable and shows obvious signs of decomposition after preservation in an ice-chest during about two days. At the atmospheric temperature, its stability appears to be controlled largely by unascertained catalytic influences. When cautiously heated, it becomes successively dark yellow and red, and ultimately detonates. It does not react with iron in the presence of ether, but immediately forms ferric thiocyanate after addition of a drop of water. The isolated liquid substance, on the other hand, reacts instantaneously with iron. In its initial phase the hydrolysis of disulphur dithiocyanate by water appears to be analogous to that of sulphur chloride: $S_2(SCN)_2 + 2H_2O \rightarrow HO \cdot S \cdot S \cdot OH + 2HCNS$, but reaction proceeds subsequently in accordance with the schemes: $HO \cdot S \cdot S \cdot OH + 2HSCN \rightarrow 2S + 2H_2O + (SCN)_2$ and $3(SCN)_2 + 4H_2O \rightarrow 5HSCN + H_2SO_4 + HCN$. Disulphur dithiocyanate reacts with piperidine in the presence of carbon tetrachloride, giving piperidine thiocyanate, $C_5H_{11}N \cdot HSCN$, colourless leaflets, m. p. 95° , and piperidine disulphide, m. p. $64-64.5^\circ$, b. p. $160-161^\circ/11$ mm. The reaction is closely analogous to that which occurs under similar conditions between sulphur chloride and piperidine. When dissolved in carbon disulphide, sulphur chloride reacts with dimethylaniline in such a manner that di-*p*-dimethylaminophenyl disulphide constitutes about three-quarters of the isolated sulphides, the remainder being a mixture of the corresponding mono- and tri-sulphides. With disulphur dithiocyanate under similar conditions, the equilibrium is displaced in the direction of the mono- and tri-sulphides, which in this case compose about two-thirds of the isolated sulphides, the remaining third consisting of disulphide. Free sulphur is not formed in either reaction.

It appears therefore that disulphur dithiocyanate is a type of sulphur haloid intermediate between sulphur bromide and the controversial sulphur iodide. The thiocyano-radicle preserves its stability and halogen nature when united to the $\cdot S \cdot S \cdot$ group. H. W.

Alkylthiol Thiocyanates. II. HANS LECHER and MAX WITTEWER (*Ber.*, 1922, **55**, [B], 1474-1480; cf. Lecher and Simon, A., 1921, i, 414).—The preparation of further examples of alkylthiol thiocyanates is recorded. The substances appear particularly valuable for synthetic purposes, since the negative substituent has not a pronounced substituting or de-sulphurising action, as is the case with the chlorine atom. They have been applied in the preparation of mixed disulphides.

Ethylthiol thiocyanate, $Et \cdot S \cdot S \cdot C \cdot N$, is prepared by the action of an excess of thiocyanogen dissolved in ether on an ethereal solution of ethyl mercaptan: $EtSH + (SCN)_2 = Et \cdot S \cdot SCN + HSCN$; unused thiocyanogen and thiocyanic acid are removed by washing the ethereal solution with ice-cold water. It is a colourless liquid, b. p. $52^\circ/1.5$ mm., with an exceedingly unpleasant odour. It is very unstable, and becomes noticeably decomposed when preserved during a quarter to half an hour in an ice-chest; it is more stable in dry ethereal solution. *Phenylthiol thiocyanate* like-

wise decomposes readily. It cannot be purified by distillation in a vacuum, and, at the atmospheric temperature, is a yellow liquid which solidifies to a colourless, crystalline solid when strongly cooled. β -Naphthylthiol thiocyanate forms small, pale yellow crystals, m. p. $64.5-65^\circ$ (corr.) after softening at $63-64.5^\circ$; it may be preserved unchanged for several weeks.

Phenyl ethyl disulphide, EtS·SPh, a colourless liquid with a faint, unpleasant odour, b. p. 123° (corr.)/14 mm., $d_4^{22.8}$ 1.1119, is prepared by the action of an ethereal solution of thiophenol on a solution of ethylthiol thiocyanate in ice-cold ether. β -Naphthyl ethyl disulphide is a pale yellow liquid, b. p. 162° /2 mm. *Phenyl β -naphthyl disulphide* (from β -naphthylthiol thiocyanate and thiophenol) crystallises in colourless needles, m. p. $75-76^\circ$. H. W.

Formation of Hydrogen Cyanide from Nitrogen and Hydrocarbons in the Electric Arc. A. KOENIG and W. HUBBUCH (*Z. Elektrochem.*, 1922, **28**, 202—223).—The formation of hydrogen cyanide from acetylene and nitrogen in a water-cooled arc under reduced pressure has been investigated. The concentration of acetylene was kept very low. Keeping the rate of flow of the gas mixture constant (3 litres per hour) the consumption of energy by the arc, gas pressure, and composition were systematically varied. It is shown that mixtures containing less than 2 vol.% of acetylene were quantitatively converted into hydrogen cyanide without any formation of carbon. With higher concentrations of acetylene, there was a considerable separation of carbon, and the yield of hydrogen cyanide was smaller. The energy yield was only 0.5—1.5 grams per kilowatt hour. Further experiments, designed to test the possibility of a commercial synthesis of hydrogen cyanide from nitrogen and hydrocarbons, were carried out at atmospheric pressure in a high tension arc which was rotating in a magnetic field. In these experiments, the rate of flow of the gas mixture was 10, 20, 50, and 100 litres per hour. The following mixtures were passed through the arc: (1) nitrogen with 1—3% acetylene, (2) nitrogen with 1—9% of 50% acetylene-hydrogen mixture, (3) nitrogen with 1—19% of a 1:2 mixture of acetylene and hydrogen, (4) 7:3 nitrogen-hydrogen mixture with 3—11% of acetylene, (5) 1:1 nitrogen-hydrogen mixture with 4—12% of acetylene, (6) nitrogen with 1—5.6% of ethylene and (7) nitrogen with 2—15% of methane. The energy and material yields with various compositions of the mixtures and various rates of flow are plotted on curves. It is shown that with a relatively slow rate of flow, that is, with the highest temperature, methane which shows the least tendency to deposit carbon gives a practically constant yield of 40% hydrogen cyanide irrespective of its concentration within the limits 2—11%. Ethylene and acetylene mixed with hydrogen show definite maxima in the yields at the point where the deposition of carbon commences. Mixtures of pure acetylene with nitrogen give a maximum yield of hydrogen cyanide in the region where there is a heavy deposition of carbon. With a more rapid rate of flow of the gases, the yields are reversed, methane giving a smaller

yield than the other hydrocarbons, and in these circumstances the yield of hydrogen cyanide from ethylene is much poorer, so that high yields may only be obtained when acetylene is used with a high rate of flow. Very good yields, both with respect to energy and material, are obtained when a mixture of 30% of hydrogen and 70% of nitrogen is passed with 7—8% of acetylene at the rate of 20 l. per hour through the arc. In this case, there is no deposition of carbon. With a very rapid rate of flow (up to 100 l. per hour), the energy yield, from mixtures of nitrogen, hydrogen, and acetylene, with a great excess of nitrogen, reaches a maximum of 10—11 grams of hydrogen cyanide per kilowatt hour. J. F. S.

Simple Cyano- and Cyanuric Compounds. III. Malononitrile and its Halogenation. ERWIN OTT and BERNHARD LÖPMANN (*Ber.*, 1922, **55**, [B], 1255—1261).—The bromination of malononitrile dissolved in water has been examined by Hesse, who isolated a small amount of a crystalline substance, m. p. 123—124°, which he considered to be dibromomalononitrile, whilst the main product of the action was an oil which could not be purified. A repetition of his experiments has led to different results. The solid material is shown to be dibromosuccinonitrile; exceptional difficulties are encountered in the analysis of this substance, but its constitution is placed beyond doubt by its hydrolysis to dibromosuccinic acid and reduction of the latter to succinic acid. The liquid product consists of dibromomalononitrile, which can be purified readily by distillation under diminished pressure. It has b. p. 49.2°/10 mm., m. p. +3°. It is a highly reactive substance, which is transformed by alkali iodide in neutral aqueous solution into the unstable *di-iodomalononitrile*, and is reduced quantitatively by an acidified solution of potassium iodide to malononitrile and iodine.

The action of chlorine on malononitrile proceeds on similar lines, but the dichloro-compound has a marked tendency to unite with a further molecule of chlorine, with the formation of a tetrachloride; the formation of the latter cannot be avoided by the use of only that quantity of chlorine which is theoretically necessary. The products obtained are *dichloromalononitrile*, a mobile liquid with a very intense odour of chloropicrin, b. p. 97°/754 mm., *dichloromalononitrile dichloride*, b. p. 183—184°/759 mm. (slight decomp.), and *dichlorosuccinonitrile*, monoclinic crystals, m. p. 91°, b. p. 150°/15 mm.

Malononitrile can be obtained fairly readily and in considerable quantity if the method of Phelps and Tillotson (*A.*, 1908, i, 757) is followed for the preparation of ethyl cyanoacetate and the latter is transformed into cyanoacetamide (yield 93%) by alcoholic instead of aqueous ammonia. It appears to be a useful solvent for the determination of molecular weight by the cryoscopic method, the mean constant being 50.03. H. W.

C₁₈ Fatty Acids. V. Molecular Rearrangements in some Derivatives of Unsaturated Higher Fatty Acids. BEN H. NICOLET and JOSEPH J. PELC (*J. Amer. Chem. Soc.*, 1922, **44**, 1145—1149).—The unsaturated fatty acids examined readily give

hydroxamic acids, as do the aromatic or saturated fatty acids, and the following were prepared. Oleohydroxamic acid (cf. Morelli, A., 1908, i, 758); *elaidohydroxamic acid*, m. p. 86°; *ricinoleohydroxamic acid*, m. p. 65°; *linolohydroxamic acid*, m. p. 8—10°; *oleoacetylhydroxamic acid*, m. p. 63°; *oleodiacylhydroxamic acid*, m. p. 64—65°; *elaidoacetylhydroxamic acid*, m. p. 84°; *elaidodiacylhydroxamic acid*, m. p. 82°. These hydroxamic acids undergo the Lossen rearrangement with aqueous alkali, the change not being affected by the double bond. *Di-trans-heptadecylenylcarbamide* has m. p. 59°, *di-cis-heptadecylenylcarbamide* has m. p. 92—93°, *dihydroxyheptadecylenylcarbamide*, m. p. 57·5°, was obtained from λ -acetylricinoleoacetylhydroxamic acid, m. p. 6—8°.

The Lengfeld-Stieglitz rearrangement of the acetylhydroxamic acids with sodium ethoxide also proceeded normally, the corresponding urethane being obtained. *trans-Heptadecylenylurethane* had m. p. 42—43°, and *cis-heptadecylenylurethane* had m. p. 87—88°.

The supposed analogous rearrangement to the carbimide by the action of acetic anhydride was complicated, however, by the fact that a mixture of *cis*- and *trans*-carbimides always resulted, whichever pure hydroxamic was used. These carbimides could not be separated from one another, but were detected by conversion into the corresponding urethanes.

W. G.

The Fluorides of Organo-metallic Compounds. II. Lead Alkyl and Aryl Fluorides.

ERICH KRAUSE and ERICH POHLAND (*Ber.*, 1922, 55, [B], 1282—1289; cf. Krause, A., 1919, i, 9; Krause and Becker, A., 1920, i, 340).—Lead alkyl fluorides cannot be prepared by double decomposition between normal potassium fluoride and the necessary lead alkyl haloid, but are obtained by the action of hydrofluoric acid on lead trialkyl hydroxides, the operations being rendered exceptionally unpleasant by the physiological action of the latter substances. They are considerably more stable than the corresponding lead alkyl chlorides, and are therefore the most stable lead alkyl haloids; after a few months, a slight decomposition is generally evident, which is more marked with decreasing weight of the alkyl group. The melting points are very high and cannot be observed, since they lie invariably above the temperature of decomposition. The lead aryl fluorides are prepared by the action of normal potassium fluoride on the lead aryl bromides; they are uniformly sparingly soluble and very stable substances.

Lead trimethyl fluoride, PbMe_3F , is prepared by exactly neutralising a solution of lead trimethyl hydroxide in alcohol with a mixture of hydrofluoric acid (33%) and alcohol and spontaneous evaporation of the solution over phosphoric oxide. It crystallises in long, very slender needles, d_4^{20} 3·53, decomp. about 305°. In spite of its high temperature of decomposition, it is remarkably readily volatilised, giving a vapour with an intensely unpleasant, metallic odour. The solubilities of the substance in grams per 100 grams of methyl alcohol, ethyl alcohol, benzene, and water at 30° and 50°, respectively, are 8·24 and 99·5; 6·89 and 82·0; 0·028 and 0·87; 5·51

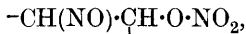
and 26.3. *Lead triethyl fluoride* forms long, thin, doubly refractive prisms, d_4^{16} 2.48, decomp. about 240° ; its solubilities in methyl alcohol, ethyl alcohol, benzene, and water at 30° and 50° are 7.24 and 90.0; 6.11 and 75.1; 0.185 and 0.60; 1.30 and 7.04. *Lead tri-n-propyl fluoride* crystallises in needles, d_4^{18} 1.56, decomp. about 235° , its solubilities in methyl alcohol, ethyl alcohol, benzene, and water at 30.1° and 50.0° , respectively, being 2.01 and 4.94; 1.21 and 3.53; 0.055 and 0.082; 0.17 and 0.23. *Lead tri-isobutyl fluoride* forms long, thin, doubly refracting prisms, d_4^{17} 1.50, decomp. about 230° ; the solubilities in methyl alcohol, ethyl alcohol, benzene, and water at 30.0° and 50.0° , respectively, are 1.76 and 2.96; 1.09 and 2.13; 0.042 and 0.071; 0.12 and 0.18. *Lead tri-isoamyl fluoride*, long, colourless needles, has d_4^{17} 1.46, decomp. about 251° , and the following solubilities in methyl alcohol, ethyl alcohol, benzene, and water at 30.1° and 50.0° ; 2.34 and 6.32; 1.73 and 4.55; 0.063 and 0.094; 0.019 and 0.022. *Lead triphenyl fluoride* is prepared by agitating lead triphenyl bromide dissolved in benzene with an aqueous solution of normal potassium fluoride. It forms colourless, microscopic needles, $d_4^{16.5}$ 1.82, decomp. about 318° . Its solubilities in methyl alcohol, ethyl alcohol, benzene, and water at 30.0° and 50.0° are, respectively, 0.36 and 1.45; 0.15 and 0.24; 0.080 and 0.092; 0.031 and 0.10. *Lead tri-p-tolyl fluoride* crystallises in hair-fine needles, decomp. about 280° . *Lead tricyclohexyl fluoride* forms microscopic spikes, $d_4^{16.5}$ 1.79, decomp. about 198° . One hundred grams of methyl alcohol, ethyl alcohol, benzene, and water dissolve 0.66, 0.39, 0.11, and 0.096 gram of the substance, respectively, at 30° .
H. W.

Attempt at a Systematic Extension of the Preparation of Organometallic Compounds. Application to Ferrous Ethyl Iodide. ANDRÉ JOB and RENÉ REICH (*Compt. rend.*, 1922, **174**, 1358—1361).—When ferrous iodide in ethereal solution is boiled with zinc ethyl iodide for six hours in the complete absence of air, a solution of *ferrous ethyl iodide*, FeEtI , is obtained. It is quantitatively decomposed by water, giving ethane and ferrous hydroxide, and by absolute alcohol giving ethane and ferrous iodoethoxide. If ferric chloride is used instead of ferrous iodide, the chloride is first instantaneously and quantitatively reduced to ferrous chloride, and this is then slowly converted into ferrous ethyl chloride.

W. G.

Compounds containing Zinc derived from Additive Products of Oxides of Nitrogen and Olefines. ALFRED SCHAARSCHMIDT, MAXIMILIAN VEIDT, and FRANZ SCHLOSSER (*Ber.*, 1922, **55**, [B], 1103—1112).—The olefine, obtained by the action of heat on paraffin chlorinated at 150° (cf. Schaarschmidt and Thiele, A., 1921, i, 1), forms an unstable additive product with nitrogen tetroxide which is reduced by zinc dust and ammonia in alcoholic solution to a mixture of an oil containing nitrogen, a solid paraffin, and a solid product, which contains one atom of zinc for every two atoms of nitrogen. Since the heterogeneous nature of the initial material renders the interpretation of the experimental

results a matter of great difficulty, the behaviour of *cyclohexene* and cetene under similar conditions has been investigated. The crude additive product of *cyclohexene* and nitrogen tetroxide is reduced to a mixture of a *liquid*, free from zinc, which could not be purified satisfactorily, but which appears to have the formula $C_6H_{11}O_2N$, and an uncrystallisable *solid* containing nitrogen, oxygen, and zinc in the atomic proportion, 2 : 4 : 1. It appears most probable that the initial additive product is either a nitro-nitrite, $-CH(NO_2) \cdot \underset{|}{CH} \cdot O \cdot NO$, or a nitroso-nitrate,



which undergoes partial hydrolysis and reduction to the oxime, giving the compound $C_6H_8 \left\langle \begin{array}{c} C:N \cdot O \cdot Zn \cdot O \cdot N:C \\ | \qquad \qquad | \\ CH \cdot OH \quad HO \cdot HC \end{array} \right\rangle C_6H_8$. If this is decomposed by being treated with hydrogen sulphide in glacial acetic acid solution, it yields the corresponding hydroxy-oxime which resembles closely the zinc-free reduction product. With cetene, the results are to some extent similar. The zinc-free *liquid* appears to have the formula $C_{16}H_{33}O_2N$, whereas the solid *product*, yellow crystals, m. p. (indefinite) 90—93°, has the composition $(C_{16}H_{32}O_2N)_2Zn$. If, however, the latter is crystallised repeatedly from ether, it yields a *substance*, $C_{32}H_{60}O_2N_2Zn$, m. p. 80—81°, which is converted by hydrogen sulphide in glacial acetic acid solution into a yellow, crystalline *compound*, $C_{16}H_{31}ON$. It appears, therefore, that, in addition to the hydroxy-oxime compound, an unsaturated oxime is also produced which contains the oxime group at the end of the chain.

Cetene-ψ-nitrosite, $C_{32}H_{64}O_6N_4$, colourless crystals, m. p. 85°, is obtained by the gradual admixture of solutions of cetene and nitrogen peroxide in light petroleum at -15° to -8°.

Similar series of compounds containing aluminium and mercury in place of zinc have also been prepared. H. W.

The Structure of the Benzene Nucleus. I. Intra-nuclear Tautomerism. CHRISTOPHER KELK INGOLD (T., 1922, **121**, 1133—1143).

The Structure of the Benzene Nucleus. II. Synthetic Formation of the Bridged Modification of the Nucleus. CHRISTOPHER KELK INGOLD (T., 1922, **121**, 1143—1153).

The Influence of some Substituents in the Benzene Ring on the Mobility of Chlorine in the Side-chain in its Relation to the Problem of Substitution in the Benzene Ring. S. C. J. OLIVIER (*Rec. trav. chim.*, 1922, **41**, 301—311; cf. A., 1914, ii, 846).—In the reaction between *p*-bromobenzenesulphonyl chloride and substituted benzenes, the influence of the substituents is found to be $Me > H > Br > Cl > NO_2$, and this is, to a great extent, confirmed by the converse reaction—benzene and substituted sulphonyl chlorides—the result in the latter case being $Me > H > I > Br > Cl > NO_2$. Similar results are obtained in the case of saponification of benzyl chloride and its ring-substituted derivatives, by a large excess of water. The position of the substituents in addition

to their nature was examined and the above results amplified as follows: $p\text{-Me} > o\text{-Me} > m\text{-Me} > \text{H} > p\text{-Cl} > o\text{-Cl} > m\text{-Cl} > m\text{-NO}_2 > o\text{-NO}_2 > p\text{-NO}_2$. Thus, from knowledge of the substituent and its position, the substitution in the ring may be predicted, and the theoretical results which would be expected from the order given above are in accordance with those obtained by Holleman and his co-workers.

H. J. E.

The Labile Nature of the Halogen Atom in Organic Compounds. IV. The Tautomeric Hydrogen Hypothesis, and the Removal of the Halogen Atom from Aromatic Nitro-compounds. ALEXANDER KILLEN MACBETH (T., 1922, 121, 1116—1121).

Physico-chemical Investigation of Tetrahydronaphthalene and Decahydronaphthalene. W. HERZ and PAUL SCHUFTAN (*Z. physikal. Chem.*, 1922, 101, 269—285).—The authors have investigated a number of the physical properties of tetralin (tetrahydronaphthalene) and decalin (decahydronaphthalene). These substances are of great use as solvents and are also used as sources of heat and power and have a use as lubricants. The substances were carefully purified and the following physical constants determined: boiling point, tetralin, 207.3° , decalin, 191.7° ; vapour pressure formula, tetralin, $\log p = -2681.3/T + 1.75 \log T - 0.003214T + 5.31446$; decalin, $\log p = -2395.2/T + 1.75 \log T - 0.00270983T + 4.62719$; heat of vaporisation, tetralin, 79.32 cal./gr., decalin, 71.01 cal./gr.; Trouton constant, tetralin, 21.8, decalin, 21.1; ebullioscopic constant, tetralin, 5773, decalin, 6036; specific heat ($15\text{--}18^\circ$), tetralin, 0.403, decalin, 0.395; melting point, tetralin, $-35.0^\circ \pm 0.5^\circ$, decalin $-124^\circ \pm 2^\circ$; density, tetralin, $d_t = 0.9843 (1 - 763 \times 10^{-6}t)$, decalin, $d_t = 0.8975 (1 - 818 \times 10^{-6}t)$; coefficient of expansion ($15\text{--}25^\circ$), tetralin 0.00078, decalin, 0.00086; critical temperature, tetralin 789° , decalin, 724° ; measurements of internal friction have been made for both substances at 25° , 50° , and 75° , and the surface tension has been measured at a series of temperatures; at the boiling point the surface tension in dynes/cm. is: tetralin 17.46, decalin 15.71, and the molecular surface energy: tetralin 512.9, decalin 505.1. A number of other quantities are calculated and an account of some partition experiments is given.

J. F. S.

Stereoisomeric Derivatives of Stilbene. R. STOERMER and H. OEHLERT (*Ber.*, 1922, 55, [B], 1232—1243).—The authors describe a series of attempts to convert stable into labile stilbene derivatives by the action of ultra-violet light. In general, the experiments are greatly complicated by the formation of resinous products, and the yields are not good. In all the cases investigated the melting points of the labile are lower than those of the corresponding stable compounds, and the isomerides are not infrequently distinguished by marked differences in colour.

2 : 4-Dinitrostilbene, $\text{CHPh}:\text{CH}\cdot\text{C}_6\text{H}_3(\text{NO}_2)_2$, is converted by exposure in benzene solution to the rays of a quartz-mercury lamp to the extent of 20% into allo-2 : 4-dinitrostilbene, large,

transparent, lemon-yellow crystals, m. p. 127° ; the solubility of the labile and stable compounds in benzene at 20° is, respectively, 11.79% and 3.7%. 4-Nitro-2-aminostilbene and 2-nitro-4-aminostilbene do not suffer a similar transformation in benzene solution. Their acetyl derivatives are likewise unchanged. The attempted partial reduction of *allo*-2 : 4-dinitrostilbene by ammonium sulphide in the presence of alcohol results partly in the production of stable 2 : 4-dinitrostilbene and partly in the formation of stable 2-nitro-4-aminostilbene. Stable 2 : 4-dinitrostilbene, m. p. 140° , is partly reduced by phenylhydrazine at 100° to 4-nitro-2-aminostilbene, but another portion undergoes a remarkable change to a red, crystalline *variety*, m. p. 140° (m. p. when mixed with the yellow stable 2 : 4-dinitrostilbene, 140°). Either form, on protracted exposure to sunlight, appears to pass into a brown modification, m. p. 140° , so that here a remarkable instance of colour trimorphism is possibly presented. *allo*-2 : 4-Dinitrostilbene is transformed by bromine into the dibromide of the stable modification.

The most suitable solvent for the isomerisation of 4-nitrostilbene is chloroform, since resinification occurs to only a slight extent, although the yields of *allo*-4-nitrostilbene, large, brownish-yellow, quadratic crystals, m. p. 65° , leave much to be desired. It is reduced by ferrous sulphate and ammonia to *allo*-4-aminostilbene, which could be isolated only as a yellowish-red liquid. When dissolved in alcohol and treated with hydrochloric acid, it gives the hydrochloride of the stable isomeride, m. p. 245° , but by cautious acetylation or benzylation it can be transformed into *allo*-4-acetylaminostilbene, yellow crystals, m. p. 134° , and *allo*-4-benzoylamino-stilbene, broad needles, m. p. 154° .

2-Nitro-4-cyanostilbene is converted to a small extent by exposure to ultra-violet light into cyanophenylisatogen, m. p. 224° (cf. Pfeiffer, A., 1916, i, 327).

2-Nitrostilbene-4-carboxylic acid is isomerised to a small extent in benzene solution to *allo*-2-nitrostilbene-4-carboxylic acid, pale yellow, crystalline aggregates, m. p. 158° . The conversion occurs to a greater extent with the esters; *methyl* *allo*-2-nitrostilbene-4-carboxylate forms coarse, apparently rectangular crystals, m. p. 91° , whereas the corresponding *ethyl* ester could only be obtained as a liquid which, when hydrolysed, gave a mixture of the stereo-isomeric acids.

Stable *methyl* 2-aminostilbene-4-carboxylate, lemon-yellow, flat needles, m. p. 130° , is obtained by the reduction of the corresponding nitro-ester with ferrous sulphate and ammonia; the *diazonium* salt is described. *Methyl* *allo*-2-aminostilbene-4-carboxylate, large dark yellow or pale brown needles, m. p. 95° , is prepared similarly from the *allonitro*-ester.

H. W.

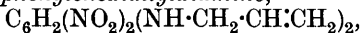
Dinitrodiphenylamine. R. C. MORAN (U.S. Pat. 1401631).—Dinitrodiphenylamine is prepared by combining a halogenodinitrobenzene with aniline by heating to 90 — 100° with sodium carbonate or sodium hydrogen carbonate in the absence of solvents or added water.

CHEMICAL ABSTRACTS.

Action of certain Primary Bases on 5-Bromo-1 : 2 : 4-trinitrobenzene. M. GIUA and A. ANGELETTI (*Gazzetta*, 1922, 52, i, 316—322).—Since 5-bromo-1 : 2 : 4-trinitrobenzene contains a nitro-group in the 1-position and a labile hydrogen atom (A., 1921, i, 551), the action on it of bases may give rise to two series of compounds: (1) $C_6H_2Br(NO_2)_3 + 2NH_2R = C_6H_2Br(NO_2)_2 \cdot NHR + NH_2R, HNO_2 \rightarrow R \cdot OH + N_2 + H_2O$, and (2) $C_6H_2Br(NO_2)_3 + 4NH_2R = C_6H_2(NO_2)_2(NHR)_2 + NH_2R, HBr + R \cdot OH + N_2 + H_2O$. In the case of primary aromatic amines, the preceding equations become: (1a) $C_6H_2Br(NO_2)_3 + 3NH_2R = C_6H_2Br(NO_2)_2 \cdot NHR + NR:N \cdot NHR + 2H_2O$ and (2a) $C_6H_2Br(NO_2)_3 + 5NH_2R = C_6H_2(NO_2)_2(NHR)_2 + NR:N \cdot NHR + NH_2R, HBr + 2H_2O$. The reaction (1) or (1a) has been investigated for a number of bases, and reaction (2) for allylamine, 2 mols. of the latter and 1 mol. of the bromonitro-compound yielding an oily product difficult to purify. The negative grouping of 5-bromo-1 : 2 : 4-trinitrobenzene causes the nitro-group in position 1 to react first, the bromine atom reacting only when the base is in excess and the heating prolonged.

5-Bromo-2 : 4-dinitroethylamine, $C_6H_2Br(NO_2)_2 \cdot NH_2Et$, prepared by the action of ethylamine, forms small, lustrous, orange-yellow prisms, m. p. 105—106°, and in alcoholic solution gives a red coloration with alkalis.

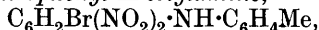
2 : 4-Dinitro-*m*-phenylenediallyldiamine,



crystallises in long, lustrous, pale yellow needles, m. p. 139—140°, dissolves in concentrated sulphuric acid with a yellow coloration, and in alcoholic solution gives a brick-yellow coloration with alkalis.

5-Bromo-2 : 4-dinitrodiphenylamine, prepared from aniline and 5-bromo-1 : 2 : 4-trinitrobenzene, forms garnet-red prisms, m. p. 156° (cf. Jackson and Cohoe, A., 1901, i, 585).

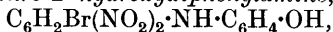
5-Bromo-2 : 4-dinitrophenyl-*m*-tolylamine,



obtained by the action of *m*-toluidine, crystallises in red prisms, m. p. 152°, and gives a dark red coloration with either alkalis in alcoholic solution or concentrated sulphuric acid.

5-Bromo-2 : 4-dinitrophenyl-*p*-tolylamine, prepared from *p*-toluidine, forms pale yellow prisms, m. p. 164—165°, and gives a red coloration with alkalis in alcoholic solution, and a red solution with hot concentrated sulphuric acid.

5-Bromo-2 : 4-dinitro-2'-hydroxydiphenylamine,

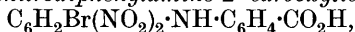


prepared from *o*-aminophenol, forms red prisms, m. p. 203—204°, dissolves in hot, concentrated sulphuric acid giving an intense blue solution, and in alcoholic solution yields a dark red coloration with alkalis.

5-Bromo-2 : 4-dinitro-3'-hydroxydiphenylamine, $C_{12}H_8O_5N_3Br$, prepared from *m*-aminophenol, crystallises in red prisms, m. p. 173—174°, dissolves in hot, concentrated sulphuric acid to a deep, reddish-brown solution, and in alcoholic solution gives a dark red coloration with potassium hydroxide.

5-Bromo-2 : 4-dinitro-4'-hydroxydiphenylamine, prepared from *p*-aminophenol, forms garnet-red prisms, m. p. 215—216°, gives a brownish-red solution in hot, concentrated sulphuric acid, and in alcoholic solution yields a dark red coloration with alkali.

5-Bromo-2 : 4-dinitrodiphenylamine-2'-carboxylic acid,

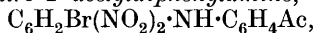


prepared from anthranilic acid, crystallises in garnet-yellow prisms, m. p. 274—276°, forms a yellow solution in hot, concentrated sulphuric acid, and in alcoholic solution gives a reddish-brown coloration with excess of alkali.

5-Bromo-2 : 4-dinitrodiphenylamine-3'-carboxylic acid, prepared from *m*-aminobenzoic acid, forms reddish-yellow needles, m. p. 245°, and gives a red coloration with alkali in excess.

5-Bromo-2 : 4-dinitrodiphenylamine-4'-carboxylic acid, prepared from *p*-aminobenzoic acid, crystallises in lustrous, reddish-yellow prisms, m. p. 247°, and with excess of alkali yields an intense, dark red coloration.

5-Bromo-2 : 4-dinitro-4'-acetyldiphenylamine,



prepared from *p*-aminoacetophenone, forms orange-yellow prisms, m. p. 167—168°, dissolves in cold concentrated sulphuric acid to a red solution, and in alcoholic solution gives a dark red coloration with alkalis.

T. H. P.

The Dihydronaphthalene Series. III. The Oxidation and Bromination of 5 : 8-Dihydro- α -naphthylamine. FREDERICK MAURICE ROWE and JOHN STANLEY HERBERT DAVIES (T., 1922, 121, 1000—1007).

Preparation of Amino-phenols or Aromatic Amino-acids.

WILLIAM LEWCOCK, WILLIAM GORDON ADAM, NORMAN EDWARD SIDERFIN, and WILLIAM LYLE GALBRAITH (Brit. Pat. 179753).—Amino-phenols or aromatic amino-acids may be obtained in good yield by the reduction of nitro- or azo-phenols or aromatic acids, with hydrogen sulphide in presence of an alkali carbonate, at about 100°. The compound to be reduced may be dissolved wholly or in part in a solution of the alkali carbonate, or the latter may be added to an already prepared solution of the alkali phenoxide, or salt. The hydrogen sulphide need not be pure but may, for example, be employed in the form of the waste gases from the ammonia scrubbers of gas-works, containing only about 15% of hydrogen sulphide together with a large proportion of carbon dioxide.

G. F. M.

Preparations in the Naphthalene Series. R. SCHOLL [with CHRISTIAN SEER and RICHARD WEITZENBOCK] (*Monatsh.*, 1921, 42, 405—409).—*5-Iodo-1-nitronaphthalene* was prepared by the action of potassium iodide on a solution of 5-nitronaphthalene-diazonium chloride; it forms fine, straw-yellow needles, m. p. 164°. When reduced with tin and hydrochloric acid, it gives *5-iodo- α -naphthylamine*, colourless leaflets, m. p. 75—75.5°. The *sulphate* forms fine needles, becoming red in the air and decomposing at 205—215°. The *hydrochloride* forms fine needles becoming blue

on exposure to light. 5-Iodo- α -naphthol was obtained by boiling a 20% sulphuric acid solution of 5-iodo-1-diazonaphthalene; it is volatile in steam and crystallises from hot water in fine, white needles, m. p. 131—132°. The yield of iodonaphthol was small, the principal product being a resin from which a substance, dark red needles, m. p. 228—245°, was obtained, probably a di-iodo-azonaphthol. By methylation of 5-iodo-1-naphthol with methylsulphate in alkaline solution, 5-iodo- α -naphthyl methyl ether was obtained, as needles, m. p. 78—79°. By heating 5-iodo-1-nitronaphthalene with copper powder, 5:5'-dinitro-1:1'-dinaphthyl was obtained, bright brown leaflets, m. p. 228—228.5°.

1:8-Dibromo-2:7-dihydroxynaphthalene was obtained by brominating 2:7-dihydroxynaphthalene in cold acetic acid; it forms aggregates of white needles, m. p. 156—158°, decomposition starting at 130°. Its dibenzoyl derivative forms white needles from acetic acid, m. p. 209°.

[With ARTHUR ERTL.]—5-Nitro- α -naphthonitrile, previously prepared by nitrating α -naphthonitrile, was obtained by the action of potassium cuprocyanide on 5-nitro-1-diazonaphthalene. 5-Nitro-1-diazonaphthaleneimide was also obtained in a new way from 5-nitro-1-diazonaphthalene and hydroxylamine or potassium hydroxylamine sulphonate. The sodium salt of normal 5-nitronaphthalene-1-diazonium hydroxide begins to decompose below 100° and couples with β -naphthol in alkaline solution. The sodium salt of *iso*-5-nitronaphthalene-1-diazonium hydroxide does not couple with alkaline β -naphthol; it forms long, dark yellow needles, decomposing at about 165°. E. H. R.

The Configuration of Ring Systems in Space. H. G. DERX (*Rec. trav. chim.*, 1922, **41**, 312—342; cf. Böeseken, A., 1921, i, 843).—In applying the boric acid method in order to determine the space configuration of the *cyclohexane*-1:2-diols, no positive result was obtained (Böeseken and van Giffen, A., 1920, ii, 219), and a further investigation, including also 1:2-diols derived from tetrahydronaphthalene and from *cycloheptane*, is here reported. The results obtained indicate that homocyclic rings containing more than five carbon atoms exist, not in one plane, but in three dimensions. Of these diols, the isomeride having the lower melting point yields with acetone a condensation product, $C_7H_{12} < \begin{smallmatrix} O \\ \diagup \quad \diagdown \\ O \end{smallmatrix} > CMe_2$,

showing it to possess the *cis*-configuration; this is confirmed in the case of the *cyclohexane*diols by the existence of the *trans*-isomeride in two optically active forms. The two *cycloheptane*-1:2-diols both form condensation products with acetone (cf. Böeseken and Derx, A., 1921, i, 663), and both increase the conductivity of solutions of boric acid, the increase in the case of the *cis*-isomeride being three times as great as in that of the *trans*-isomeride. The author draws the conclusion that annular tension does not exist in six-atom carbon rings; further, that in all determinations of molecular configuration in the case of rings, the three-dimensional structure should be taken into account.

H. J. E.

a a 2

Catalytic Action of Benzyl Alcohol. J. JACOBSON (*Compt. rend. Soc. Biol.*, 1921, **85**, 299—300; from *Chem. Zentr.*, 1921, iii, 1463).—Benzyl alcohol diminishes the reducing action of Fehling's solution and interferes with the starch-iodide reaction.

G. W. R.

[Preparation of] Dihydroxyphenylmethylaminoethanol Hydrochloride. W. N. NAGAI (U.S. Pat. 1399144).—Diacetyl-protocatechualdehyde is condensed with nitromethane in slightly alkaline solution, the product being then reduced with zinc and acetic acid in the presence of formaldehyde, and hydrochloric acid added. The substance is crystalline and has hæmostatic properties.

CHEMICAL ABSTRACTS.

Xanthosterol. H. DIETERLE (*Arch. Pharm.*, 1922, **259**, 244—245).—Xanthosterol, isolated from the bark of *Xanthoxylon Budrunga* is not considered to be identical with lupeol isolated by Goodson (A., 1921, i, 488) from *X. macrophyllum*, as, although the m. p. of xanthosterol, its benzoate, and monobromide lie in each case just below those of lupeol and its corresponding derivatives, xanthosterol cannot be regarded as an impure lupeol, since the mixed melting points do not lie between the melting points of the xanthosterol and lupeol derivatives, but a depression of the m. p. is observed in each case.

G. F. M.

Japanese Bird-lime. II. HIDEKICHI YANAGISAWA and NORIKAZU TAKASHIMA (*J. Pharm. Soc. Japan*, 1922, 179—189; cf. A., 1921, i, 760).—To the product of the saponification of bird-lime prepared from *Trochodendron aralioides* with alcoholic potash were added first dilute alcohol and then water, by which caoutchouc, trochol ($C_{26}H_{44}O_2, \frac{1}{2}C_2H_6O, \frac{1}{2}H_2O$), and a small quantity of phytosterol were separated. To the alkaline mother-liquor, a calcium salt was added and the resulting precipitate extracted with ether. From the ether-soluble portion, oleic acid, a semi-liquid acid of unknown nature, resins, trochol, and a phytosterol-like substance were isolated. The latter forms white needles, m. p. 145—155°, and yields two *acetates*, of which the one, $C_{26}H_{43}OAc$, crystallises in white needles, m. p. 190°, and gives on hydrolysis *trochophytosterol*, $C_{26}H_{43}\cdot OH$, m. p. 172—175°; the other forms white needles, m. p. 155—158°. The salt insoluble in ether was decomposed with hydrochloric acid and the liberated acids were converted into their ethyl esters; these proved to be palmitic ester with a small quantity of cerotic ester. By washing the crude ester with sodium carbonate solution, a new acid, *trochic acid*, $C_{31}H_{50}O_5$, was isolated, as a white powder, m. p. 225°; it exists in the bird-lime in the free state. By treatment with acetic anhydride, it gives a substance of m. p. 185—190°.

K. K.

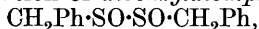
Composition of Bird-lime. II. YUSHICHI NISHIZAWA (*J. Chem. Soc. Japan*, 1922, **43**, 154—172; cf. Yanagisawa, A., 1921, i, 760).—Two alcohols were isolated by saponification of bird-lime. The more fusible *alcohol*, $C_{30}H_{50}O$, forms lustrous scales, m. p. 180°, b. p. 250—255°/0.2 mm., $[\alpha]_D^{25} + 75.77^\circ$, in a mixture of chloroform

and alcohol; the *acetate* forms colourless scales, m. p. 212° . By oxidation with chromic acid, it gives a crystalline solid, $C_{34}H_{48}O_2$, m. p. 162° , b. p. $270^{\circ}/0.2$ mm. (approx.); it yields an *oxime*, $C_{30}H_{48}O:N\cdot OH$, crystallising in needles, m. p. 253° .

The alcohols obtained from bird-lime ($d\ 0.97-0.98$) prepared from *Trochodendron aralioides* were separated as their *acetates*, of which one forms rhombic crystals, m. p. 217° , whilst the other crystallises in needles, m. p. 190° . When hydrolysed, the former gave a dihydric alcohol, *trochodiol*, $C_{29}H_{50}O_2$, crystallising with EtOH from alcohol, rhombic prisms, m. p. 252° , $[\alpha]_D^{20} + 20.3^{\circ}$, in a mixture of chloroform and alcohol, whilst the latter acetate yields a monohydric *alcohol*, forming needles, m. p. 210° . *Trochodiol phenylcarbamate*, $C_{29}H_{48}\cdot O\cdot CO\cdot NPh$, crystallises in rhombic prisms, m. p. 165° . K. K.

Rupture of Bridge Linkings. CARL WAHL (*Ber.*, 1922, 55, [B], 1449—1457).—Although little systematic work has been done on the subject, the bridge linkings in the ether groups, $:C\cdot O\cdot C:$ and $:C\cdot S\cdot C:$, are generally regarded as very stable. The unstabilising effect of phenyl and acetyl or benzoyl groups on the sulphur bridge is now demonstrated.

Benzyl acetonyl sulphide, $CH_2Ph\cdot S\cdot CH_2\cdot COMe$, a colourless liquid, b. p. $155-156^{\circ}/17$ mm., is prepared in good yield by the action of sodium benzyl mercaptan on chloroacetone in the presence of alcohol, anhydrous ether, or benzene, and is conveniently purified through the *sodium hydrogen sulphite* compound. It is oxidised with violence by nitric acid to benzaldehyde and sulphuric acid, a similar change being effected by permanganate and glacial acetic acid, or, less readily, by hydrogen peroxide. It is converted by sodium and alcohol into sodium sulphide, and is reduced by sodium in the presence of moist ether or by zinc dust and acetic acid to benzyl mercaptan. An alcoholic solution of the sulphide yields ammonium chloride and benzyl mercaptan when treated with hydroxylamine hydrochloride, but if the effect of the hydrochloric acid is avoided by the addition of sodium acetate, an *oxime* appears to be formed. It readily adds two atomic proportions of bromine without evolution of hydrogen bromide. It gives a colourless, crystalline, additive *compound* with mercuric chloride. When dissolved in cold glacial acetic acid and treated cautiously with hydrogen peroxide (30%), it yields *benzylacetonylsulphoxide*, colourless, lustrous leaflets, m. p. 125° , which is very sensitive towards rise in temperature. The unrestrained action of hydrogen peroxide and glacial acetic acid on the sulphide proceeds vigorously and leads to the formation of *dibenzyldisulphoxide*,



m. p. 108° . The sulphide yields a *semicarbazone*, m. p. 123° , and a *phenylhydrazone*, colourless needles, m. p. 155° , which could not be converted into an indole derivative by anhydrous zinc chloride.

Benzyl phenacyl sulphide, $CH_2Ph\cdot S\cdot CH_2\cdot C\cdot OPh$, is prepared in 90% yield by the addition of solid phenacyl bromide to sodium benzyl sulphide in the presence of absolute alcohol. It crystallises

in colourless needles which generally melt sharply at 89° , but appears to contain a small proportion of bromine-free impurities which cannot be removed. It gives an additive compound with mercuric chloride. Its behaviour towards oxidising agents is similar to that of benzyl acetyl sulphide, but it is somewhat less sensitive. It gives a *phenylhydrazone*, needles, m. p. 80.5° . *Benzylphenacylsulphoxide* crystallises in colourless leaflets, m. p. 133° .

The sulphides can be converted into sulphones by potassium permanganate and acetic acid if care is taken to avoid the use of an excess of the latter; the yields are satisfactory. *Benzylacetyl-sulphone*, $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{COMe}$, crystallises in colourless needles, m. p. 89° , whereas *benzylphenacylsulphone*, $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{COPh}$, forms colourless, lustrous leaflets, m. p. 113° . The sulphones are transformed by prolonged treatment with boiling alcoholic potassium hydroxide solution (20%) into benzoic or acetic acid and benzyl-methylsulphone, m. p. 127° . *Benzylacetyl-sulphone* gives a *phenylhydrazone*, $\text{CH}_2\text{Ph}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CMe}\cdot\text{N}\cdot\text{NHPh}$, needles, m. p. 121° ; a *semicarbazone*, colourless leaflets, m. p. 189° , and an *oxime*, colourless needles, m. p. 151° . The *phenylhydrazone*, slender needles, m. p. 151.5° , and *oxime*, colourless needles, m. p. 163° , of benzyl phenacyl sulphone are described. H. W.

γ -Diallylaminopropyl *p*-Aminobenzoate. O. KAMM and E. H. VOLWILER (U.S. Pat. 1388573).—Diallylamino-esters of aromatic acids containing a benzene nucleus are prepared by dissolving benzyl chloride or a substituted benzyl chloride in benzene, heating for an hour in a reflux apparatus with a diallylamino-alcohol, and then treating the reaction mixture with dilute acid to dissolve basic compounds, and making the aqueous layer alkaline with sodium hydroxide. The ester can be extracted and dissolved in hydrochloric acid. γ -Diallylaminopropyl *p*-aminobenzoate hydrochloride has local anæsthetic properties, and has m. p. 138° ; β -diallylaminopropyl *p*-aminobenzoate hydrochloride has m. p. 158 — 160° . CHEMICAL ABSTRACTS.

Some Dialkylated Benzyl Cyanides [Phenylacetone nitriles] and the Corresponding Alcohols, Amides, Amines, and Acids. JOSEPH BLONDEAU (*Compt. rend.*, 1922, **174**, 1424—1426).—Phenyldialkylacetone nitriles of the type $\text{CPhRR}'\cdot\text{CN}$ were prepared by the method of Bodroux and Taboury by the action of sodamide and the alkyl iodide. α -Phenyl- α -methylbutyronitrile, $\text{CMeEtPh}\cdot\text{CN}$, b. p. 119 — $120^{\circ}/15$ mm. and 239° , and α -phenyl- α -benzylbutyronitrile, $\text{CH}_2\text{Ph}\cdot\text{CEtPh}\cdot\text{CN}$, b. p. $201^{\circ}/17$ mm., have been prepared. These nitriles on hydrolysis gave first the amides and then the acids, of which α -phenyl- α -methylbutyramide, m. p. 74° , and α -phenyl- α -benzylbutyramide, m. p. 119° ; α -phenyl- α -methylbutyric acid, m. p. 60° , and its methyl ester, b. p. $120^{\circ}/16$ mm., and ethyl ester, b. p. 124 — $125^{\circ}/14$ mm., and α -phenyl- α -benzylbutyric acid, m. p. 140° , and its methyl ester, m. p. 61° , b. p. 196 — $197^{\circ}/16$ mm., have been prepared. The amides on reduction with sodium and absolute alcohol gave the corresponding alcohols with a certain amount of the corresponding amines. The following are described :— β -phenyl-

β -ethylbutanol, b. p. 136—137°/13 mm., and 260—261°, giving a benzoyl derivative, b. p. 210°/18 mm., and a phenylurethane, m. p. 70°; β -phenyl- β -methylbutanol, b. p. 138°/23 mm., and 246°, giving a benzoyl derivative, b. p. 202—204°/12 mm., m. p. 46°, and a phenylurethane; β -phenyl- β -benzylbutanol, b. p. 11°/17 mm., giving a benzoyl derivative, and a phenylurethane, m. p. 117°; β -phenyl- β -ethylbutylamine, b. p. 137—139°/23 mm., and its hydrochloride; β -phenyl- β -methylbutylamine, b. p. 112—113°/11 mm., and its hydrochloride; β -phenyl- β -benzylbutylamine, b. p. 193°/10 mm., and its hydrochloride. W. G.

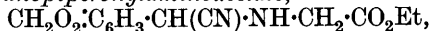
Synthesis of N-Alkylideneamino-acids and their Conversion into N-Alkylamino-acids by Hydrogenation. HELMUTH SCHEIBLER and PAUL BAUMGARTEN (*Ber.*, 1922, 55, [B], 1358—1379).—Somewhat unexpectedly, it has been observed that the condensation of aldehydes with ethyl aminoacetate does not in all cases lead to the production of alkylideneaminoacetic esters in even moderate yield. A more successful synthesis depends on the condensation of the sodium hydrogen sulphite compounds of the requisite aldehyde or ketone with ethyl aminoacetate in accordance with the scheme $\text{CHR}(\text{O}\cdot\text{SO}_2\text{Na})\cdot\text{OH} + \text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} = \text{CHR}(\text{O}\cdot\text{SO}_2\text{Na})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{H}_2\text{O}$. The product is subsequently treated with potassium cyanide, giving the cyano-ester, $\text{SO}_2\text{Na}\cdot\text{O}\cdot\text{CHR}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{KCN} = \text{CN}\cdot\text{CHR}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{KNaSO}_3$. The latter is transformed by a molecular proportion of alkali hydroxide and alkali ethoxide in absolute ethyl-alcoholic solution into the alkali salt of the alkylideneamino-acid, from which, by hydrogenation, the alkylamino-acid is prepared. It is remarkable that the cyano-esters give the alkylideneamino-acids when acted on by a single equivalent of potassium hydroxide in absolute ethyl-alcoholic solution; the reaction probably occurs in accordance with the scheme $\text{CN}\cdot\text{CHR}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et} + \text{KOH} = \text{EtOH} + \text{CN}\cdot\text{CHR}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{K} \rightarrow \text{KCN} + \text{NH} < \begin{smallmatrix} \text{CH}_2\cdot\text{CO} \\ \text{CHR} \end{smallmatrix} > \text{O} \rightarrow \text{R}\cdot\text{CH}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. The sodium salts of the alkylideneaminoacetic acids are transformed by acetic anhydride or acetyl chloride into N-acetyl compounds, the reaction being expressed by the scheme $\text{CHR}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\cdot\text{Na} + \text{Ac}_2\text{O} = \text{CHR}\cdot\text{NAc} < \begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix} > \text{CO} + \text{AcONa}$.

Benzaldehyde reacts energetically with ethyl aminoacetate but the direct isolation of the product of the reaction was not practicable. Reduction of the crude substance with aluminium amalgam in moist ethereal solution or with sodium and alcohol leads to the production of ethyl benzylaminoacetate, b. p. 175—179°/50 mm., the identity of which is confirmed by its conversion into benzylglycine hydrochloride, m. p. 214—216° (corr., decomp.). Simultaneous reduction and acetylation is effected by alternate addition of sodium amalgam and acetic anhydride to an aqueous suspension of the crude product whereby N-acetyl-N-benzylglycine, $\text{CH}_2\text{Ph}\cdot\text{NAc}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$,

colourless aggregates of needles, m. p. 126·5° (corr.), is produced. (See also below.) As judged from the quantity of the reduced ester obtained, the yield of condensation product does not exceed 19% of that theoretically possible. The condensation of piperonal with ethyl-aminoacetate follows a similar course; the crude product is transformed by successive reduction and treatment with hydrochloric acid into *piperonylglycine hydrochloride*, small, colourless leaflets, m. p. 224°.

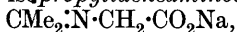
A suspension of benzaldehyde sodium hydrogen sulphite in water is treated with ethyl aminoacetate at 0° and a concentrated aqueous solution of potassium cyanide is subsequently added; *ethyl cyanobenzylaminoacetate*, $\text{CN}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, separates as a pale yellow liquid which cannot be distilled without decomposition, even under diminished pressure, and is identified as the hydrochloride, m. p. 83·5° (corr., decomp.). [Stadnikof (A., 1909, i, 106) gives m. p. 82°.] The yield is 97% of that theoretically possible. The nitrile ester is converted by cold, concentrated sulphuric acid into the *amido-ester*, $\text{NH}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, colourless, lustrous needles, m. p. 135°. The latter is hydrolysed completely with evolution of ammonia by sodium hydroxide, but only the ester group is affected by treatment with a hot aqueous suspension of freshly precipitated copper hydroxide which forms the *copper salt*, $(\text{NH}_2\cdot\text{CO}\cdot\text{CHPh}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{O})_2\text{Cu}$, sky-blue, anhydrous crystals. *Benzylideneglycine*, $\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, is obtained by the action of sodium hydroxide or preferably potassium hydroxide on the cyano-ester in absolute ethyl-alcoholic solution, but the brown, viscous syrup which solidifies to a glassy mass cannot readily be purified from sodium or potassium cyanide. *Sodium benzylideneaminoacetate*, a colourless, crystalline powder, is prepared in quantitative yield by the action of equivalent quantities of sodium hydroxide and ethoxide on the cyano-ester; it is somewhat unstable and is readily hydrolysed by warm water, with the production of benzaldehyde. The corresponding *silver, copper, barium, and calcium salts* are described. *N-Acetyl-N-benzylidenebetaine*, $\text{CHPh}\cdot\text{NAc}\langle\text{CH}_2\rangle\text{CO}$, colourless, lustrous needles, has m. p. 103—104°; it is hydrolysed by boiling water to benzaldehyde and aceturic acid, m. p. 206°. *N-Benzylideneglycine* is reduced by sodium and boiling ethyl alcohol to *N-benzylglycine hydrochloride*, m. p. 214—216° (corr.), whereas its sodium salt is transformed by sodium amalgam and acetic anhydride into *N-acetyl-N-benzylglycine*, m. p. 126·5° (corr.) (see above).

Ethyl N-α-cyanopiperonylaminoacetate,



is a viscous, yellow liquid which is characterised as the *hydrochloride*, a colourless, crystalline powder, m. p. 150—152° (corr.) after incipient decomposition at about 115° in a sealed capillary. Its conversion into *3:4-methylenedioxybenzylideneglycine*, a pale brown, viscous syrup which solidifies to a glassy mass, and *sodium piperonylideneaminoacetate* and the reduction of the latter to *N-piperonylglycine hydrochloride*, small, colourless needles, m. p. 224° (corr., decomp.), are described.

A similar series of changes starting from acetone sodium bisulphite leads to the production of *ethyl N- α -cyanoisopropylaminoacetate*, $\text{CN}\cdot\text{CMe}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, an almost colourless liquid [*hydrochloride*, small, colourless crystals, m. p. 87° (corr.) in a sealed capillary], of *sodium N-isopropylideneaminoacetate*,



a colourless, finely crystalline, very hygroscopic powder, and of *N-isopropylglycine hydrochloride*, colourless, lustrous, hygroscopic crystals, m. p. $203\text{--}204.5^\circ$ (corr.) after previous softening, from which *isopropylglycine*, hard irregularly-shaped crystals, m. p. $192\text{--}193^\circ$ (corr., decomp.), is prepared by the action of moist silver oxide.

H. W.

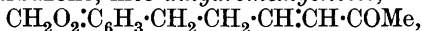
3-Hydroxy-*o*-toluic Acid. YASUHIKO ASAHINA and YOSHIO KONDO (*J. Pharm. Soc. Japan*, 1922, 264—271).—3-Hydroxy-*o*-toluic acid was obtained by the fusion of hydrangenol and phyllodulcin with potassium hydroxide, and was also prepared from 4-bromo-*o*-toluic acid by Jacobsen's method. Finally, 3-nitro-*o*-toluic acid, m. p. $151\text{--}152^\circ$, was reduced to the corresponding amino-acid, m. p. $125\text{--}126^\circ$, which was diazotised and boiled with dilute hydrochloric acid, when 3-hydroxy-*o*-toluic acid, m. p. $169\text{--}170^\circ$, was formed, and proved to be identical with that from hydrangenol and phyllodulcin. This process is somewhat tedious, and gives a smaller yield than that obtained by Jacobsen's method.

K. K.

The Catalytic Hydrogenation of Methysticin. H. GOEBEL (*Ber. deut. Pharm. Ges.*, 1922, 32, 115—124).—By the catalytic hydrogenation of methysticin,



only the double bond adjacent to the benzene nucleus is eliminated, with the formation of *dihydromethysticin*, m. p. $117\text{--}118^\circ$, which on hydrolysis with alcoholic potassium hydroxide gives the corresponding *dihydromethystic acid*, yellow needles, m. p. $133\text{--}134^\circ$. The constitution of the latter follows from its conversion, on oxidation with alkaline permanganate, into methylenedioxyphenylpropionic acid, m. p. 172° . That the keto-group of methysticin remains unchanged during the hydrogenation is shown by converting dihydromethysticin, which itself, like methysticin, gives no semicarbazone, into *dihydromethysticole*,



by boiling dihydromethystic acid with 5% hydrochloric acid. The ketone boils at $195\text{--}200^\circ/13\text{ mm.}$, and gives a *semicarbazone*, m. p. $149\text{--}150^\circ$. Although dihydromethysticin itself could not be further hydrogenated, the potassium salt of dihydromethystic acid, or of methystic acid, was converted into *tetrahydromethystic acid* by hydrogen and a palladium catalyst. This substance forms white needles, m. p. $137\text{--}138^\circ$, and was converted by boiling with 5% hydrochloric acid into *tetrahydromethysticole*, an oily liquid, b. p. $200\text{--}210^\circ/13\text{ mm.}$, forming a *semicarbazone*, m. p. $164\text{--}165^\circ$. The hydrogenation of the potassium salt of methystic acid takes place in two stages, and by using an old partly poisoned

*a a**

catalyst the intermediate *dihydromethystic acid* was isolated. It formed fine needles, m. p. 140—141°, and, as on oxidation it gave piperonal and piperonic acid, it is evident that in this case it is the double bond of methysticin farthest removed from the benzene nucleus that has been eliminated by the hydrogenation. On boiling with 15% hydrochloric acid, *dihydromethysticole*, b. p. 140—150°/10 mm., was obtained. Its *semicarbazone* melts at 160—161°.

G. F. M.

The Aldehydosalicylic Acids and their Derivatives.

EDWARD JOHNSON WAYNE and JULIUS BEREND COHEN (T., 1922, 121, 1022—1029).

The Formation of Cyclic Compounds from Hydroaromatic Dicarboxylic Acids.

A. WINDAUS and W. HÜCKEL (*Nachr. Ges. Wiss. Göttingen, Math.-physik. Klasse*, 1920, 11, [ii], 181—187).—Baeyer's strain theory explains the well-known stability of alicyclic compounds with five and six atoms in the ring, especially noticeable with dicarboxylic acids heated at 300° with acetic anhydride. In this paper, the reaction is applied to hydroaromatic dicarboxylic acids, with the view of determining their constitution and the applicability of Baeyer's theory. *cis*- and *trans*-cycloHexane-1:2-dicarboxylic acid gave two different inner anhydrides, the *trans* changing to the *cis* form at higher temperatures. Homophthalic acid prepared by the oxidation of indene with potassium permanganate (Heusler and Schieffer, A., 1899, i, 365) forms white crystals, m. p. 178°, and may be catalytically reduced to *trans*-2-carboxycyclohexane-1-acetic acid, clustered prisms from water, m. p. 146° (*dianilide*, fine needles, m. p. 252°). By heating with acetic anhydride at 240° and distilling at 25 mm., a crystalline distillate was obtained of which the portion soluble in light petroleum gave an anhydride, m. p. 38°; on recrystallisation from water, probably *cis*-2-carboxycyclohexane-1-acetic acid, m. p. 128—129°, was obtained. The latter, therefore, behaves towards Blanc's reaction like an acid of the glutaric series. *o*-Carboxy- β -phenylpropionic acid, obtained by the oxidation of Δ^1 -dihydronaphthalene with potassium permanganate (Straus and Lemmel, A., 1913, i, 256), on catalytic hydrogenation gave an acid, m. p. 103° (*dianilide*, lustrous leaves, m. p. 159°), which, when slowly heated, gave probably *trans*-2-carboxycyclohexane-1-propionic acid, m. p. 143° (*dianilide*, m. p. 205—206°). When heated with acetic anhydride, the acid, m. p. 103°, gave a distillate which, when treated with ether and sodium carbonate, yielded *hexahydro- α -hydrindone*, b. p. 216°/758 mm., in 55% yield [*semicarbazone*, clustered needles from alcohol, m. p. 214—215° (decomp.); *oxime*, m. p. 79—80°]. Thus, *cis*-2-carboxycyclohexane-1-propionic acid under Blanc's reaction behaves like an acid of the adipic series.

CHEMICAL ABSTRACTS.

The Two Isomeric Phthalyl Chlorides. JULIUS VON BRAUN and WILHELM KAISER (*Ber.*, 1922, 55, [B], 1305—1310).—The physico-chemical investigations of Ott (A., 1912, i, 828) have

enabled satisfactory formulæ to be ascribed to the two phthalyl chlorides, but, apart from a recent observation by Pfeiffer (this vol., i, 341), scarcely any chemical differences between the two isomerides have been noted. The author has therefore examined their behaviour towards the salts of dithiocarbamic acid which have been shown previously (A., 1904, i, 90) to react readily with the normal acid chloride complex in accordance with the equation $R \cdot COCl + NR_2 \cdot H, HS \cdot CS \cdot NR_2 = NR_2 \cdot H, HCl + R \cdot CO \cdot S \cdot CS \cdot NR_2$. The intensely coloured dithiourethanes immediately decompose in the case of the chlorides of fatty acids in accordance with the scheme $R \cdot CO \cdot S \cdot CS \cdot NR_2 = R \cdot CO \cdot NR_2 + CS_2$, whereas the aryl compounds are rather more stable. *s*-Phthalyl chloride would therefore be expected to give a dark yellow thio-derivative, $C_6H_4(CO \cdot S \cdot CS \cdot NR_2)_2$, which would possess some degree of stability. The behaviour of the *as*-chloride can be predicted with less certainty, but it appears most probable that colourless or faintly coloured, very unstable substances of the type $C_6H_4 < \begin{smallmatrix} C(S \cdot CS \cdot NR_2) \\ CO \end{smallmatrix} > O$ would be initially formed which would decompose primarily into unsymmetrical phthalamides, $C_6H_4 < \begin{smallmatrix} C(NR_2)_2 \\ CO \end{smallmatrix} > O$, from which the symmetrical derivatives would immediately be obtained. The predictions are completely fulfilled by experiment.

The cautious addition of *s*-phthalyl chloride to an ice-cold mixture of piperidine, water, and carbon disulphide causes the separation of *N*-piperidyl-*s*-phthalyl dithiourethane, $C_6H_4(CO \cdot S \cdot CS \cdot C_5NH_{10})_2$, a brilliant yellow powder, m. p. 123°, which is converted slowly in the cold, but rapidly on warming into carbon disulphide and *phthalyl*-*NN'*-*dipiperidide*, $C_6H_4(CO \cdot C_5NH_{10})_2$, m. p. 52–54°, which is identical with the product obtained from *s*-phthalyl chloride and piperidine by the Schotten-Baumann reaction. When *as*-phthalyl chloride is treated in a similar manner, a very faint yellow coloration is developed; the products of the change are piperidine hydrochloride and *phthalyl*-*NN'*-*dipiperidide*. Exactly analogous observations are made when piperidine is replaced by dimethylamine. The symmetrical chloride gives *N*-dimethyl-*s*-phthalyl dithiourethane, a yellow powder, m. p. 107°, which is readily converted into carbon disulphide and *NN'*-tetramethyl-phthalamide, $C_6H_4(CO \cdot NMe_2)_2$, colourless crystals, m. p. 121–122°. With *as*-phthalyl chloride only a very pale yellow colour is developed and the products of the action are dimethylamine hydrochloride and tetramethylphthalamide. H. W.

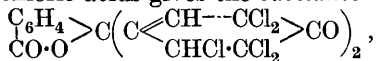
Chloro- and Bromo-derivatives of Phenolphthalein. A. THIEL and FR. MÜLLER (*Ber.*, 1922, **55**, [B], 1312–1321; cf. Thiel, A., 1914, ii, 285).—The authors have commenced a study of the influence of systematic halogenation of phenolphthalein on its behaviour as indicator. The present communication deals with substances containing chlorine or bromine in the side nuclei. The usual method for the preparation of phenolphthaleins (condensation of phthalic anhydride with phenols in the presence of a suitable

agent) cannot be utilised in these cases, since it is too largely dependent on unknown and at present uncontrollable factors, and, further, can only lead usefully to symmetrical derivatives. The general method consists in condensing 4'-hydroxybenzoylbenzoic acid or a halogenated derivative of it with phenol or a halogenated phenol in the presence of stannic chloride. 4'-Hydroxybenzoylbenzoic acid is prepared conveniently from phenolphthaleinoxime, which is smoothly hydrolysed by dilute sulphuric acid into the ketonic acid and *p*-aminophenol. Application of the reaction to unsymmetrically substituted halogenated phenolphthaleins shows that the oxime nitrogen in the form of the amino-group is eliminated in combination with the nucleus which is free from or contains least halogen.

The full description of the behaviour of halogenated phenolphthaleins as indicators is recorded elsewhere. It may, however, be noted that the tinctorial power diminishes regularly with increasing halogen content to such an extent that the maximal coloration produced in aqueous solution at the atmospheric temperature by a tetrahalogenated compound is only one-hundredth of that produced by phenolphthalein. The tint developed in alkaline solution is not appreciably affected as long as one side nucleus remains unsubstituted, but becomes violet and finally bluish-violet when both rings are substituted.

The following substances are described: *o*-3':5'-Dichloro-4'-hydroxybenzoylbenzoic acid, colourless crystals, m. p. 241°; *o*-3':5'-dibromo-4'-hydroxybenzoylbenzoic acid, m. p. 248°; *o*-3'-chloro-4'-hydroxybenzoylbenzoic acid, colourless crystals, m. p. 212°; 3'-chlorophenolphthalein, m. p. 201° (the melting points of the phthaleins described in this communication are all somewhat indefinite owing to decomposition); 3'-bromophenolphthalein, m. p. 118°; 3':5'-dichlorophenolphthalein, a colourless powder, m. p. 220°; 3':5'-dibromophenolphthalein, a pale yellow, crystalline powder, m. p. 238°; 3':5':3''-trichlorophenolphthalein, a colourless substance, m. p. 122°; 3':5':3''-tribromophenolphthalein, a colourless compound, m. p. 124°.

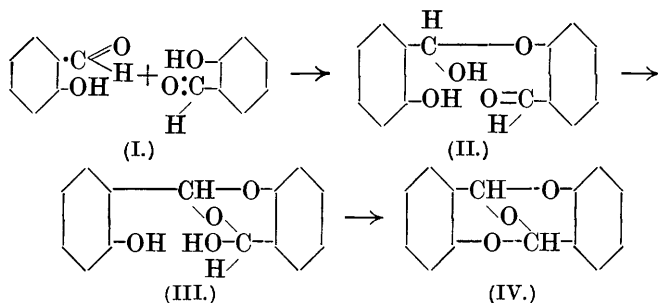
Chlorination of a suspension of phenolphthalein in glacial acetic and fuming hydrochloric acids gives the substance



m. p. 218°, which is reduced by tin and hydrochloric acid to 3':5':3''-tetrachlorophenolphthalein, m. p. 225°. Its constitution follows from the observation that it is converted by the oxime fusion into *o*-3':5'-dichloro-4'-hydroxybenzoylbenzoic acid.

H. W.

The Structure of Disalicylaldehyde. ROGER ADAMS, M. F. FOGLER, and C. W. KREGER (*J. Amer. Chem. Soc.*, 1922, **44**, 1126—1133).—Disalicylaldehyde is considered to have the constitution shown in the formula IV, and may be called 5:11:13-dibenzo-bisdioxan. The mechanism for the formation from salicylaldehyde is considered to be as follows:



If this explanation is correct the reason why various acid chlorides cause the reaction to take place is clear. A small amount of acid chloride reacts first with the hydroxyl of the salicylaldehyde, giving hydrochloric acid. This mineral acid then catalyses steps II and III. Finally, the remainder of the acid chloride acts as a dehydrating agent and thus gives step IV. In support of this view, it is shown that salicylaldehyde is unaffected by cold acetic anhydride even after long standing. If, however, to this mixture is added a drop of concentrated sulphuric acid an immediate reaction occurs and disalicylaldehyde is at once formed. Other acids may be used in place of the sulphuric acid. It should be noted, however, that sulphuric acid can bring about the reverse change and if a mixture of pure disalicylaldehyde and excess of acetic anhydride and one drop of sulphuric acid is left for some time at the ordinary temperature crystals of salicylaldehyde triacetate separate.

Finally, in support of the above view as to the mechanism of the conversion of salicylaldehyde into disalicylaldehyde, it is shown that saligenin readily condenses with benzaldehyde in the presence of a little acid, benzoic acid being the best in order to control the reaction. The product is 2-phenyl-1:3-benzodioxan, m. p. 54° (annexed formula). When dissolved in acetic anhydride and treated with a drop of sulphuric acid, this compound decomposes in the same way as disalicylaldehyde and gives benzylidene diacetate and saligenin resin. W. G.

Cobalt Compounds of α -Oximinoketones. G. PONZIO (*Gazzetta*, 1922, 52, i, 285—288).—Tschugaev (A., 1907, i, 830; 1908, i, 554) found that treatment of α -benzilmonoxime with a cobaltous salt yields the cobaltic compound, $\text{Co}(\text{ON}:\text{CPh}\cdot\text{COPh})_3$, and assumed that this property of giving compounds of trivalent cobalt is common to all α -oximinoketones. The author finds that this generalisation is not justified, since the action of aqueous cobaltous acetate solution on aqueous or alcoholic solutions of the α -oximinoketones, $\text{R}^1\cdot\text{CO}\cdot\text{C}(\text{NOH})\cdot\text{CO}\cdot\text{R}^2$ or $\text{R}^1\cdot\text{CO}\cdot\text{CH}:\text{NOH}$, where R^1 and R^2 represent Me or Ph, yields cobaltous and not cobaltic compounds. The cobaltous salts of the α -oximinoketones described below are all more or less soluble in many of the ordinary organic solvents and separate in well-defined crystals of an abnormal reddish-brown colour, forming orange-red powders. They do not

respond to the reactions for cobaltous ions and must be regarded as highly stable complex salts of the type
$$\begin{array}{c} R^1 \cdot C : NO \\ R^2 \cdot C = O \end{array} \rightarrow Co \leftarrow \begin{array}{c} NO : C \cdot R^1 \\ O = C \cdot R^2 \end{array}$$
 in which the co-ordination number of the cobalt is 4.

It is therefore evident that Tschugaev's considerations on tervalent cobalt compounds of the α -oximinoketones are valueless. Further, as the author has obtained the cobaltous salts of oximinoacetylacetone and oximinoacetophenone and has confirmed the existence of the cobaltic salt of α -benzilmonoxime, the configurations of the oximino-compounds cannot, contrary to Tschugaev's suggestion, be related to their capacity to form metallic salts. Indeed, oximinoacetylacetone does not exist in geometrical isomerides, whilst oximinoacetophenone has the β - or anti-structure and α -benzilmonoxime the syn-form.

The *cobaltous* salt of *oximinoacetylacetone*, $Co(ON : CAc \cdot CO \cdot CH_3)_2$, crystallises in large, blood-red prisms, m. p. 164° , and dissolves easily in the cold in concentrated sulphuric acid and in sodium or ammonium hydroxide solutions, giving a dark orange-red coloration.

Cobaltous oximinobenzoylacetone, $Co(ON : CAcBz)_2$, forms flattened, orange-brown needles, m. p. 220° (decomp.), and dissolves in cold concentrated sulphuric acid or sodium or ammonium hydroxide, forming yellow solutions.

Cobaltous oximinoacetophenone, $Co(ON : CHBz)_2$, forms orange-brown laminæ, begins to change at about 100 — 120° , and decomposes, sometimes violently, at 240 — 244° , with sublimation of benzoic acid; it dissolves in cold concentrated sulphuric acid to an orange-red solution, but is insoluble in sodium or ammonium hydroxide solution.

Cobaltic α -benzilmonoxime, $Co(ON \cdot CPhBz)_3$, obtained, but not described, by Tschugaev (*loc. cit.*), crystallises in reddish-brown prisms and decomposes violently at 195° or sometimes at a somewhat higher temperature; it dissolves in cold concentrated sulphuric acid to a reddish-brown solution, but is insoluble in potassium or ammonium hydroxide solution.

Cupric oximinoacetylacetone, $Cu(ON : CAc)_2$, obtained similarly to the preceding salts, forms an olive-green powder, decomposes violently at about 140° , and dissolves in sodium hydroxide solution, giving a greenish-yellow, in ammonia solution a greenish-blue, in dilute hydrochloric acid a yellow, and in dilute acetic acid a green, coloration. As it gives some of the reactions of cupric ions, it must be regarded as a less stable complex salt than the cobaltous salts of the α -oximinoketones.

T. H. P.

Two $\alpha\alpha\beta\beta$ -Substituted Propiophenones and their Products of Decomposition by Sodamide. (MME) PAULINE RAMART and G. ALBESCO (*Compt. rend.*, 1922, **174**, 1289—1291).—Substituted ketones of the types $CHPh_2 \cdot CR_2 \cdot CPh$ and $CHPhEt \cdot CR_2 \cdot CPh$ may be prepared by the condensation of mixed organo-magnesium derivatives with phenyl styryl ketones and alkylation of the resulting compounds by means of sodamide. In the alkylation the first alkyl group is introduced easily, but the second only with difficulty.

$\beta\beta$ -Diphenylpropiophenone gives with sodamide and methyl iodide first $\beta\beta$ -diphenyl- α -methylpropiophenone and then $\beta\beta$ -diphenyl- $\alpha\alpha$ -dimethylpropiophenone, m. p. 90° . Under similar conditions, β -phenyl- β -ethylpropiophenone gives β -phenyl- $\alpha\beta$ -diethylpropiophenone, m. p. 68° , and β -phenyl- $\alpha\alpha\beta$ -triethylpropiophenone, b. p. $180^\circ/10$ mm. Both these ketones are decomposed by sodamide, two reactions occurring to almost equal extent, namely:

$$\text{CHPh}_2\cdot\text{CR}_2\cdot\text{COPh} + \text{NH}_2\text{Na} \rightarrow \text{CHPh}_2\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NH}_2 + \text{C}_6\text{H}_6$$

$$\text{CHPh}_2\cdot\text{CR}_2\cdot\text{COPh} + \text{NH}_2\text{Na} \rightarrow \text{CHPh}_2\cdot\text{CHR}_2 + \text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}_2$$

Thus $\beta\beta$ -diphenyl- $\alpha\alpha$ -dimethylpropiophenone gave $\gamma\gamma$ -diphenyl- β -methylpropane, b. p. $145^\circ/13$ mm., benzamide, $\beta\beta$ -diphenyl- $\alpha\alpha$ -dimethylpropionic acid in the form of its amide and some tetraphenylethane. β -Phenyl- $\alpha\alpha\beta$ -triethylpropiophenone gave δ -phenyl- γ -ethylhexane, $\text{CHPhEt}\cdot\text{CHEt}_2$, b. p. $205^\circ/740$ mm., benzamide and β -phenyl- $\alpha\alpha\beta$ -triethylpropionic acid, m. p. 82° . W. G.

The Reactivity of Doubly-conjugated Unsaturated Ketones.
III. Unsymmetrical Hydroxy- and Methoxy-derivatives.
 JOHANNES SYBRANDT BUCK and ISIDOR MORRIS HEILBRON (T., 1922, 121, 1095—1101).

***o*-Quinones and 1 : 2-Diketones. V. Benzils of the Superoxide Type [ψ -Benzils].** A. SCHÖNBERG and O. KRAEMER (Ber., 1922, 55, [B], 1174—1194).—In general, the benzils are yellow substances, but 4 : 4'-diethoxybenzil (Vorländer, A., 1911, i, 865) and 2 : 2'-dimethoxybenzil (Irvine, T., 1907, 91, 541) are colourless. Further examination of these and similar substances has disclosed the existence of a class of benzils in which the dicarbonyl group is present in the peroxide form, $\begin{smallmatrix} \text{R}\cdot\text{C}\cdot\text{C}\cdot\text{R} \\ | \quad | \\ \text{O}-\text{O} \end{smallmatrix}$. These com-

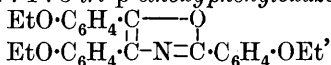
pounds are colourless, but melt to a yellow liquid and give yellow solutions. The phenomenon is reversible since colourless crystals are deposited when the yellow solutions are concentrated or cooled. It can be explained by the assumption of a reversible transformation of the peroxide into the ketonic form. The colourless compounds are converted by solution in concentrated sulphuric acid into intensely coloured derivatives of the ketonic modification. The colourless benzils react very slowly with and are sometimes almost inactive towards the typical dicarbonyl reagents such as *o*-diamines. In contrast to the coloured benzils which contain the dicarbonyl group in the ketonic form, the colourless substances are very stable towards hydrogen peroxide in acid solution.

2 : 2'-Dimethoxy-5 : 5'-dimethylbenzil, colourless leaflets, m. p. 183° , is prepared by the oxidation of a boiling alcoholic solution of the corresponding benzoin with Fehling's solution. It is converted by phenylhydrazine into the corresponding osazone, $\text{C}_{30}\text{H}_{30}\text{O}_2\text{N}_4$, yellow crystals, m. p. 197° . It is not affected by aqueous or ethereal ammonia at 200° and does not condense with *o*-phenylenediamine or naphthalene-1 : 2-diamine. It is converted by a boiling mixture of glacial acetic and aqueous hydrobromic acids (50%) into 2-hydroxy-2'-methoxy-5 : 5'-dimethylbenzil, prisms, m. p. (indefinite) 113° ,

which is re-converted into the dimethoxy-compound by treatment with methyl sulphate.

2 : 2'-Dimethoxybenzil, m. p. 130° (cf. Irvine, *loc. cit.*), is similarly prepared by the oxidation of 2 : 2'-dimethoxybenzoin with Fehling's solution. It gives a *dioxime*, colourless prisms, decomp. 235° (indefinite), and a *diphenylosazone*, $C_{28}H_{26}O_2N_4$, yellow prisms, m. p. 198—199°. It is stable towards aqueous ammonia and *o*-diamines. With hydrobromic and acetic acids it yields 2-*hydroxy-2'-methoxybenzil*, colourless, lustrous prisms, m. p. 120°.

4 : 4'-Diethoxybenzil (cf. Vorländer, *loc. cit.*) is conveniently prepared by the action of aluminium chloride on a solution of phenetole and oxalyl chloride in carbon disulphide. It is converted by drastic treatment with concentrated aqueous ammonia into *p*-ethoxybenzoic acid and 2 : 4 : 5-*tri-p-ethoxyphenyloxazole*,



colourless needles, m. p. 82°. With naphthalene-1 : 2-diamine in boiling glacial acetic acid solution it slowly gives 2 : 3-*di-p-ethoxyphenyl- $\alpha\beta$ -naphthaquinoxaline* (annexed formula), needles, m. p. 155°.

It is converted by a mixture of nitric acid (*d* 1.48) and sulphuric acid (*d* 1.70) into 3 : 3'-*dinitro-4 : 4'-diethoxybenzil*, lustrous, yellow leaflets, m. p. 216°, which is transformed by naphthalene-1 : 2-diamine hydro-

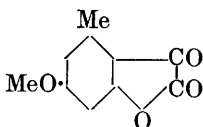
chloride into 2 : 3-*di-m-nitro-p-ethoxyphenyl- $\alpha\beta$ -naphthaquinoxaline*, yellow needles, m. p. 178°. 3 : 3'-Dibromo-4 : 4'-diethoxybenzil crystallises in pale yellow needles, m. p. 208°. 4 : 4'-*Dihydroxybenzil*, m. p. 235°, after previous softening (*dibenzoate*, yellow needles, m. p. 170°) can be obtained only with difficulty and in poor yield by the action of hydrobromic acid on 4 : 4'-diethoxybenzil, but is readily prepared by the corresponding treatment of 4 : 4'-dimethoxybenzil.

Ethylbenzene is converted by oxalyl chloride and aluminium chloride in the presence of carbon disulphide into *p*-ethylbenzoic acid instead of the desired 4 : 4'-diethylbenzil.

Diphenyl ether is transformed by oxalyl chloride into 4 : 4'-*di-phenoxybenzil*, pale yellow, silky leaflets, m. p. 116°, in which the position of the phenoxy groups is established by its oxidative hydrolysis by hydrogen peroxide to *p-phenoxybenzoic acid*, m. p. 159°. With *o*-tolylenediamine hydrochloride, the benzil yields 2 : 3-*di-p-phenoxyphenyl-6-methylquinoxaline*, yellow aggregates of prisms, m. p. 149°, whilst with naphthalene-1 : 2-diamine hydrochloride it gives 2 : 3-*di-p-phenoxyphenyl- $\alpha\beta$ -naphthaquinoxaline*, yellow crystals, m. p. 157°.

Oxalyl chloride and 3 : 5-dimethoxytoluene give 6-*methoxy-4-methyl-2 : 3-diketocoumaran* (annexed formula), lustrous, yellow crystals, m. p. 165°; the same compound is obtained by the similar treatment of 5-hydroxy-3-methoxytoluene.

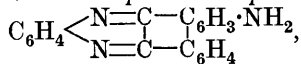
In contrast to the colourless 2 : 2'-dimethoxybenzil and 2 : 2'-dimethoxy-5 : 5'-dimethylbenzil,



the yellow diketones, 4:4'-dimethyl-, 4:4'-dimethoxy-, and 3:4:3':4'-dimethylenedioxy-benzils react readily with naphthalene-1:2-diamine hydrochloride in boiling glacial acetic acid solution, giving, respectively, 2:3-di-*p*-tolyl- $\alpha\beta$ -naphthaquinoxaline, needles, m. p. 183°, 2:3-di-*p*-methoxyphenyl- $\alpha\beta$ -naphthaquinoxaline, yellow needles, m. p. 161°, and 2:3-di-*mp*-methylenedioxyphenyl- $\alpha\beta$ -naphthaquinoxaline, yellow crystals, m. p. 205°.

Piperil is converted by aqueous ammonia at 120° into 2:4:5-tri-*mp*-methylenedioxyphenyloxazole, $N \begin{smallmatrix} \swarrow C(C_6H_3:O_2CH_2) \cdot O \\ \searrow C(C_6H_5:O_2CH_2) : C(C_6H_3:O_2CH_2) \end{smallmatrix}$, slender, colourless needles, m. p. 170—171°. H. W.

The Phenanthrene Series. XXXIII. Preparation of Derivatives of Phenanthraquinone and Phenanthrene from 2-Nitrophenanthraquinone. JULIUS SCHMIDT and OTTO SPOUN (Ber., 1922, 55, [B], 1194—1211).—Phenanthraquinone is converted by boiling nitric acid (*d* 1.4) into a mixture of 2-nitrophenanthraquinone, yellow needles, m. p. 258—260°, and 4-nitrophenanthraquinone, m. p. 176—177°, which can be separated by taking advantage of the much smaller solubility of the former in boiling alcohol (cf. Werner, A., 1902, i, 437). 2-Nitrophenanthraquinone is reduced smoothly by Werner's method (*loc. cit.*) to 2-aminophenanthraquinone, dark bluish-violet needles which are not completely molten below 320°; it is characterised by its transformation by *o*-phenylenediamine hydrochloride in boiling aqueous alcoholic solution into 2-aminophenanthraphenazine,



pale yellow needles, m. p. 240° (*hydrochloride*, matted needles, m. p. 298—300°), and by the formation of a *NN*-diacetyl compound, a pale green powder, m. p. 206—208°. 2-Aminophenanthraquinone is converted smoothly into 2-hydroxyphenanthraquinone when it is suspended in concentrated hydrochloric acid and diazotised; subsequently sufficient water is added to give a clear solution, which is heated to its boiling point and then cooled, when the hydroxy-compound separates in almost quantitative yield. The only drawback to the method lies in the relatively very large quantity of water which is necessary. 2-Hydroxyphenanthraquinone is converted by *o*-phenylenediamine hydrochloride into 2-hydroxyphenanthraphenazine, pale brown, microscopic crystals, m. p. 258—259°, and by semicarbazide hydrochloride into the monosemicarbazone, brownish-red crystals, m. p. 263—265° (decomp.).

2-Hydroxyphenanthraquinone is converted by boiling nitric acid (*d* 1.35) into 3:4-dinitro-2-hydroxyphenanthraquinone, a tile-red powder which slowly decomposes above 220°; it cannot be crystallised conveniently, and is best purified by taking advantage of its acidic character, which enables it to dissolve in sodium hydrogen carbonate solution (the *sodium* salt is described). The presence of the three substituents on the same nucleus is proved by oxidation of the compound by sulphuric acid and potassium dichromate to phthalic acid, whilst the fact that one nitro-group is present in

position 4 is established by the production of 4-aminophenanthrene, m. p. 104—105°, by drastic treatment of the substance with red phosphorus and fuming hydriodic acid (*d* 2.05). The preparation of 3:4-dinitro-2-hydroxyphenanthraquinone, pale brown, microscopic crystals, m. p. 251° (decomp.), of 3:4-dinitro-2-hydroxyphenanthraquinone monoxime, brown crystals, m. p. 211° (decomp.), and of 3:4-dinitro-2-hydroxyphenanthraquinone monosemicarbazone, reddish-brown crystals which do not melt below 270°, is described. Reduction of the nitroquinone with phenylhydrazine and subsequent acetylation of the product gives 3:4-dinitro-2-hydroxyphenanthraquinol diacetate, m. p. 232° (decomp.). 3:4-Dinitro-2-hydroxyphenanthraquinone is reduced by tin and hydrochloric acid to 3:4-diamino-2-hydroxyphenanthraquinone, which is isolated in the form of its hydrochloride. The latter is converted by diazotisation and subsequent boiling with water into 2:3:4-trihydroxyphenanthraquinone, a reddish-brown substance which is completely molten at 235° after incipient decomposition at about 186°. The isolation of the substance is beset with unusual difficulties. It is most definitely characterised by converting it into 2:3:4-trihydroxyphenanthraquinone, dark brown, microscopic crystals, m. p. 255—258° (decomp.), or into its monosemicarbazone, a brownish-red powder which decomposes gradually above 270°.

The bromination of 2-hydroxyphenanthraquinone has been examined, but the process is somewhat inconvenient by reason of the insolubility of the substance in the usual media. The action of bromine on a suspension of the compound in water leads to the formation of a mixture of mono-, di-, and tri-bromo-derivatives, from which only dibromohydroxyphenanthraquinone, reddish-brown crystals, m. p. 255°, could be isolated in an approximately homogeneous condition.

2-Nitrophenanthraquinone is converted by phosphorus pentachloride into a mixture of 9:9-dichloro-2-nitrophenanthrone, yellow needles or leaflets, m. p. 186°, and 10:10-dichloro-2-nitrophenanthrone, pale yellow needles, m. p. 162—163°, which are separated by taking advantage of their widely differing solubilities in benzene. (For the present, the position of the chlorine atoms in the respective compounds is assigned arbitrarily.) The former is reduced by granulated tin and concentrated hydrochloric acid to 2-amino-10-hydroxyphenanthrene, $\text{NH}_2 \cdot \text{C}_6\text{H}_3 \cdot \text{C} \begin{smallmatrix} \text{OH} \\ | \\ \text{C}_6\text{H}_4 \cdot \text{CH} \end{smallmatrix}$, m. p. 221° (the hydrochloride, dibenzoyl derivative, almost colourless crystals, m. p. 225—226°, and diacetyl compound [$+\frac{1}{2}(\text{CH}_3\text{CO})_2\text{O}$], large rhombohedra, m. p. 182°, are described). When treated similarly, 10:10-dichloro-2-nitrophenanthrone yields 2-amino-9-hydroxyphenanthrene, almost colourless, microscopic crystals, m. p. 194—195° (decomp.), the benzoyl derivative of which has m. p. 160° (decomp.). H. W.

Trimethylcamphorylmethylammonium Bromide. H. RUPE (U.S. Pat. 1399082). — Trimethylcamphorylmethylammonium bromide is prepared by heating camphorylbromomethane with an ethereal-alcoholic solution of trimethylamine under pressure for

fifteen hours, cooling, dissolving the desired product (after its precipitation with ether) in chloroform, and reprecipitating it with ether. It forms colourless leaflets, m. p. 192° . On further heating above the m. p., trimethylammonium bromide is separated, which again melts with decomposition at 250° . CHEMICAL ABSTRACTS.

Oxidation of Menthone by Ferric Chloride. YASUHIKO ASAHINA and SABURO MITUHORI (*J. Pharm. Soc. Japan*, 1922, 255—263).—By oxidation of menthone with ferric chloride, buchucamphor is produced. A mixture of 50 grams of menthone, 280 of grams crystallised ferric chloride, and 500 c.c. of 50% acetic acid is gently boiled until the brown colour of the solution is changed to dark green; the oily layer is then separated from the aqueous and distilled with steam, filtered, and the oily filtrate shaken with sodium hydroxide solution. On acidifying, crystals of buchucamphor separate from the filtrate. Buchu-camphor, after recrystallisation from alcohol, has m. p. 82° , and gives a green coloration with ferric chloride. Attempts to prepare the oxime by the methods of Kondakov and Bjalobreczeski (A., 1897, i, 227), and Semmler and Mackenzie (A., 1906, i, 373) were unsuccessful. Buchu-camphor reacts, however, easily with phenylcarbimide, forming buchucamphor phenylurethane, m. p. 113° (Semmler and Mackenzie gave 41°).

When oxidised with potassium permanganate in acetone solution, buchucamphor gave a syrup, which on cooling changed into white needles, m. p. 129° ; from it a semicarbazone, m. p. 217° , was obtained. The product is perhaps identical with Semmler and Mackenzie's diketonic acid. By distilling the crude oxidation product, an unsaturated ketonic acid, m. p. $104\text{--}105^{\circ}$, was obtained.

K. K.

Resin Constituents. VIII. The Amyrins from Elemi Resin. II. α -Amyrin.

ALOIS ZINKE, ALFRED FRIEDRICH, OTTO JOHANNSEN, and RUDOLF RICHTER (*Monatsh.*, 1921, 42, 439—445; cf. A., 1921, i, 39).—When α -amyrin benzoate is distilled, benzoic acid is split off and a hydrocarbon $C_{28}H_{46}$ $\begin{smallmatrix} \text{CH} \\ | \\ \text{CH} \end{smallmatrix}$ is formed. The latter could not be isolated, but forms a crystalline dibromide, $C_{30}H_{48}Br_2$, white, prismatic needles, m. p. $259\text{--}260^{\circ}$. The name α -amyrene is proposed for the hydrocarbon, instead of α -amyrilen, the name given by Vesterberg (*loc. cit.*) to a probably identical hydrocarbon obtained by the action of phosphorus pentachloride on α -amyrin. Vesterberg's α -amyrone, or, better, α -amyranone, was prepared by oxidation of α -amyrin with chromic acid; it forms crystalline plates or spherical aggregates, m. p. 124° , sintering at 115° . Its oxime, $C_{30}H_{48}ON$, has m. p. 234° . The α -amyranone is very resistant to oxidation and is therefore of little use for elucidating further the structure of α -amyrin. It cannot be obtained in the enol form, but by heating with benzoyl chloride forms a benzoate, α -amyrenol benzoate, $C_{37}H_{52}O_2$, fine leaflets, m. p. $197\text{--}198^{\circ}$. Bromo- α -amyrin was oxidised to bromo- α -amyranone, fine, white leaflets, m. p. 190° ; its oxime has m. p.

236.5°. *Bromo- α -amyrenol benzoate* crystallises in leaflets, m. p. 226—227°. A loose compound appears to be formed between α - and β -amyrin benzoates, rendering their separation difficult.

E. H. R.

Resin Constituents. IX. The Decomposition of *d*-Siaresinolic Acid and Lubanyl Benzoate. ALOIS ZINKE, FRANZ HANSELMAYER, and WILHELMINE EHMER (*Monatsh.*, 1921, **42**, 447—452; cf. A., 1918, i, 398).—By oxidation of *d*-siaresinolic acid in acetic acid solution with Kiliani's mixture (A., 1902, i, 46), and also by oxidising *l*-prabangic acid (A., 1921, i, 351) with potassium permanganate in alkaline solution, a new crystalline acid was obtained, $C_{21}H_{30}O_5$, m. p. 285—286° (decomp.). The acid is dibasic, but neither a crystalline methyl ester nor a hydroxylamine derivative could be obtained.

The formula suggested by Zinke and Drzimal for lubanyl benzoate (A., 1921, i, 187) has been confirmed by fusion with potassium hydroxide, when protocatechuic acid was obtained. The preparation of vanillin from the benzoate afforded further evidence of the correctness of the formula.

E. H. R.

Capularin, a Glucoside from Jute Leaf. HARIDAS SAHA and KUMUD NATH CHOUDHURY (T., 1922, **121**, 1044—1046).

Castelin, a New Glucoside from *Castela Nicholsoni*. LOUIS PIERRE BOSMAN (T., 1922, **121**, 969—972).

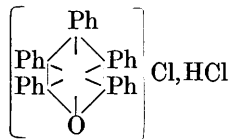
Furfurylidene-1-methylcyclohexan-2-one and some of its Derivatives and the Mono- and Di-furfurylidenecyclohexanones. (MLLE) N. WOLFF (*Compt. rend.*, 1922, **174**, 1469—1471; cf. A., 1921, i, 514).—Furfuraldehyde condenses with 1-methylcyclohexan-2-one to give 3-furfurylidene-1-methylcyclohexan-2-one, $C_4OH_3 \cdot CH \cdot C_6H_7MeO$, m. p. 51°, R_a 58.30°, R_D 58.96°, R_B 61.21°, which when reduced with sodium amalgam yields 3-furfuryl-1-methylcyclohexan-2-one, $C_4OH_3 \cdot CH_2 \cdot C_6H_8MeO$, b. p. 146°/16 mm., R_a 53.60°, R_D 53.92°, R_B 54.82°. The first named compound condenses with magnesium phenyl or *p*-tolyl bromide giving respectively phenylfuryl-2-keto-3-methylcyclohexylmethane, $C_4OH_3 \cdot CHPh \cdot C_6H_8MeO$, b. p. 206°/16 mm., R_a 79.03°, R_D 79.39°, R_B 80.70°, and *p*-tolylfuryl-2-keto-3-methylcyclohexylmethane, $C_4OH_3 \cdot CH(C_6H_4Me) \cdot C_6H_8MeO$, b. p. 220°/16 mm., R_a 82.96°, R_D 84.52°, R_B 86.61°.

With cyclohexanone, furfuraldehyde gives 1-furfurylidenecyclohexan-2-one, m. p. 47°, R_a 52.86°, R_D 54.69°, R_B 57.62°, and 1:3-difurfurylidenecyclohexan-2-one, $C_6H_6O \cdot (CH \cdot C_4OH_3)_2$, m. p. 145°, R_a 78.39°, R_D 85.81°, R_B 95.41°.

W. G.

Pyrylium Compounds. XI. Pentaphenylpyrylium Salts. The Formulation of Salts of Dyes. W. DILTHEY [with H. KAFFER] (*Ber.*, 1922, **55**, [B], 1275—1279; cf. A., 1921, i, 429).—Benzamarone, $CHBzPh \cdot CHPh \cdot CHPhBz$, is converted by phos-

phorus pentachloride in the presence of boiling chlorobenzene into the 2 : 3 : 4 : 5 : 6-*pentaphenylpyrylium* salt (annexed formula), yellow needles, m. p. (indefinite) 248—254°, which does not lose the molecular proportion of hydrogen chloride completely when preserved over lime. The nature of the attachment of the chlorine atoms is deduced from the transformation of the hydrochloride into the iron salt, $C_{35}H_{25}OCl_4Fe$, yellow, lustrous needles, m. p. 286—287°, and into the *perchlorate*, $C_{35}H_{25}O_5Cl$, m. p. 294°. The *picrate*, $C_{41}H_{27}O_8N_3$, has m. p. 157°. An alcoholic solution of the hydrochloride is converted by sodium carbonate solution at 0° into a mixture of $\alpha\epsilon$ -diketo- $\alpha\beta\gamma\delta\epsilon$ -pentaphenyl- Δ^{β} -pentene,



almost colourless needles, m. p. 149—151°, which is readily reconverted into pyrylium salts and tetraphenylfuran, pale yellow leaflets, m. p. 172°.

The communication concludes with a reply to Kehrmann (A., 1921, i, 447) with regard to the relative probability of the formulation of the salts of dyes (cf. Dilthey, A., 1920, i, 324). H. W.

A Synthesis of isoBrazilein and certain Related Anhydro-pyranol Salts. II. Synthesis of isoHæmatein. HERBERT GRACE CRABTREE and ROBERT ROBINSON (T., 1922, 121, 1033—1041).

3 : 6-Tetramethyldiaminocyanoselenopyronin. M. BATTEGAY and G. HUGEL (*Bull. Soc. chim.*, 1922, [iv], 31, 440—444).—In proof of the constitution of 3 : 6-tetramethyldiaminoselenopyronin (cf. A., 1920, i, 629), the corresponding selenoxanthone has been prepared indirectly. If the selenopyronin is oxidised by alkaline permanganate the only product is an amorphous, yellow compound. If, however, the selenopyronin is heated with aqueous potassium cyanide at 65° for ten minutes, a *leucocyanoselenopyronin* is obtained, and if this is oxidised by ferric chloride and hydrochloric acid, 3 : 6-tetramethyldiaminocyanoselenopyronin, is obtained as its *hydrochloride*, which is readily converted into a crystalline *nitrate*, from which by decomposition with potassium cyanide the free base may be obtained. If the cyanoselenopyronin is warmed with aqueous sodium hydroxide, 3 : 6-tetramethyldiaminoselenoxanthone, m. p. 261°, is obtained giving coloured salts with concentrated acids which are easily hydrolysed by water.

W. G.

Syntheses in the Benzofuran Group. 6-Methylcoumaran-2-one and 3-Methyl-6-isopropylcoumaran-3-one. I. EFISIO MAMELI (*Gazzetta*, 1922, 52, i, 322—337).—*o*-Tolyloxyacetic and 3-methyl-6-isopropylphenoxyacetic acid undergo ring-closure when treated with either phosphorus pentachloride or aluminium chloride. The chloride of the original acid represents the first product of the reaction and the new ring is formed by elimination of the chlorine atom and of a nuclear hydrogen atom and is five-membered,

the alkyl substituents of the benzene ring playing no part. The final products are 6-methylcoumaran-2-one and 3-methyl-6-*iso*-propylcoumaran-3-one, respectively.

6-Methylcoumaran-2-one has m. p. 89–90°; the semicarbazone, m. p. 238–240°; oxime, m. p. 152°, and benzylidene derivative, m. p. 111–112° (cf. Stoermer and Bartsch, A., 1901, i, 94; Auwers, A., 1916, i, 496; 1919, i, 216, 217; Higginbotham and Stephen, T., 1920, **117**, 1534).

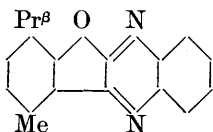
3-Methyl-6-*iso*propylcoumaran-2-one yields the original 3-methyl-6-*iso*propylphenoxyacetic acid when treated with potassium hypobromite, and treatment of its *isonitroso*-derivative with an acid gives 3-methyl-6-*iso*propylcoumaran-1:2-dione, which forms *o*-thymotic acid when oxidised by means of hydrogen peroxide and undergoes condensation with *o*-phenylenediamine to 5-methyl-2-*iso*propylcoumarophenazine. In some respects, the heterocyclic ring of 3-methyl-6-*iso*propylcoumaran-2-one behaves differently from those of other coumaranones. Thus, the action of hydrolysing or oxidising agents usually results in opening of the heterocyclic ring by rupture of the linking between the methylene and carbonyl groups, *o*-hydroxybenzoic acids being formed, whereas in the present case this ring resists the action of such agents. Further, the action of hydrochloric acid on oximinocoumaranones mostly effects rupture of the ring between the oxygen atom and the C:NOH group and yields *o*-hydroxybenzoylformic acids, but, as stated above, in the present instance the corresponding coumarandione is formed, just as with the oximino-derivatives of acyclic ketones, hydrindones, hydroxythionaphthens, and benzopyrones.

3-Methyl-6-*iso*propylcoumaran-1:2-dione dissolves in cold alkali hydroxide or carbonate solution and is reprecipitable by means of acid. Similar lactonic behaviour is shown by thionaphthaquinone and by β -naphthafuran-1:2-dione and certain dialkylcoumarandiones. As regards the opening of the heterocyclic ring, this dione exhibits behaviour intermediate to that of coumaran-1:2-dione, which is converted into *o*-hydroxybenzoylformic acid by the action of moisture, and that of β -naphthafuran-1:2-dione, which is dissolved slowly by cold and rapidly by hot sodium hydroxide solution. Thus, replacement of the methylene group in the heterocyclic ring of the coumaranone by carbonyl to give the coumarandione causes this ring to open more easily and in a different manner.

6-Methylcoumaranone azine, $C_{18}H_{16}O_2N_2$, prepared by the action of hydrazine hydrate, forms a golden-yellow, crystalline powder, m. p. 223–224°, which begins to darken at 205° and afterwards becomes almost black, and decomposes at 230°.

3-Methyl-6-*iso*propylcoumaran-2-one, $C_{12}H_{14}O_2$, crystallises in long, slender, silky, white needles, m. p. 60°, and gradually becomes oily. It gives a fluorescent solution in alcohol and a greenish-yellow solution in concentrated sulphuric acid, and it decolorises permanganate in presence of sodium carbonate. The oxime, $C_{12}H_{15}O_2N$, crystallises in white scales, m. p. 155–156°; the semicarbazone, $C_{13}H_{17}O_2N_3 \cdot H_2O$, forms a white, crystalline mass, m. p. 191° (decomp.); the benzylidene derivative, $C_{19}H_{18}O_2$,

separates in reddish-yellow needles, m. p. 134° ; the *piperonylidene* derivative, $C_{20}H_{18}O_4$, long, deep yellow, silky needles, m. p. 162° ; the *oximino*-derivative, $C_{12}H_{13}O_3N$, forms tufts of yellow prisms, or slender needles, or regular rhombic plates, m. p. 164 – 165° , decomposes at 200° , and yields an *acetyl compound*, $C_{14}H_{15}O_4N$, crystallising in straw-yellow flocks, m. p. 127° .



3 - *Methyl* - 6 - *isopropylcoumaran* - 1 : 2 - *dione*, crystallises in bright yellow needles, either interlaced or in stellate aggregates, m. p. 105 – 106° .

Methylisopropylcoumarophenazine (annexed formula), forms either orange-red or yellow crystals, m. p. 217° , and dissolves in acids, giving yellow salts. T. H. P.

Syntheses in the Cinchona Series. VII. 5 : 8-Diamino-dihydroquinine and 5 : 8-Diamino-6-methoxyquinoline and their Conversion into the Corresponding Aminohydroxy- and Dihydroxy-bases. WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1922, **44**, 1073–1079).—It has previously been shown that the aminoazo-dyes prepared from 5-aminodihydroquinine and 5-amino-6-methoxyquinoline are easily converted by acids into the corresponding hydroxyazo-dyes (A., 1921, i, 44). This also applies to the 5 : 8-diamino-derivatives, and there is evidence that the amino-group in position 5 is more labile than that in position 8. Again, it was found that the substitution of a methoxyl group in position 6 is a determining factor as regards the lability of the amino-groups.

8-*p*-Sulphobenzeneazo-5-aminodihydroquinine, on reduction with stannous chloride and hydrochloric acid, gives 5 : 8-*diaminodihydroquinine*, an amorphous powder, m. p. 125 – 140° (decomp.), which is very unstable in light and air and rapidly dissolves in dilute acids, giving red solutions from which crystalline salts can be obtained. The *tetrahydrobromide* and the *basic sulphate* were prepared. Diaminodihydroquinine, when boiled with hydrochloric acid, yielded 5 : 8-*dihydroxydihydroquinine*, which is very unstable and is best isolated as its *dihydrochloride*, m. p. 208 – 211° (decomp.), or its *dihydrobromide*. 8-*Amino-5-hydroxydihydroquinine* is obtained as its *stannichloride* by the reduction of 5-hydroxy-8-benzeneazodihydroquinine with stannous chloride and hydrochloric acid.

5-Amino-6-methoxyquinoline, when coupled with diazotised sulphanilic acid, yields 8-*p-sulphobenzeneazo-5-amino-6-methoxyquinoline*, from which on reduction with ammonium sulphide 5 : 8-*diamino-6-methoxyquinoline*, m. p. 163 – 164° (decomp.), is obtained. When the latter compound is warmed for thirty minutes on a water-bath with 10% hydrochloric acid, 8-*amino-5-hydroxy-6-methoxyquinoline*, m. p. 180 – 182° (decomp.), is obtained, and it may also be prepared from 8-benzeneazo-5-hydroxy-6-methoxyquinoline by the action of ammonium sulphide. 8-*p*-Sulphobenzeneazo-5-amino-6-methoxyquinoline, when heated in acetic acid solution with hydrochloric acid is converted into 8-*p-sulphobenzene-*

azo-5-hydroxy-6-methoxyquinoline, and 5 : 8-diamino-6-methoxyquinoline, if boiled for three hours with hydrochloric acid, yields 5 : 8-dihydroxy-6-methoxyquinoline. 5 : 8-Diaminoquinoline, on the other hand, is recovered unchanged after boiling for three hours with hydrochloric acid.

W. G.

Syntheses in the Cinchona Series. VIII. The Hydrogenation of Dihydrocinchonine, Cinchonine, and Dihydroquinine.

WALTER A. JACOBS and MICHAEL HEIDELBERGER (*J. Amer. Chem. Soc.*, 1922, **44**, 1079—1090).—Dihydrocinchonine, when reduced with sodium and amyl alcohol, yielded a mixture of hexahydrocinchonine and two epimeric hexahydrodeoxycinchonines, in the last of which the alcohol group as well as the quinoline ring had suffered reduction. The relationship of these compounds to the products obtained by reduction with zinc and hydrochloric acid and by the reduction of cinchonine have been elucidated.

Dihydrocinchonine, when reduced in boiling amyl alcohol with sodium, gave a mixture of bases in the form of an oil, and these were separated by fractional crystallisation of their dihydrochlorides. In this way, the following bases and their derivatives were obtained. α -Hexahydrodeoxycinchonine, m. p. 106—107° (corr.), $[\alpha]_D^{25} +212-217^\circ$, giving a dihydrochloride, $[\alpha]_D^{24} +69.2^\circ$, a nitroso-derivative as its hydrochloride, m. p. 203—205°, $[\alpha]_D^{27} +68.0^\circ$; an acetyl derivative as its hydrochloride, m. p. 235—237°, $[\alpha]_D^{27} +37.0^\circ$, a benzoyl derivative as its hydrochloride, m. p. 215—220°, $[\alpha]_D^{27} +13.0^\circ$, and 6-benzeneazo- α -hexahydrodeoxycinchonine, m. p. 153—156°. β -Hexahydrodeoxycinchonine, m. p. 106—106.5°, $[\alpha]_D^{25} +18.15^\circ$, giving a dihydrochloride, m. p. 237—240°, $[\alpha]_D^{26} +84.0^\circ$, a nitroso-derivative, m. p. 92.5—93.5° (corr.), $[\alpha]_D^{28} +107.0^\circ$, and its hydrochloride, m. p. 209—211°, $[\alpha]_D^{29} +68.4^\circ$, a benzoyl derivative as its hydrochloride, m. p. 232—234°, $[\alpha]_D^{27} +95.0^\circ$. Hexahydrocinchonine dihydrobromide, $[\alpha]_D^{27} +50.0^\circ$. It is probable that one of the hexahydrodeoxycinchonines described above corresponds with that of Freund and Bredenberg (cf. A., 1915, i, 159), but the hexahydrocinchonine described probably differs from that of Skita and Brunner (cf. A., 1916, i, 835).

Dihydrocinchonine dihydrochloride reacts with phosphorus pentachloride in chloroform solution to give chlorodihydrocinchonine, m. p. 70°, $[\alpha]_D^{24} +36.4^\circ$, and its hydrochloride, m. p. 227—228°, $[\alpha]_D^{23} +48.8^\circ$, which on reduction yields dihydrodeoxycinchonine, m. p. 59.5—60° (corr.), $[\alpha]_D^{30} +113.8^\circ$, and its hydrochloride, m. p. 197—199°, $[\alpha]_D^{24} +69.3^\circ$. Dihydrodeoxycinchonine when reduced with sodium in amyl alcohol gave the two epimeric hexahydrodeoxycinchonines described above.

A repetition of von Norwall's work on the reduction of cinchonine itself by sodium and amyl alcohol (cf. A., 1895, i, 631) resulted in the formation of α -tetrahydrodeoxycinchonine, m. p. 116.5—117.5° (corr.), $[\alpha]_D^{31} +209.0^\circ$, together with a mixture of β -tetrahydrodeoxycinchonine and tetrahydrocinchonine, which were not isolated as such, but were further reduced to the corresponding hexahydro-derivatives.

Dihydroquinine, when reduced in the same manner as the other compounds, yielded mainly *hexahydroquinine*, which could not be isolated as such but as its *dihydrochloride*, m. p. 271—273°, $[\alpha]_D^{25} - 36.5^\circ$, as *nitrosohexahydroquinine hydrochloride*, m. p. 212—213°, $[\alpha]_D^{31} - 85.1^\circ$, and as *benzoylhexahydroquinine*, m. p. 160—160.5°, $[\alpha]_D^{26} - 115.2^\circ$. W. G.

Syntheses in the Cinchona Series. IX. Certain Quinicine and Benzoylcinchona Salts, Crystalline Ethyldihydrocupreine (Optochin) Base, and other Derivatives. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1922, **44**, 1091—1098).—The following miscellaneous cinchona derivatives, used as initial materials for various investigations, are described. Dihydroquinicine sulphate (cf. Hesse, A., 1888, 69) has m. p. 174—176°, $[\alpha]_D^{21.5} - 8.3^\circ$; N-methylquinicine dihydrochloride, m. p. 153—155°, $[\alpha]_D^{23} + 16.6^\circ$; N-methyldihydroquinicine hydrochloride, m. p. 150—153°, $[\alpha]_D^{26.5} - 9.4^\circ$; N-ethyldihydroquinicine hydrochloride, m. p. 202—204°, $[\alpha]_D^{23} + 68.1^\circ$; N-ethyldihydroquinicine hydrochloride, m. p. 202°, $[\alpha]_D^{27} - 14.4^\circ$; N-benzoyldihydroquinicine hydrochloride, m. p. 161—164°, $[\alpha]_D^{24.5} - 65.9^\circ$; ethyldihydrocupreicine (optotoxin) sulphate, m. p. 164—166°, $[\alpha]_D^{28} - 7.8^\circ$; dihydrocupreicine hydrobromide, m. p. 213—215°, $[\alpha]_D^{21.5} - 5.4^\circ$.

Glycine derivatives of quinicine, described are: *quinicylglycine-anilide dihydrochloride*, m. p. 190°, and *quinicylglycine-p-hydroxy-anilide hydrogen sulphate*, m. p. 212—215°.

The following hydrochlorides of certain benzoylated cinchona alkaloids are described. *Benzoylcinchonidine dihydrochloride*, m. p. 208—211°; *benzoyldihydrocinchonidine hydrochloride*, m. p. 185—190°, $[\alpha]_D^{27.5} + 124.9^\circ$; benzoylquinine dihydrochloride (cf. Wunsch, A., 1895, i, 118), m. p. 229—232° (decomp.), $[\alpha]_D^{22} + 88.7^\circ$; *benzoyldihydroquinine hydrochloride*, m. p. 235—240° (decomp.), $[\alpha]_D^{24} + 140.6^\circ$.

Cinchotenine methyl ester, m. p. 243—244.5° (decomp.), $[\alpha]_D^{22} + 118.7^\circ$; *cinchotenine ethyl ester hydrochloride*, and *cupretenine methyl ester dihydrochloride*, m. p. 200°.

Ethyldihydrocupreine (optochin) was obtained in a crystalline form from toluene and had m. p. 123—128°, $[\alpha]_D^{25} - 136.2^\circ$. *Ethyldihydrocupreine ethyl bromide* had m. p. 185°, $[\alpha]_D^{25} - 111.8^\circ$. *Dihydroquinine ethyl bromide* had m. p. 188—190°, $[\alpha]_D^{25.5} - 111.1^\circ$. Hydrobromocinchonidine (cf. Leger, A., 1919, i, 451) had m. p. 176—177° (decomp.), $[\alpha]_D^{21.5} - 226.8^\circ$, and *hydrobromocupreine dihydrobromide* had m. p. 197—203° (decomp.), $[\alpha]_D^{21} - 161.8^\circ$. W. G.

Syntheses in the Cinchona Series. X. Dihydrocinchonicinol and the Dihydroquinicins. MICHAEL HEIDELBERGER and WALTER A. JACOBS (*J. Amer. Chem. Soc.*, 1922, **44**, 1098—1107).—It has been found possible to reduce the ketonic group in cinchona alkaloids of the type of cinchonicine and quinicine, by means of palladium and hydrogen, the products being mixtures of stereoisomerides of a new type of alkaloids to which the authors have assigned the names dihydrocinchonicinols and dihydroquin-

icinols. In general, the *d*-forms proved easier to isolate, and a number of *d*-bases, one of the *l*-bases, and numerous salts of the *d*- and *l*-forms are described. The restoration of the secondary hydroxyl group in the case of the dihydroquinicins resulted in the restoration of the blue fluorescence of the bases when dissolved in excess of nitric or sulphuric acids, thus supporting Kaufmann's statement that the alkyloxy-group and the secondary hydroxyl group are necessary to produce this phenomenon (cf. A., 1913, i, 763, 1222).

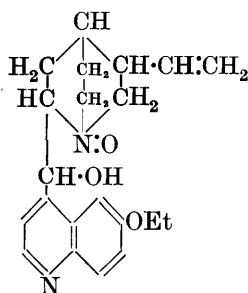
From the reduction of cinchonine oxalate *d*-dihydrocinchoninolsulphate, m. p. 223—224°, $[\alpha]_D^{25} + 63.6^\circ$, and the *l*-isomeride, m. p. 232—234°, $[\alpha]_D^{25} - 57.3^\circ$, were obtained.

Derivatives obtained from quinine were *d*-dihydroquinicinsulphate, m. p. 115°, $[\alpha]_D^{25} + 100.7^\circ$; *d*-dihydroquinicinsulphate, m. p. 80°, $[\alpha]_D^{25} + 87.1^\circ$; *d*-dihydroquinicinsulphate dihydrochloride, m. p. 212—214°, $[\alpha]_D^{25} + 151.8^\circ$ and its *l*-isomeride, m. p. 170°, $[\alpha]_D^{25} - 117.7^\circ$; *d*-N-methyldihydroquinicinsulphate, m. p. 165.5—166°, $[\alpha]_D^{25} + 93.9^\circ$, and its *d*-hydrobromide, m. p. 218—223°, $[\alpha]_D^{25} + 80.2^\circ$, its *d*-dihydrochloride, m. p. 190°, $[\alpha]_D^{25} + 145.7^\circ$, and its *methiodide*, m. p. 225—227°, $[\alpha]_D^{25} + 68.7^\circ$; *l*-N-methyldihydroquinicinsulphate, m. p. 136.5—137.5°, $[\alpha]_D^{25} - 24.9^\circ$, and its *dihydrochloride*, m. p. 232—235° (decomp.), $[\alpha]_D^{25} + 1.45^\circ$, and its *methiodide*, m. p. 253—254° (decomp.), $[\alpha]_D^{25} - 50.0^\circ$. *d*-N-Ethyldihydroquinicinsulphate, m. p. 140—141°, $[\alpha]_D^{25} + 91.7^\circ$, and its *hydrochloride*, m. p. 135°, $[\alpha]_D^{25} + 85.4^\circ$, its *dihydrochloride*, m. p. 250° (decomp.), $[\alpha]_D^{25} + 142.6^\circ$, and its *methiodide*, m. p. 135°, $[\alpha]_D^{25} + 62.9^\circ$. *l*-N-Ethyldihydroquinicinsulphate dihydrochloride, m. p. 237—238°, $[\alpha]_D^{25} - 16.7^\circ$.

Derivatives obtained from dihydrocupreicine were *d*-O-ethyl-dihydrocupreicinsulphate, m. p. 105—110°, $[\alpha]_D^{25} + 100.2^\circ$, and its *hydrochloride*, m. p. 209—210°, $[\alpha]_D^{25} + 81.1^\circ$, and *dihydrochloride*, m. p. 192—194°, $[\alpha]_D^{25} + 149.2^\circ$. *d*-N-Methyl-O-ethyldihydrocupreicinsulphate, m. p. 136.5—137°, $[\alpha]_D^{25} + 88.2^\circ$, and *d*-N : O-diethyldihydrocupreicinsulphate, m. p. 110—111°, $[\alpha]_D^{25} + 87.1^\circ$. W. G.

Action of Hydrogen Peroxide on Cinchona Alkaloids.

EDMUND SPEYER and ALFRED GUSTAV BECKER (*Ber.*, 1922, 55, [B], 1321—1329).—Quinine is converted by hydrogen peroxide



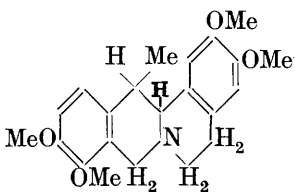
(30%) into an amine oxide which is characterised by its ability to liberate iodine from acidified potassium iodide solution and its re-conversion into quinine by the action of sulphurous acid. Since pyridine and analogous bases do not react with hydrogen peroxide in this manner, it appears valid to conclude that the oxygen atom is attached to the tervalent nitrogen atom of the piperidine complex and to ascribe the annexed formula to quinine oxide. Dihydroquinine, quinidine, dihydrocupreine, and ethyldihydrocupreine behave in a similar manner, but cinchonine does not appear to yield an amine oxide.

Quinine oxide, needles, m. p. 195—196°, has $[\alpha]_D -31.44^\circ$ and -29.87° when dissolved in chloroform ($c=2.481$ and 6.207 , respectively). It gives a *dihydrochloride*, leaflets, m. p. 138—140°, a *dinitrate*, colourless rods ($+3H_2O$), m. p. (anhydrous) 152—153° (decomp.), a normal *sulphate*, silky needles, m. p. 146°, after softening at 140°, a *hydrogen sulphate*, needles ($+2H_2O$), m. p. (anhydrous) 165—167°, after becoming pale yellow at 130° and softening at 140°, a *monopicrate*, yellow needles, m. p. 158°, after softening at 156° and a *diperchlorate*, pale brown leaflets, m. p. 193°, after previous softening.

Dihydroquinine oxide is prepared as a yellow liquid by the action of hydrogen peroxide on dihydroquinine or by the catalytic hydrogenation of quinine oxide in the presence of palladium; the *dinitrate* is described.

Quinidine oxide crystallises in coarse octahedra, m. p. 205°; it yields a *picrate*, matted needles, m. p. 152°. *Dihydrocupreine oxide* forms coarse prisms, m. p. 198—202°, after becoming discoloured above 185°. *Ethylidihydrocupreine oxide* crystallises in needles, m. p. 150°, after softening at 135°; its *dinitrate* forms colourless rods, decomp. 153°. H. W.

The Constitution of Corydaline. J. GADAMER and F. VON BRUCHHAUSEN (*Arch. Pharm.*, 1922, **259**, 245—249).—In agreement with the conclusions of Späth and Lang (this vol., i, 168), the authors now accept for corydaline the formula annexed, since dehydrocorydaline, obtained by the removal of four hydrogen atoms by treatment with mercuric acetate, gives Cannizzaro's reaction when it is warmed with 30% sodium hydroxide solution, 2 mols. being converted thereby by auto-reduction and auto-oxidation into 1 mol. of *oxydehydrocorydaline*, $C_{22}H_{23}O_5N$, m. p. 228—228.5°, and 1 mol. of *dihydrodehydrocorydaline*. This could not occur with the formula previously proposed. G. F. M.



Ecgonine. J. GADAMER and C. JOHN (*Arch. Pharm.*, 1922, **259**, 241—244; cf. this vol., i, 167).—*Anhydroecgonine ethyl ester* is obtained as an oil, b. p. 137—139°/11 mm., $d_4^{20} 1.0721$, $n_D^{20} 1.49615$; it forms a crystalline *hydrochloride*, m. p. 243—244°. By the action of sulphuric acid, or better chlorosulphonic acid in the cold on *l*-ecgonine the *sulphuric ester* is obtained as a white, crystalline substance, m. p. 258—260°, $[\alpha]_D -85^\circ$; *aurichloride*, $C_9H_{15}O_6NS \cdot HAuCl_4 \cdot 2H_2O$, m. p. 110° (152—153°, anhydrous). Treatment of anhydroecgonine with cold sulphuric acid did not give the corresponding derivative. G. F. M.

Morphine. EDMUND SPEYER and GÜNTHER BECKER (*Ber.*, 1922, **55**, [B], 1329—1339).—In previous communications (A., 1911, i, 76, 909; 1915, i, 580) the conversion of morphine oxide by acetic anhydride and sulphuric acid into morphinehydrateoxide-

sulphonic acid and reduction of the latter by sulphurous acid to morphinehydratesulphonic acid has been described. If this nomenclature is correct, reduction of the latter acid should yield a dihydromorphinehydratesulphonic acid; actually, however, α -dihydromorphinesulphonic acid, $C_{17}H_{21}O_6NS$, decomp. above 360° after darkening between 338° and 350° , is obtained (the same acid is prepared from morphinehydrateoxidesulphonic acid), so that it is evident that the water in "morphinehydratesulphonic acid" is present as water of crystallisation; this is shown experimentally to be the case by heating it during several hours at 170 – 180° , whereby a molecular proportion of water is expelled without further decomposition taking place. The terms morphinesulphonic acid and oxidodimorphinesulphonic acid are therefore to be substituted for the older expressions.

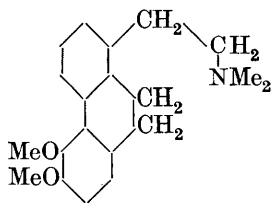
Catalytic reduction of sodium morphineoxidesulphonate leads to the formation of "ordinary" dihydromorphinesulphonic acid, decomp. above 360° after blackening between 301° and 306° . This acid is distinguished from α -dihydromorphinesulphonic acid [prepared by catalytic reduction of the oxidodimorphinesulphonic acid or of morphinesulphonic acid (see above)] by crystalline form and more sparing solubility.

Dihydromorphine is transformed by hydrogen peroxide into dihydromorphine N-oxide, plates, decomp. 261° after softening at 257° , which is converted by acetic anhydride and concentrated sulphuric acid into NN'-oxidobisdihydromorphinesulphonic acid, $C_{31}H_{44}O_{15}N_2S_2$, prisms, decomp. above 360° after blackening at 334° . Sulphurous acid transforms the latter into dihydromorphinesulphonic acid.

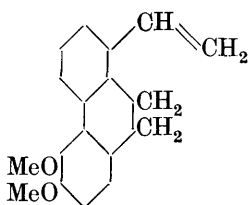
Potassium morphinesulphonate is converted by methyl iodide into codeinesulphonic acid methohydroxide, needles, decomp. 284° after softening at 282° (cf. Freund and Speyer, A., 1911, i, 909). Similarly, α -dihydromorphinesulphonic acid gives dihydrocodeinesulphonic acid methohydroxide, leaflets, decomp. 280 – 286° (cf. Speyer and Wieters, this vol., i, 170).

H. W.

The Course of the Decomposition of apoMorphine by Reduction by Emde's Method. FRANZ FALTIS and MATHILDE KRAUSZ (*Monatsh.*, 1921, 42, 377–385).—In a previous paper on the structure of isochondodendrine (Faltis and Neumann, this vol., i, 569), it was concluded that when a benzylisoquinoline derivative is reduced by Emde's method with sodium amalgam (A., 1912,



i, 801), rupture of the isoquinoline ring occurs in one way only, whilst Hofmann's method gives a mixture of inactive α - and active β -methines. To confirm this observation, experiments have been made with a benzylisoquinoline base of known constitution, apomorphine. Dimethyldihydroapomorphine methochloride gave, by Emde's method, dimethyldihydroapomorphimethine, transparent tablets, m. p. 70.5 – 71.5° (annexed formula).



Its *methiodide* has m. p. 240° . When boiled with sodium hydroxide solution, the methiodide decomposed, giving trimethylamine and *dimethoxyvinyl-dihydrophenanthrene* (annexed formula), brush-like crystals, m. p. $83\cdot5-84^{\circ}$ (corr.). Unlike the known dimethoxyvinylphenanthrene, this dihydro-derivative does not form a picrate. When the methochloride of dimethyldihydroapomorphimethine was reduced with sodium amalgam, it gave, apparently, a mixture of dimethoxyethyl- and -vinyl-dihydrophenanthrenes. Wijs's method of estimating the ethylene linkings by determining the iodine number proved valuable in the analysis of the nitrogen-free products. A number of examples of the application of this method are given.

E. H. R.

Strychnos Alkaloids. XXXII. Transformations of the Quinones from Brucinesulphonic Acid. I. HERMANN LEUCHS and KURT FRICKER (*Ber.*, 1922, **55**, [B], 1244—1254).—In extension of the work of Leuchs and Geiger (*A.*, 1909, i, 828), the red quinone obtained by the action of 5*N*-nitric acid on brucinesulphonic acid I has been investigated further. As by-product, a nitro-compound was isolated previously to which the formula $C_{21}H_{23}O_{10}N_3S$ was ascribed; this is now amended to $C_{21}H_{21}O_{10}N_3S$. The substance is shown to be a nitroquinone which is smoothly reduced by sulphur dioxide to a nitroquinol, the formula of which can now be resolved in the following manner:

$C_{16}H_{16}\{C(OH) \dots C(OH); :C:NO_2; :N; HO_3S; :NH; HO_2C; CH(OH)\}$.

The red quinone, $C_{21}H_{20}O_7N_2S$, is characterised further by its conversion into a *semicarbazone*, $C_{22}H_{23}O_7N_5S$, pale brown needles, and by reduction with tin and hydrochloric acid to the *aminophenol*, $C_{21}H_{23}O_6N_3S$, short, colourless needles, the *hydrochloride* of which is also described. The quinol, $C_{21}H_{22}O_7N_2S$, gives a *di-acetate*, colourless, slender needles.

The nitroquinone from brucinesulphonic acid I is obtained in the form of a tetrahydrate, yellow, lustrous needles, a *dihydrate*, rectangular or hexagonal prisms, and as the anhydrous compound, $C_{21}H_{21}O_{10}N_3S$. During its production, the $-CO:N$ group of brucine and brucinesulphonic acid appears to undergo transformation into the $\cdot CO_2H$ and NH groups, since it yields an *ethyl ester*, dark yellow, domatic prisms. The quinone group, however, remains intact, since the substance gives a *monosemicarbazone*, yellow leaflets, and a *monoxime*, slender yellow needles, which is almost quantitatively reconverted by warm *N*-nitric acid into the nitroquinone. The oxime is convertible into an *ethyl ester*, dark yellow, rectangular prisms which is transformed by methyl-alcoholic ammonia at 100° into the *methyl ester* of the *nitroquinoneoximeimine*, $C_{22}H_{25}O_9N_5S$, dark yellow needles. Reduction of the nitroquinoneoxime by tin and hydrochloric acid gives the *hydrochloride* of the *diaminophenol*, $C_{21}H_{26}O_7N_4S \cdot HCl$, almost colourless, oblique prisms or plates. Similar reduction of the nitroquinone and treatment of the product

with ethyl alcohol gives the *hydrochloride* of the *amino-quinol* ester, $C_{23}H_{29}O_8N_3S.HCl$, hexagonal plates (the *dihydrate* is also described).

The nitro-quinone is reduced by sulphurous acid at 90° to the corresponding *nitro-quinol*, the *monohydrate*, $C_{21}H_{23}O_{10}N_3S.H_2O$, dark violet, rectangular prisms, the *dihydrate* and *hydrochloride* of which are described; it is readily re-oxidised to the nitro-quinone by 2*N*-nitric acid or ferric chloride. It yields a *monoethyl* ester, violet leaflets or coarse, blackish-violet, prismatic rods, a *di-ethyl* ester, aggregates of violet leaflets and a *tri-acetyl* derivative, pale yellow, rhombic platelets. The latter is converted by ethyl alcoholic hydrogen chloride into the *ethyl* ester of the *N-monoacetylnitroquinol*, $C_{25}H_{29}O_{11}N_3S$, brownish-yellow leaflets. H. W.

Reduction of Pyridine with Zinc Dust and Acetic Anhydride.

II. OTTO DIMROTH and FRITZ FRISTER (*Ber.*, 1922, **55**, [B], 1223—1232; cf. Dimroth and Heene, this vol., i, 48).—In the previous communication it was mentioned incidentally that 1 : 1'-diacetyltetrahydro-4 : 4'-dipyridyl, obtained by the reduction of pyridine with zinc dust and acetic anhydride, is frequently contaminated by the presence of an orange-yellow, crystalline compound. This is now shown to be 1 : 1'-diacetyldihydro-4 : 4'-dipyridyl. It crystallises in orange-coloured leaflets or needles, m. p. 284° (instead of 248° as previously erroneously reported). The substance is readily oxidised by air to 4 : 4'-dipyridyl and the process is quantitative when effected with lead tetra-acetate in acetic anhydride solution or by bromine in chloroform (whereby dipyridyl perbromide is produced). The same 1 : 1'-diacetyldihydro-4 : 4'-dipyridyl is obtained readily by the reduction of 4 : 4'-dipyridyl with zinc dust and acetic anhydride. It is very possible that dihydro-4 : 4'-dipyridyl is the initial product of the reduction of 4 : 4'-dipyridyl by metals in acid solution but this supposition is not looked on as proved definitely; in any case the authors do not see any reason to suppose with Weitz and Ludwig (this vol., i, 365) that the radicle 4 : 4'-dipyridinium is present.

The formation of diacetyldihydropyridyl occurs irregularly during the preparation of the corresponding tetrahydro-compound, but the maximum amounts are secured when the mixtures are stirred too long in contact with air at a high temperature. The obvious explanation that the tetrahydro-compound is oxidised by atmospheric oxygen through the dihydro-substance to dipyridyl could not be experimentally confirmed. On the other hand, the dihydro-derivative is produced freely when the tetrahydro-substance is heated with an equivalent amount of dipyridyl in acetic anhydride solution at 100° ; simultaneously, pyridine is formed. It appears therefore that the dihydrodipyridyl is produced entirely by the reduction of dipyridyl and that the tetrahydro-compound is oxidised to pyridine, and not to dihydrodipyridyl.

According to the experimental conditions, oxidation of 1 : 1'-diacetyltetrahydro-4 : 4'-dipyridyl leads to the production of dipyridyl or pyridine; the opinion expressed previously (*loc. cit.*)

that this oxidation is preceded by dissociation into radicles is now abandoned.

The peculiar blue coloration which is observed when a solution of diacetyltetrahydrodipyridyl in glacial acetic acid is warmed has been investigated further. It is found that different specimens of the substance give this effect with very varying intensity, and that it is not exhibited by material which has been washed with dilute acetic acid and methyl alcohol immediately before use. It is due to adherent dipyridyl which is formed readily by the autoxidation of diacetyltetrahydrodipyridyl at a rate which is greatly influenced by the presence of catalytic impurities. H. W.

Dialkylamides of Nicotinic Acid. M. HARTMANN and M. SEIBERTH (U.S. Pat. 1403117).—*Nicotinodiethylamide* is prepared by heating nicotinyl chloride for two hours at 160° with diethylamine hydrochloride, dissolving the reaction mass in water, adding potassium hydroxide, extracting with ether, and evaporating the ether after drying the solution with an alkali hydroxide. After distillation in a vacuum, it is a yellowish oil, b. p. 280° or 175°/25 mm. *Nicotinodipropylamide* is a yellow oil, b. p. 184°/17 mm. *Nicotinopiperidide* is a thick oil, b. p. 310°.

CHEMICAL ABSTRACTS.

2 : 4-Diphenylpyridine. C. GASTALDI (*Gazzetta*, 1922, 52, i, 305—307; cf. this vol., i, 573).—2 : 4-Diphenylpyridine, $C_{17}H_{13}N$, crystallises in elongated, colourless plates, m. p. 69°, exhibits slight basic properties and dissolves in concentrated sulphuric acid to a solution showing faint blue fluorescence. The *hydrochloride* (2 : 4-diphenylpyridinium chloride) forms slender, colourless needles and decomposes when heated; the *platinichloride*, $(C_{17}H_{13}N)_2 \cdot H_2PtCl_6$, crystallises in orange needles with irregular ends, m. p. 238° (decomp.); the *picrate*, $C_{17}H_{13}N \cdot C_6H_3O_7N_3$, forms thin, yellow plates or stouter prisms, m. p. 187° (decomp.); the *methiodide* (2 : 4-diphenyl-1-methylpyridinium iodide), $C_{18}H_{16}NI$, crystallises in very long, yellow needles, m. p. 210° (decomp.), and forms colourless aqueous solutions. T. H. P.

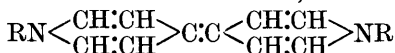
Some Derivatives of Indolinone. OLDŘICH TOMIČEK (*Chem. Listy*, 16, 1—4, 35—39).—Brunner's reaction whereby indolinones are prepared from the phenylhydrazides of fatty acids (A., 1896, i, 625; 1897, i, 100, 438; 1898, i, 90), is tried with the phenylhydrazides of β -phenylpropionic acid, and found to give good yields. By its means, a number of benzylindolinones were prepared.

Phenylpropionylphenylhydrazine was converted into 3-benzyl-2-indolinone, m. p. 132°. Its 1-acetyl derivative, m. p. 82°, was prepared, also the 5 : 7-dibromo-derivative, m. p. 194°. 3-Benzyl-1-methyl-2-indolinone, m. p. 95—96°, was prepared by the Brunner reaction from phenylpropionylphenylmethylhydrazine, m. p. 102°, obtained from *as*-phenylmethylhydrazine. 3-Benzyl-7-methyl-2-indolinone, m. p. 196°, was prepared from phenylpropionyl-*o*-tolylhydrazine, m. p. 122°. Its monobromo-derivative has m. p. 191°.

3-Benzyl-5-methyl-2-indolinone, m. p. 149·5°, was prepared from phenylpropionyl-p-tolylhydrazine, m. p. 120°. Its monobromo-derivative, m. p. 198°, was also obtained. 3-Benzyl-4(or 6)-methyl-2-indolinone, m. p. 209°, was obtained from phenylpropionyl-m-tolylhydrazine, m. p. 125°. It was expected that a mixture of the 4- and 6-methyl derivatives would be formed, but only one product was obtained; which of the two it is, it is not yet possible to state with certainty. R. T.

isoQuinoline and the isoQuinoline-Reds. JOHN EDMUND GUY HARRIS and WILLIAM JACKSON POPE (T., 1922, **121**, 1029-1033).

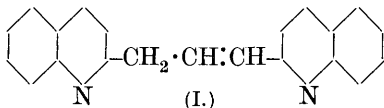
1:1'-Dimethyltetrahydro-4:4'-dicollidyl [1:2:4:6:1':2':4':6'-Octamethyltetrahydro-4:4'-dipyridyl]. BRUNO EMMERT and OTTO WERB (*Ber.*, 1922, **55**, [B], 1352-1358).—In a previous communication (A., 1920, i, 331), the blue coloration of alcoholic solutions of 1:1'-dialkyltetrahydro-4:4'-dipyridyls has been attributed to the formation of an alkylpyridinium radicle, $R\cdot NC_5H_5$. The more recent observations of Emmert and Parr (this vol., i, 179) that 4:4'-dipyridyldiisobutyl iodide and 4:4'-dipyridyldiisoomyl iodides in addition to much alkylpyridinium iodide are formed by the action of iodine on the blue solutions of 1:1'-diisobutyl- and 1:1'-diisoomyltetrahydro-4:4'-dipyridyls suggests a different interpretation, since one of the substances,



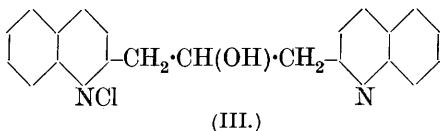
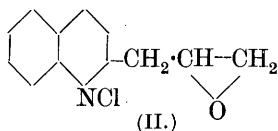
or $RN \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} > C:C < \begin{array}{c} \text{CH:CH} \\ \text{CH:CH} \end{array} NR$, must also be present in the solution; either must be coloured, and, possibly, be the cause of the blue colour of the solutions. To test this point, a dialkyltetrahydrodipyridyl derivative has been prepared in which the labile hydrogen atoms in position 4 are replaced by alkyl groups; this cannot in consequence give such a dialkyldihydrodipyridyl compound. Its alcoholic solution does not become coloured under the action of air or oxygen. The sensitive blue coloration of other dialkyltetrahydrodipyridyls must therefore be attributed to the formation of dialkyldihydropyridyls, and it is no longer necessary to assume the rupture of the bond between the pyridine nuclei with the formation of radicles.

2:4:6-Trimethylpyridine is converted into its methiodide (the *platinichloride* is described) which is reduced by sodium amalgam in aqueous solution and in an atmosphere of carbon dioxide to 1:2:4:6:1':2':4':6'-octamethyltetrahydro-4:4'-dipyridyl, $NMe \begin{array}{c} \text{CMe:CH} \\ \text{CMe:CH} \end{array} > CMe:CMe < \begin{array}{c} \text{CH:CMe} \\ \text{CH:CMe} \end{array} NMe$, colourless, rhombic crystals, m. p. 154-155°, which resinifies rapidly if exposed to air, more slowly in an atmosphere of carbon dioxide. An alcoholic solution of the substance decolorises iodine, with the formation of amorphous products in which crystalline material is present in too small quantity to permit further examination. H. W.

A New Red Quinoline Colouring Matter. M. GIUA (*Gazzetta*, 1922, 52, i, 349—351).—Condensation of quinoline with epichlorohydrin in presence of sodium hydroxide yields an intense dark-red, semi-oily mass which, especially in a desiccator over sulphuric acid, tends to solidify. From the resin thus obtained, alcohol extracts a red compound which dissolves in acids, forms a platinum-



chloride, etc., and is probably represented by the annexed formula. The first product of the reaction is most likely the salt-like compound II, which unites with a second molecule of quinoline under the condensing action of the alkali, giving the compound III, the latter then losing the halogen atom and a molecule of water and undergoing transposition to the compound I :



The red compound, which may be obtained also by condensation of quinoline with α -dichlorohydrin in presence of potassium hydroxide, unites with bromine to give a bromide of high melting point.

The compound (I), $C_{21}H_{16}N_2$, forms a brownish-red solid turning pale yellow in the light, softens at 193° , and is completely fused at 220° ; it dissolves in mineral acids and in acetic acid giving intensely wine-red salts. The *picrate*, $C_{21}H_{16}N_2 \cdot C_6H_3O_7N_3$, forms a brick-red powder; the *platinichloride*, $(C_{21}H_{16}N_2)_2 \cdot H_2PtCl_6$, a dark yellow precipitate dissolving in concentrated hydrochloric acid to a green solution; the *aurichloride*, $C_{21}H_{17}N_2 \cdot HAuCl_4$, a golden-yellow, crystalline powder, and the *nitrate*, $C_{21}H_{17}O_3N_3$, a yellow powder.

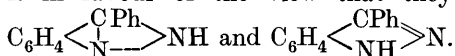
T. H. P.

Bromo-derivatives of Glyoxaline. ISIDORE ELKANAH BALABAN and FRANK LEE PYMAN (T., 1922, 121, 947—958).

Benzylalkylbarbituric Acids. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1922, 44, 1141—1145).—A series of ethyl benzylalkylmalonates has been prepared either by alkylating the monobenzylmalonic esters or by benzylating the monoalkylmalonic esters. From these ethyl esters the corresponding benzylalkylbarbituric acids have readily been obtained by heating the malonic ester with sodium ethoxide and carbamide in alcoholic solution in an autoclave at 105° for five hours. In this series benzylethylbarbituric acid was found to have the strongest physiological action, but contrary to expectations the hypnotic effect was accompanied by symptoms of tetanus instead of the antispasmodic effect commonly attributed to the benzyl group. New compounds described are : *Ethyl benzylethylmalonate*, b. p. 160 — $170^\circ/9$ mm., *ethyl benzylisopropylmalonate*, b. p. 170 — $180^\circ/12$ mm., *ethyl benzyl-n-butylmalonate*, b. p. 177 — $185^\circ/10$ mm., *ethyl benzylisobutyl-*

malonate, b. p. 177—187°/10 mm., ethyl benzylisoamylmalonate, b. p. 180—190°/10 mm. 5-Benzyl-5-methylbarbituric acid, m. p. 207°, 5-benzyl-5-ethylbarbituric acid, m. p. 206—207°, 5-benzyl-5-n-propylbarbituric acid, m. p. 210°, 5-benzyl-5-n-butylbarbituric acid, m. p. 195°, 5-benzyl-5-isobutylbarbituric acid, m. p. 255°, and 5-benzyl-5-isoamylbarbituric acid, m. p. 194—196°. W. G.

3-Phenylindazole and 2-Hydroxy-3-phenylindazole. K. VON AUWERS and K. HÜLTENES (*Ber.*, 1922, **55**, [B], 1112—1138).—The recent isolation of stereoisomeric derivatives of 2-acylindazoles (Auwers, A., 1919, i, 455; Auwers and Duesberg, A., 1920, i, 638; Auwers and Schwegler, A., 1920, i, 640), has led to a re-examination of 3-phenylindazole which has been obtained previously (Auwers and Sondheimer, A., 1896, i, 503) in two modifications with different melting points the inter-relationship of which has not been elucidated completely. It is now found that the balance of evidence is in favour of the view that they are structural isomerides,



The new examination of the inter-conversion of the 3-phenylindazoles, m. p. 107—108° and 115—116°, respectively, by recrystallisation or under the action of heat confirms in the main the previous observations (*loc. cit.*), excepting that the changes do not appear to occur with such absolute uniformity as assumed previously. The two modifications give the same hydrochloride and (with acetic anhydride) the same acetyl derivative from which the form, m. p. 107—108°, is obtained by hydrolysis. On the other hand, the phenylindazoles appear to give different picrates which are distinguished from one another in colour, crystalline form, and melting point. The two salts, however, melt indefinitely; on recrystallisation, the melting points approximate to one another without becoming sharp. It appears as if mixtures are formed in every case which tend to pass on crystallisation into a common equilibrium mixture. When triturated with ammonia, the salts give only 3-phenylindazole, m. p. 107—108°.

2-Nitroso-3-phenylindazole, lustrous, greenish-yellow needles, m. p. 91—92°, is prepared readily by the addition of a nitrite solution to 3-phenylindazole dissolved in glacial acetic acid.

The alkylation of indazole leads, according to the experimental condition and the particular alkyl haloid used, to 1- or 2-derivatives or to mixtures of them (Auwers and Schaich, A., 1921, i, 806). Similar relationships are observed with 3-phenylindazole, but, in general, the tendency towards the production of 1-compounds is more marked than with the parent substance. Thus, whereas indazole gives almost exclusively 2-alkyl derivatives when treated with alkyl haloid at 100°, 3-phenylindazole gives, in addition, considerable amounts of the 1-isomerides. Indazole is converted by alkyl haloid and alcoholic alkoxide into about equal quantities of the two isomerides, whereas the main product from 3-phenylindazole is the 1-compound. The difference is not so marked in the case of the action of alkyl iodides on the silver salts, since the

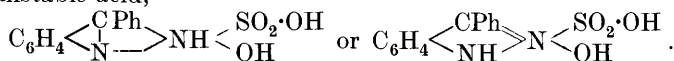
course of the change is here governed mainly by the nature of the alkyl group. The following individual compounds have been examined: 3-phenyl-2-methylindazole, lustrous, apparently monoclinic crystals, m. p. 47—49° (*picrate*, pale yellow needles or granules, m. p. 186—187°); 3-phenyl-1-methylindazole, large, rhombic crystals, m. p. 78·5—80°, b. p. about 207°/12 mm. (*picrate*, very unstable, red crystals, m. p. 91—95°); 3-phenyl-1:2-dimethylindazolium iodide, $C_{15}H_{15}N_2I$, colourless crystals, m. p. 189—190°, which is converted by loss of methyl iodide under the action of heat exclusively into 3-phenyl-1-methylindazole; 3-phenyl-2-ethylindazole, a yellow liquid, b. p. 193—195°/10 mm. (*picrate*, yellow needles, m. p. 160—162°); 3-phenyl-1-ethylindazole, which, unexpectedly, decomposes when distilled in a vacuum (the *picrate* is dark red and very unstable); 3-phenyl-2-allylindazole *picrate*, yellow crystals, m. p. 138—140°; 3-phenyl-1-allylindazole, a yellow liquid, b. p. 215—216°/15 mm. (the corresponding red *picrate* is very unstable).

3-Phenylindazole closely resembles indazole in its behaviour towards chloroformic esters, by which it is smoothly converted into 3-phenylindazole-2-carboxylic esters. The latter are completely hydrolysed by cold alcoholic alkali hydroxide solutions to 3-phenylindazole; at an elevated temperature they lose carbon dioxide, giving 3-phenyl-1- and -2-alkylindazoles and products of further decomposition. Methyl 3-phenylindazole-2-carboxylate forms lustrous, flattened needles, m. p. 112—113°, whilst the corresponding *ethyl* ester crystallises in colourless needles, m. p. 83—84°.

It has been shown previously (*loc. cit.*) that 2-hydroxy-3-phenylindazole is the main product of the action of sodium sulphite on diazotised *o*-aminobenzophenone, and that the substance is unstable and passes under the prolonged influence of boiling solutions of sodium hydroxide or carbonate into small quantities of benzophenone and nitrogen and a compound, m. p. about 212°. The latter is now shown to be 3-hydroxy-2-phenylindazole, since it is identical with the product obtained by Freundler (A., 1907, i, 158) from hydrazobenzene-*o*-carboxylic acid and phosphoryl chloride (cf. Heller, A., 1917, i, 219). Its constitution is established further by its oxidation by chromic acid in acetic acid solution to azobenzene-*o*-carboxylic acid. Its *methyl ether*, leaflets with a blue fluorescence, m. p. 95—96°, acetyl derivative, m. p. 90—91°, and benzoyl derivative, colourless, slender needles, m. p. 180—181°, are described. The formation of 3-hydroxy-2-phenylindazole from 2-hydroxy-3-phenylindazole appears to be analogous to the Beckmann transformation, but is regarded as occurring by the direct change in position of the radicles.

Sodium 3-phenylindazole-2-sulphonate, colourless, lustrous leaflets (the corresponding barium, lead, and silver salts are described) is obtained under certain definite experimental conditions, which are fully described in the original, when diazotised *o*-aminobenzophenone is subjected to the action of sodium sulphite. The salt is stable towards boiling water and alkali hydroxide solutions, but is hydrolysed by dilute mineral acids to the salt of 3-phenylindazole and sulphuric acid. It is transformed by the addition of

concentrated hydrochloric acid to its cold concentrated solution into 3-phenylindazole-2-sulphonoxide, $\text{C}_6\text{H}_4\langle\text{CPh}\rangle\text{N}\text{---}\text{NH}\langle\text{SO}_2\text{O}\rangle$ or $\text{C}_6\text{H}_4\langle\text{CPh}\rangle\text{NH}\rangle\text{N}\langle\text{SO}_2\text{O}\rangle$, colourless needles, m. p. 195—196°. The substance is insoluble in water or in solutions of alkali hydroxides, is neutral in reaction and is hydrolysed by boiling acids, alkali hydroxides, or even by water, into 3-phenylindazole and sulphuric acid. It is also formed by the action of ethyl chlorosulphonate on 3-phenylindazole or its silver salt. It is remarkable that the alcoholic solution of the sulphonoxide has an acid reaction and liberates carbon dioxide from carbonates. The phenomena are not caused by hydrolysis, and appear to be due to the formation of an unstable acid,



Attempts are also described to prepare sulphonoxides from other indazoles. Sodium 3-methylindazole-2-sulphonate is, however, converted by concentrated hydrochloric acid into the corresponding *sulphonic acid*, m. p. (anhydrous) 185—190°; the *dihydrate*, slender, colourless needles, has m. p. 102—103°, then immediately resolidifies, softens, and evolves gas at 140—150°, and finally melts at 179·5—180·5° (m. p. of 3-methylindazole sulphate). The immediately evolved gas is sulphur dioxide, due to a subsidiary reaction. Somewhat unexpectedly, 3-methylindazole and indazole are transformed into the corresponding sulphates when mixed with ethyl chlorosulphonate without any special precautions. Possibly the 2-sulphonic acids of the bases are initially formed and subsequently hydrolysed by atmospheric moisture. This hypothesis is supported by the observation that anhydrous 3-methylindazole-2-sulphonic acid is converted into 3-methylindazole sulphate when heated in contact with the atmosphere at 100°, whereas it remains unchanged in the absence of air.

H. W.

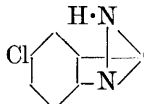
Halogenated Indazoles and Stereoisomerism of Free Indazoles. K. VON AUWERS and H. LANGE (*Ber.*, 1922, 55, [B], 1139—1173).—In extension of previous investigations on the stereoisomerism of 2-acylindazoles (Auwers, A., 1919, i, 455; Auwers and Duesberg, A., 1920, i, 638; Auwers and Schwegler, A., 1920, i, 640), the halogenated indazoles have now been prepared and examined. The first portion of the present communication is devoted to an account of the halogenation of indazoles under varying experimental conditions, and the elucidation of the constitution of the substances so prepared. It is shown that the two rings of indazole are attacked with approximately equal readiness by halogens, which enter it in the 3- and 5-positions. Direct chlorination and bromination yield therefore mainly a 3 : 5-di-derivative, whereas the preparation of mono-substitution products cannot be achieved in this manner. Monohalogenated indazoles with chlorine, bromine, or iodine in the 3-position are obtained from indazole silver

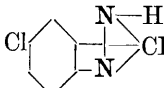
and the respective halogen; probably the halogen atom attaches itself first to the nitrogen, to which the silver was united, and isomerisation subsequently occurs in the established manner. Mono-halogenated derivatives with the chlorine or bromine atom in the 5-position are prepared by the action of the halogens on 2-acetyl-indazoles, in which the presence of the acyl group prevents the entry of the halogen atom into the 3-position. Methyl groups attached to one of the two nitrogen atoms attract the halogen to their vicinity and facilitate its entry. 2-Methylindazole thus yields a 3-monobromo-derivative and 1-methylindazole gives a 3:5:7-tribromo-compound, whereas indazole itself only acquires two bromine atoms, even when treated energetically. The chemical nature of indazoles is little affected by the entry of a halogen atom into the benzene nucleus; thus, the 5-halogenated derivatives are somewhat weaker bases than the parent substance, but are readily soluble in 2*N*-hydrochloric acid, combine with picric acid, and are insoluble in solutions of alkali hydroxides. Halogenation in the pyrazole ring, on the other hand, has a powerful influence on the chemical character of the indazoles, the 3-halogenated derivatives dissolving readily in dilute sodium hydroxide solution and being therefore markedly acidic. The degree of acidity diminishes in the order chloro-, bromo- to iodo-derivative. Basic character is little marked in these compounds, since they only dissolve with difficulty even in concentrated hydrochloric acid, and do not give picrates. The behaviour of the 3:5-di-derivatives is somewhat remarkable. As is to be expected, they are very weak bases which are dissolved only with difficulty by concentrated hydrochloric acid and do not give picrates. On the other hand, they appear to be weaker acids than the 3-monohalogenated compounds since they dissolve only in hot solutions of alkali hydroxides from which they separate unchanged on cooling.

The new observations of the stereoisomerism of the 2-acetyl derivatives of indazole completely confirm those made previously (*loc. cit.*). The acetyl compounds of 5-bromo- and 5-iodo-indazoles in addition to the stable forms give labile varieties which, like the corresponding chloro-compounds, are relatively very stable at the atmospheric temperature, but are transformed into the stable modifications slowly at the temperature of the water-bath, rapidly at higher temperatures. On the other hand, it was not found possible to isolate labile acetyl derivatives from 3:5-dichloro-, 3:5-dibromo-, 3-chloro-, or 3-iodo-indazoles. It appears, therefore, that the presence of any substituent in position 3 inhibits the existence of labile 2-acetyl compounds or, at any rate, that such substances are so unstable that they pass immediately into the stable isomerides, even under the mild experimental conditions adopted.

Remarkable observations are recorded with 5-chloro- and 5-bromo-indazoles. The former, m. p. 119—120°, has been obtained by Auwers and Schwegler (A., 1920, i, 642) by the spontaneous decomposition of the nitroso-compound of *p*-chlorobenz-*o*-toluidide. The same substance was obtained also initially by the hydrolysis of the stable acetyl compound of 5-chloroindazole. After a few

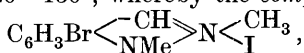
minutes, re-determination of the melting point showed that it had risen to 143—144°, and that this had also occurred with Schwegler's product. A second experiment also yielded 5-chloroindazole, m. p. 119—120° (by hydrolysis of the acetyl derivative), but subsequently the laboratory was found to have become "infected," and only the modification of higher melting point could be isolated. Similar results were obtained with 5-bromoindazole. The substance has been prepared previously by several chemists according to widely differing methods and the melting point 124—125° has been uniformly assigned to it. This is now confirmed. When, however, a specimen was preserved for several weeks the melting point was found to have risen to 132—133°, and subsequently it was not found possible to isolate the variety of lower melting point. The balance of the evidence is in favour of the view that stereo-

isomeric pairs of substances of the type  and

 are here encountered.

The following individual substances are described. 3:5-Dichloroindazole, matted, silky needles, m. p. 240°, prepared by adding chlorine water to indazole dissolved in dilute hydrochloric acid or by passing gaseous chlorine into a solution of indazole in glacial acetic acid; the constitution of the compound is established by its production by the chlorination of 3- or 5-chloroindazole. Its *acetyl* derivative crystallises in slender, colourless needles, m. p. 122—123°. 3-Chloroindazole, m. p. 148° (*acetyl* derivative, m. p. 67°). Stable 5-chloroindazole, colourless, lustrous needles, m. p. 143—144°; the labile and stable modifications give the same *picrate*, m. p. 194—195°. 3:5-Dibromoindazole, m. p. 243—244° (*acetyl* derivative, small, lustrous needles, m. p. 132°). 5-Bromoindazole (labile form, m. p. 124—125°, stable *variety*, m. p. 132—133°; both modifications yield the same *picrate*, m. p. 195—196°). The stable *acetyl* derivative of 5-bromoindazole crystallises in colourless, highly refractive needles, m. p. 143—144°, whereas the labile *modification* (from 5-bromoindazole, silver, and *acetyl* chloride in the presence of anhydrous ether or from 5-bromoindazole and *acetyl* chloride in the presence of pyridine) forms colourless leaflets, m. p. 137—138°; a mixture of the two forms has m. p. 113°. 3-Bromoindazole, m. p. 141—142° (*acetyl* derivative, colourless needles, m. p. 83—84°). 5-Bromo-1-methylindazole, plates or leaflets, m. p. 111—112° (by the action of bromine water on an ice-cold solution of 1-methylindazole in 2*N*-hydrochloric acid). The constitution of the compound is established by methylating 5-bromoindazole in the presence of alkali and transforming the mixture of bases into the corresponding *picrates* which are separated by taking advantage of their differing solubilities in ether. The base obtained by the decomposition of the more readily soluble *picrate* (m. p. 124—126°) is identical with the product just described. 5-Bromo-1-methyl-

indazole is also prepared by heating 3 : 5-dibromoindazole with methyl iodide at 120—150°, whereby the *compound*,



m. p. 221° (decomp.), is produced, which when heated above its melting point, loses methyl iodide and gives 5-bromo-1-methylindazole. More drastic bromination of 1-methylindazole leads to the production of mixtures containing a dibromo-derivative, which was not isolated in the pure condition, but in all probability is 3 : 5-dibromo-1-methylindazole, and 3 : 5 : 7-tribromo-1-methylindazole, colourless, lustrous needles, m. p. 168—168·5°. 3-Bromo-2-methylindazole, long, colourless needles or lustrous leaflets, m. p. 82—83°, is prepared by the direct bromination of 2-methylindazole, whereas 5-bromo-2-methylindazole, lustrous needles, m. p. 97—97·5°, cannot be obtained in this manner, but is derived from the methylation of 5-bromoindazole (see above). 3 : 5-Dibromo-2-methylindazole, lustrous leaflets, m. p. 133—134°, is prepared from 5-bromo-2-methylindazole and an excess of bromine in glacial acetic acid solution. 3-Bromo-5-methylindazole crystallises in soft, matted needles, m. p. 158—159°.

Ethyl indazole-3-carboxylate is converted by acetic anhydride into the corresponding *acetyl* derivative, m. p. 89·5—90·5°, which does not appear to exist in a labile modification.

5-Bromoindazole-3-carboxylic acid, pale yellow, matted needles, m. p. 303—305° (decomp.), is obtained readily by the bromination of indazole-3-carboxylic acid dissolved in glacial acetic acid at the atmospheric temperature; its *acetyl* compound crystallises in pale yellow needles, m. p. 220—223°. Ethyl indazole-3-carboxylate is converted by bromine into the *compound* $\text{C}_{10}\text{H}_9\text{O}_2\text{N}_2\text{Br}_2$, reddish-brown needles, m. p. about 105°, which is converted by a solution of sodium sulphite into *ethyl 5-bromoindazole-3-carboxylate*, m. p. 230—232° (*acetyl* derivative, slender, colourless needles, m. p. 166—167°).

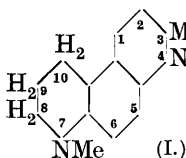
3-Iodoindazole, colourless needles, m. p. 142°, is prepared by the action of iodine on indazole silver in the presence of ether; its *acetyl* derivative crystallises in colourless, lustrous needles, m. p. 93—94°, and does not appear to yield a labile modification. 5-Nitroindazole is reduced by ferrous sulphate and ammonia to 5-aminoindazole, colourless needles, m. p. 170—172°, after previous softening and darkening, which is transformed by successive diazotisation and treatment with potassium iodide into 5-iodoindazole, colourless leaflets, m. p. 157—159°. The corresponding stable *acetyl* derivative (from the iodo-compound and acetic anhydride) forms coarse, yellow crystals, m. p. 144—145°; treatment of 5-iodoindazole with acetyl chloride in the presence of pyridine appears to give a labile acetyl compound, which, however, has not yet been isolated in the homogeneous condition. H. W.

The Course of the Quinaldine Synthesis with 6-Amino-tetrahydroquinoline and 6-Aminokairolone. J. LINDNER (*Monatsh.*, 1921, 42, 421—438).—These experiments were started with the object of determining in which direction ring formation

would take place when the quinaldine synthesis was applied to 6-aminotetrahydroquinoline or 6-aminokairolin (6-amino-1-methyl-tetrahydroquinoline), the point having a bearing on the problem of the distribution of double bonds in polynuclear systems. It was found that only the phenanthrene type of derivative was formed, not the anthracene type.

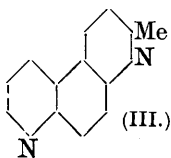
6-Amino-1-methyltetrahydroquinoline was prepared by reduction of 6-nitroso-1-methyltetrahydroquinoline. It has b. p. 163—165°/11 mm., and darkens rapidly in air. The position of the amino-group is inferred from analogy with 6-nitrosotetrahydroquinoline. By the quinaldine synthesis was obtained 3:7-dimethyl-

7:8:9:10-tetrahydro- ψ -phenanthroline (annexed formula I). The base crystallises with 1 mol. of water in rhombic four- or six-sided tablets, sulphur-yellow in colour, m. p. 69°. The water is difficult to remove; the anhydrous base has m. p. 52°. The *monohydrochloride* has an intense red colour, and crystallises in six-sided



tablets. The *dihydrochloride* is colourless. The *platinichloride*, $C_{14}H_{16}N_2 \cdot H_2PtCl_6 \cdot H_2O$, is a reddish-yellow, crystalline powder, sparingly soluble in water. Demethylation of (I) was accomplished by heating the hydriodide of the base in a stream of carbon dioxide at 160—200°. The demethylated base, 3-methyltetrahydro- ψ -phenanthroline (II), was difficult to purify; its m. p. is probably above 70°. It crystallises with $2\frac{1}{2}H_2O$. Its *monohydrochloride* is red, and forms a crystalline mass by evaporation of its alcoholic solution; the *dihydrochloride* is colourless, deliquescent, and difficult to crystallise. By reduction with hydriodic acid and red phosphorus, 3-methyloctahydro- ψ -phenanthroline was obtained. The base could not be crystallised, but the *dihydrochloride*, $C_{13}H_{18}N_2 \cdot 2HCl$, forms fine, white crystals which sublime without melting. The same octahydro-compound was obtained by reduction of (I), demethylation occurring during reduction. By exhaustive reduction the *tetradecahydro*-compound was obtained, which was isolated as its *platinichloride*, $C_{13}H_{24}N_2 \cdot H_2PtCl_6 \cdot H_2O$. By oxidation of the demethylated base (II), with mercuric acetate, four hydrogen atoms were removed, and 3-methyl- ψ -phenanthroline was obtained. It could not be completely purified; the free base had m. p. 98—109°, the tetrahydrate 74—82°.

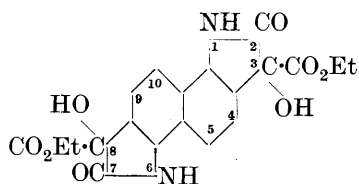
To confirm the supposed structure of the last compound (annexed formula III), it was prepared by carrying out the quinaldine synthesis on 6-aminoquinoline. The m. p. of the hydrated form ($4H_2O$) was 84—85° and of the anhydrous base 115°. The identity of the two preparations was established thereby proving that the synthesis takes the same course with the 6-amino-1-methyltetrahydroquinoline as with 6-aminoquinoline.



E. H. R.

A Naphthalenic Di-isatin. JH. MARTINET and F. VACHER (*Bull. Soc. chim.*, 1922, [iv], **31**, 435—440).—1:5-Naphthylene-

diamine condenses with ethyl mesoxalate in acetic acid solution to give *ethyl ββ-naphthabisdioxindole-3 : 8-dicarboxylate* (annexed



formula), decomp. about 300°, which gives a *diacetyl* and a *tetraacetyl* derivative, both forming colourless crystals. When hydrolysed with aqueous sodium hydroxide in the absence of air and subsequently acidified with hydrochloric acid, the ester yields

1 : 5-naphthabisdioxindole. If the saponification is carried out in the presence of air with constant agitation, the product is *1 : 5-naphthadi-isatin*, which gives a *monophenylhydrazone* and a *diphenylhydrazone*. The corresponding *sodium* and *potassium isatates* are soluble in water, giving yellow solutions. W. G.

Addition of Hydrazoic Acid to Derivatives of Carbodi-imide. R. STOLLÉ (*Ber.*, 1922, 55, [B], 1289—1297).—A preliminary description of the preparation of tetrazoles by the action of sodium azide on derivatives of carbodi-imide.

Carbodiphenylimide and carbodi-*p*-tolylimide are converted by sodium azide in boiling absolute alcoholic solution into 5-anilino-1-phenyl-1 : 2 : 3 : 4-tetrazole, m. p. 161°, and 5-*p*-toluidino-1-*p*-tolyl-1 : 2 : 3 : 4-tetrazole, m. p. 211°, respectively. The latter substance is also prepared in good yield by the action of sodium azide and lead oxide on di-*p*-tolylthiocarbimide. By an extension of the method to the corresponding *meta*- and *ortho*-compounds, 5-*m*-toluidino-1-*m*-tolyl-1 : 2 : 3 : 4-tetrazole, coarse leaflets, m. p. 147°, and 5-*o*-toluidino-1-*o*-tolyl-1 : 2 : 3 : 4-tetrazole, needles, m. p. 152°, are obtained. 5-*Phenylhydrazino*-1-phenyl-1 : 2 : 3 : 4-tetrazole, from *ad*-diphenylthiosemicarbazide, lead oxide, and sodium azide, crystallises in yellowish-white, lustrous leaflets, m. p. 190° (decomp.). Under similar conditions, phenylthiocarbamide yields 5-amino-1-phenyl-1 : 2 : 3 : 4-tetrazole, lustrous leaflets, m. p. 159°, which appears to have been prepared previously from phenylthiocarbimide and hydrazoic acid by Oliveri-Mandalà and Noto (*A.*, 1913, i, 774), who, however, misinterpreted their reaction; it gives an *acetyl* derivative, small, matted needles, m. p. 211° (decomp.) after previous softening, and a *nitroso*-compound, decomp. about 108°. 5-Amino-1-*p*-tolyl-1 : 2 : 3 : 4-tetrazole crystallises in colourless, lustrous leaflets, m. p. 176°. Phenylthiocarbimide and *o*-tolylthiocarbimide are converted smoothly by sodium azide in the presence of boiling alcohol into 5-thiol-1-phenyl-1 : 2 : 3 : 4-tetrazole, m. p. 152°, and 5-thiol-1-*o*-tolyl-1 : 2 : 3 : 4-tetrazole, m. p. 131° (decomp.).

Sodium thiocyanate is obtained by the interaction of sodium azide and carbon disulphide in boiling alcoholic solution.

Oxanilideimide chloride and sodium azide give 1 : 1'-*diphenylbis*-5 : 5'-tetrazole, $\begin{array}{c} \text{N} \cdot \text{NPh} \\ || \quad || \\ \text{N} \text{---} \text{N} \end{array} \text{C} \cdot \text{C} \begin{array}{c} \text{NPh} \cdot \text{N} \\ || \quad || \\ \text{N} \text{---} \text{N} \end{array}$, needles, m. p. 212°.

H. W.

b b *2

The Reaction of Benzylidenebenzhydrazide Chloride and Dibenzhydrazide Chloride with Sodium Azide. R. STOLLÉ and A. NETZ (*Ber.*, 1922, **55**, [B], 1297—1305).—Benzylidenebenzhydrazide chloride reacts with sodium azide in boiling ethyl- or methyl-alcoholic solution with the formation of 1-benzylidene-imino-5-phenyl-1 : 2 : 3 : 4-tetrazole, m. p. 105° (the corresponding iodochloride, $C_{14}H_{11}N_5ICl$, has m. p. 146°); reaction occurs probably in accordance with the scheme: $CPhCl:N:N:CHPh \xrightarrow{+NaN_3} N_3 \cdot CPh:N:N:CHPh + NaCl \rightarrow N \begin{smallmatrix} N:CPh \\ \diagdown \\ N \end{smallmatrix} \cdot N:N:CHPh$, but cannot be arrested at the intermediate stage. With anisylideneanishydrazide chloride in methyl-alcoholic solution it is possible to isolate both azidoanisylideneanishydrazide, slender needles, m. p. 113° (decomp.), and 1-anisylideneamino-5-anisyl-1 : 2 : 3 : 4-tetrazole, slender needles or leaflets, m. p. 147°.

Dibenzhydrazide chloride is transformed by sodium azide in boiling methyl-alcoholic solution into azidodibenzhydrazide, $N_3 \cdot CPh:N:N:CN_3 \cdot Ph$, long, slender needles, m. p. 139° (decomp.); a sodium salt, $N \begin{smallmatrix} N:CPh \\ \diagdown \\ N \end{smallmatrix} = N \cdot NNa \cdot C \begin{smallmatrix} NPh \cdot N \\ \diagup \\ N \end{smallmatrix}$ or $N \begin{smallmatrix} N:CPh \\ \diagdown \\ N \end{smallmatrix} = N \cdot N \cdot C \begin{smallmatrix} NPh \cdot N \\ \diagup \\ N \end{smallmatrix} Na$, is formed as by-product. The latter compound is the chief product when boiling ethyl alcohol is used as solvent (in addition, a compound, leaflets, m. p. 172° (decomp.), which is converted by boiling hydrochloric acid into 1-amino-5-phenyl-1 : 2 : 3 : 4-tetrazole); it is also obtained from azidodibenzhydrazide and sodium azide in the presence of boiling ethyl alcohol. The corresponding free acid, $C_{14}H_{11}N_9$, crystallises in small, slender needles, m. p. 192° (decomp.); the silver salt is described. The action of methyl iodide on the silver salt or of methyl sulphate on the sodium compound yields two methyl esters, $C_{15}H_{13}N_9$, short rods, m. p. 150° (decomp.); and coarse crystals, m. p. 124°. The silver salt is transformed by ethyl iodide into two ethyl esters, m. p. 123° and (?) 122°, respectively (mixed m. p. below 120°).

Azidodibenzhydrazide is converted by boiling ethyl alcohol into nitrogen and 1-aniloethoxymethylamino-5-phenyl-1 : 2 : 3 : 4-tetrazole, $N \begin{smallmatrix} N:CPh \\ \diagdown \\ N \end{smallmatrix} = N \cdot NH \cdot C(OEt) \cdot NPh$, rhombic plates, m. p. 144° (decomp.) after previous softening. It is transformed by dilute hydrochloric acid into ethyl alcohol, aniline, and 1-amino-5-phenyl-1 : 2 : 3 : 4-tetrazole. 1-Anilomethoxymethylamino-5-phenyl-1 : 2 : 3 : 4-tetrazole, rhombic platelets, m. p. 157°, is prepared from the azide and methyl alcohol at 100°. H. W.

The Replacement of Diazo-groups by Nitro-groups. V. VESELY and K. DVOŘÁK (*Bull. Soc. chim.*, 1922, [iv], **31**, 421—424).—For the replacement of the diazo-group by the nitro-group in the Sandmeyer reaction, the authors recommend the addition of a mixture of molecular copper or copper bronze and an alkali nitrite to the solution of the diazonium salt. Such a mixture gives as good a yield as the double copper sulphite and an alkali nitrite. W. G.

Action of certain Hydrazines and of Pyridine on 5-Bromo-1 : 2 : 4-trinitrobenzene. MICHELE GIUA (*Gazzetta*, 1922, 52, i, 346—349; cf. this vol., i, 649).—In the action of hydrazine hydrate on 5-bromo-1 : 2 : 4-trinitrobenzene, the 1-nitro-group is first attacked and eliminated as nitrous acid, so that secondary reactions may occur: (1) $C_6H_2Br(NO_2)_3 + 2N_2H_4 = C_6H_2Br(NO_2)_2 \cdot NH \cdot NH_2 + N_3H + 2H_2O$, (2) $C_6H_2Br(NO_2)_2 \cdot NH \cdot NH_2 + N_3H = C_6H_2(NO_2)_2(NH \cdot NH_2) \cdot N_3 + HBr$, and (3) $C_6H_2Br(NO_2)_3 + 4N_2H_4 = C_6H_2(NO_2)_2(NH \cdot NH_2)_2 + N_3H + 2H_2O + N_2H_4 \cdot HBr$. There exists, therefore, the possibility of the formation of dinitrophenylhydrazinazide, in accordance with equation (2). With excess of hydrazine hydrate, the reaction (3) takes place, whilst with 2 mols. of hydrazine hydrate and 1 mol. of the bromotrinitrobenzene the reaction is represented by equation (1). The action of phenylhydrazine gives rise to 5-bromo-2 : 4-dinitrohydrazobenzene and to 4 : 6-dinitro-1 : 3-dihydrazinobenzene, which decomposes at about 253° (cf. Borsche, A., 1921, i, 461). *as*-Phenylmethylhydrazine yields 5-bromo-2 : 4-dinitromethylhydrazobenzene, and pyridine an additive compound of the type of those obtained by Zincke from 4-chloro-1 : 3-dinitrobenzene and pyridine or quinoline.

5-Bromo-2 : 4-dinitrophenylhydrazine, $C_6H_2Br(NO_2)_2 \cdot NH \cdot NH_2$, crystallises in flattened, lustrous, pale yellow needles, m. p. 203—204°, and gives a yellow coloration with sulphuric acid and a dark red coloration with alkali in presence of alcohol.

5-Bromo-2 : 4-dinitroacetylphenylhydrazine, $C_6H_2Br(NO_2)_2 \cdot NH \cdot NHAc$, forms orange-yellow prisms, m. p. 188—189°, and in alcoholic solution gives a dark red coloration with alkali.

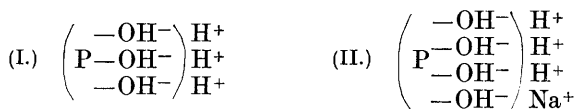
5-Bromo-2 : 4-dinitrohydrazobenzene, $C_6H_2Br(NO_2)_2 \cdot NH \cdot NHPh$, crystallises in lustrous, orange-yellow lamellæ, m. p. 154—155°, and forms intense reddish-brown salts with alkaline bases.

5-Bromo-2 : 4-dinitromethylhydrazobenzene, $C_6H_2Br(NO_2)_2 \cdot NH \cdot NMePh$, forms red prisms, m. p. 138—139°, and in alcoholic solution yields a dark red coloration with alkalis.

2 : 4 : 5-Trinitrophenylpyridinium bromide, $C_5H_5NBr \cdot C_6H_2(NO_2)_3$, crystallises in lustrous, golden-yellow lamellæ, m. p. above 300°, and gives a dark red coloration with alkalis. T. H. P.

Colloidal Chemistry of the Proteins. III. A. FODOR (*Kolloid Z.*, 1922, 30, 313—336; cf. A., 1921, i, 81, 701).—From a number of coagulation and peptisation experiments with fibrin sols, together with much previously published data, the author concludes that the dehydration of protein gels leads, exactly as in the case of a large number of inorganic gels, to the formation of new and more stable molecular structures which are characterised by a reduced tendency to enter into reactions, whilst, on the other hand, peptisation of such structure gives, owing to combination with water, reactive disperse particles. It is shown that the larger or smaller particles obtained by precipitating proteins are not to be regarded as accidental, but as structures combined with different

amounts of water and of different reactivity. The author differentiates two stages between the hydrate in which the water is weakly held and the solid swollen gel. These he terms loosely held water (micellar water, and imbibition water) and water adsorbed on the surface. The adsorbed water is regarded as held by the protein owing to it adsorbing one ion of water and giving a complex which is formulated $(P \leftrightarrow \overset{+}{H})\overset{-}{OH}$ or $(P \leftrightarrow \overset{-}{OH})\overset{+}{H}$. This complex the author terms an "enhydron." In the case of globulin, the enhydron is represented by I; this when treated with alkali becomes through adsorption an alkali enhydron and is represented by II. The character of the enhydron remains unchanged



so long as the adsorbed water is in excess of the alkali, but when the alkali is in excess the complex ceases to be an enhydron and becomes an "ekhydron." In the same way, acid-enhydrons can be formed. The changes of yeast proteins, globulin, and casein are considered on the basis of this hypothesis. J. F. S.

Discrepancies between the Observed and Calculated Potential Difference of Protein Solutions near the Isoelectric Point. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 4, 617—619).—The discrepancies previously noted (A., 1921, i, 627, 693, 822) between the observed values of the influence of the P_H on the potential difference between protein solutions inside collodion bags and protein free aqueous solution and those calculated on the basis of Donnan's theory disappear when both inside and outside solutions contain a buffer salt. This shows that the differences were due to inaccuracies in the measurement of the P_H of the outer solution near the isoelectric point of the protein. C. R. H.

The Regulation of Osmotic Pressure. II. The Effect of Albumin on the Conductivity of a Sodium Chloride Solution. WALTER W. PALMER, DANA W. ATCHLEY, and ROBERT F. LOEB (*J. Gen. Physiol.*, 1922, 4, 585—589).—At a P_H of about 3.0, increasing concentrations of albumin increase the conductivity of 0.6% sodium chloride; at a P_H of 7.3 and at the isoelectric point of albumin, the conductivity is diminished by such additions. C. R. H.

The Proteic Acids of Urine. I. The Hydroxyproteic Acids. S. EDLBACHER (*Z. physiol. Chem.*, 1922, 120, 71—84).—The barium salt of hydroxyproteic acid showed the same properties as that described by previous workers. Free hydroxyproteic acid consists of urea, and a carbohydrate, probably a tetrose, which yields an osazone, $C_{16}H_{18}O_2N_4$, m. p. 130°. By treating the substance with alcohol and ether, a compound is obtained which in many respects resembles Moor's urein. Hydroxyproteic acid does

not contain any hexone bases, but possibly traces of other amino-acids. S. S. Z.

The Colloidal Behaviour of Edestin. DAVID J. HITCHCOCK (*J. Gen. Physiol.*, 1922, 4, 597—615).—Edestin reacts like an amphoteric electrolyte and behaves otherwise in a manner entirely analogous to that described by Loeb (A., 1921, i, 627, 693) for gelatin, casein, and albumin. C. R. H.

Kinetics of Trypsin Digestion. JOHN H. NORTHROP (*J. Gen. Physiol.*, 1922, 4, 487—509).—Experiments on the rate of hydrolysis of gelatin and casein by trypsin (the rate being measured by the increase of hydrolysis products) show that this rate does not increase in proportion to the substrate concentration, but becomes constant after the latter has reached about 3%. A mixture of casein and gelatin is digested at a rate which is equal to the sum of the rates of hydrolysis of the two substances separately. The rate of digestion is unaffected by the viscosity of the solution or by the concentration of ionised protein. The effect of inhibiting substances on the hydrolysis is independent of substrate concentration, which is taken as evidence against the existence of an enzyme-substrate compound. There is evidence to show that enzyme and inhibitor form a highly dissociated compound. These results may be explained by the fact that the increase of products of hydrolysis does not give a true measure of the change in concentration of substrate. If the decrease of casein or gelatin is measured directly, the reaction is found to conform to the law of mass action, the rate of digestion being proportional to the concentration of substrate. The difference in the results obtained by the two methods is due to the fact that the reaction is not a simple one, but a series of consecutive reactions. C. R. H.

The Digestion of Histone Sulphate with Pepsin and Hydrochloric Acid. K. FELIX (*Z. physiol. Chem.*, 1922, 120, 94—102).—The histone sulphate from the thymus of the calf was digested with pepsin and hydrochloric acid and precipitated with sodium picrate. The filtrate was treated with phosphotungstic acid, and the precipitate again treated with silver baryta. The precipitate from the silver fraction contained a substance resembling the original histone, but the distribution of nitrogen in it was somewhat different, and also it did not give Millon's reaction. The filtrate from the silver fraction showed a content of 17% arginine-*N*, 13% lysine-*N*, and 70% monoamino-acid-*N*. The monoamino-acids of this fraction gave Millon's reaction. The phosphotungstic precipitate showed the presence of peptides, probably dipeptides, but no amino-acids. Lævulic acid was also found in this fraction, but its origin was traced to the pepsin preparation. S. S. Z.

The Conditions of Acidity and Thermolability of Saccharase. HANS VON EULER and KARL MYRBÄCK (*Z. physiol. Chem.*, 1922, 120, 61—70).—Purified preparations of saccharase manifested the same acidity curve as previously established with

less pure preparations. On the other hand, the purified preparations showed a greater stability towards heat. S. S. Z.

Blood Saccharase and the Antigen Properties of Yeast Saccharase. E. KNAFFL-LENZ (*Z. physiol. Chem.*, 1922, **120**, 110—125).—The injection of sucrose into rabbits did not produce a serum capable of inverting this sugar. Immunisation with potent preparations of yeast invertase yielded a serum which inhibited the inverting capacity of invertase only to a small extent. S. S. Z.

Mannanase and Levidulinase. MINORU MAYEDA (*J. Biochem. [Japan]*, 1922, **1**, 131—137).—The mannan of the food "konjak-powder" is liquefied by saprophytic bacteria, yielding "levidulin," but not mannose. Certain fungi, such as *Aspergillus niger*, liquefy mannan by their exoenzymes, but also have a distinct endoenzyme which hydrolyses "levidulin." CHEMICAL ABSTRACTS.

Enzymic Fat Synthesis. L. SPIEGEL (*Z. physiol. Chem.*, 1922, **120**, 103—109).—On incubating cellulose, dextrose, and starch with enzyme preparations from certain oil-bearing seeds, a low production of fatty substances was established. S. S. Z.

Preparation of Organic Compounds of Boron with the Aid of Boron Fluoride. II. Boron Triphenyl and Phenylboric Acid. ERICH KRAUSE and RUDOLF NITSCHKE (*Ber.*, 1922, **55**, [B], 1261—1265; cf. this vol., i, 22).—*Boron triphenyl*, BPh_3 , long, colourless, hexagonal rods, m. p. 136° , b. p. $203^\circ/15\text{ mm.}$, is readily obtained by passing gaseous boron fluoride into an ethereal solution of an excess of magnesium phenyl bromide; it is isolated by distillation of the residue left after removal of the ether, under diminished pressure in an atmosphere of nitrogen. It readily becomes oxidised on exposure to air, without, however, being inflamed; it is stable in an atmosphere of nitrogen or carbon dioxide. It is somewhat rapidly decomposed by alcohol with the formation of esters. If an excess of the Grignard reagent is avoided, the product of the reaction is composed of a mixture of boron triphenyl, *boron diphenyl fluoride*, and *boron phenyl difluoride*; the latter substances have not yet been isolated in a homogeneous condition. Crude boron phenyl difluoride is transformed by hot water into phenylboric acid, $\text{BPh}(\text{OH})_2$, which is dehydrated by exposure to phosphoric oxide to phenyl boron oxide, BPhO .

H. W.

Action of Mercuric Acetate on Nitrobenzene. J. P. WIBAUT and J. JÜRGENS (*Verslag. Akad. Wetensch. Amsterdam*, 1922, **29**, 1074—1076).—By heating mercuric acetate with nitrobenzene at 150° for three and a half hours, addition of sodium chloride, and removal of the excess of nitrobenzene by distillation with steam, a light yellow residue is obtained which is separable into *o*-nitrophenylmercuric chloride (Dimroth, A., 1902, i, 656), *mercury oo'-dinitrodiphenyl*, m. p. 206° , and a material insoluble in light petroleum from which a pure substance could not be isolated.

CHEMICAL ABSTRACTS.

Mercuriation in the Aromatic Series. I. Phenolmercuri-acetates and -hydroxides and their Derivatives. E. MAMELI (*Gazzetta*, 1922, 52, i, 352—368).—The author has investigated the monomercuri-acetates, -hydroxides, and other salts of phenolmercury obtained from ordinary phenol. Under all experimental conditions, even when a preponderance of phenoldimercuri-acetate results, both the ortho- and para-monomercuriacetates are formed. To obtain the monomercuriacetates, it is best to heat the phenol and mercuric acetate together without solvent, whilst in acetic acid solution the product consists almost solely of the dimercuriacetate. In order to determine the positions of the $\cdot\text{Hg}\cdot\text{OAc}$ group in the two monomercuriacetates obtained, these have been converted into the corresponding chlorides, for which the positions of the $\cdot\text{HgCl}$ groups have already been established (Dimroth, A., 1899, i, 54, 428; 1902, i, 656, 849). The action of iodine on *o*-phenolmercuriacetate yields, besides *o*-iodophenol, also 2:4-di-iodophenol and 2:4:6-tri-iodophenol, the reaction being probably catalysed by the mercury compound.

The isomeric phenolmonomercuriacetates have been converted into the corresponding hydroxides, bromides, iodides, nitrates, and sulphates, some of these being obtained by the action of alkali hydroxides or salts on the acetates and others by treating the phenolmercuri-oxide with acids. The action of alkali iodides on the acetate sometimes yields the mercuridiaryl compound, HgR_2 , which often decomposes, giving the original phenol, but if the reaction is carried out under mild conditions, the phenolmercuri-iodide is formed.

Phenol-o-mercuriacetate, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{Hg}\cdot\text{OAc}$, forms long needles or white, dendritic crystals composed of microscopic, hexagonal, or rhombic prisms, and melts at 157° to a turbid, red liquid which afterwards becomes clear and at $210\text{--}215^\circ$ decomposes with evolution of gas and red vapour and sublimation of mercury. By alkali hydroxide solution, it is dissolved, with formation of the corresponding hydroxide, and treatment of this alkaline solution with carbon dioxide results in the formation of the internal oxide (Dimroth, A., 1902, i, 849). By hydrogen sulphide, the acetate is not affected in aqueous suspension, but in presence of hydrochloric acid mercuric sulphide is precipitated. In aqueous acetic acid solution, the acetate is converted by sodium chloride into the corresponding chloride.

Phenol-p-mercuriacetate forms long, slender needles or dendritic masses or microscopic, triangular prisms, m. p. 165° , and decomposes at $210\text{--}215^\circ$ similarly to the ortho-isomeride.

Phenol-*o*-mercurichloride has m. p. 156° and the para-compound m. p. 222° (cf. Dimroth, *loc. cit.*).

Phenol-o-mercuribromide, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{HgBr}$, forms slender, silky needles, sometimes in bundles, m. p. $130\text{--}132^\circ$, the clear red liquid becoming turbid at 190° and solidifying and decomposing at 195° . The *mercuri-iodide* crystallises in white, stellar aggregates composed of tufts of short, microscopic prisms, m. p. 121° , the clear red liquid turning turbid at $170\text{--}180^\circ$ and decomposing at $200\text{--}210^\circ$. The

nitrate, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{HgNO}_3$, is a white, crystalline, infusible compound, blackening at about 200° . The *sulphate*, $(\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{Hg})_2\text{SO}_4$, and *hydroxide* are white, pulverulent, and infusible.

Phenol-p-mercuribromide forms scales, m. p. $144\text{--}146^\circ$, decomposing and solidifying at $200\text{--}210^\circ$. The *iodide* is obtained as a white powder, m. p. $134\text{--}135^\circ$, and decomposes at $200\text{--}210^\circ$. The *nitrate* forms white crystals and decomposes at 210° . The *sulphate* and the hydroxide are white, infusible compounds. T. H. P.

Mercury Compounds of Hydroxybenzaldehydes. THOMAS ANDERSON HENRY and THOMAS MARVEL SHARP (T., 1922, **121**, 1055—1060).

Organo-derivatives of Tin and Lead. I. Application of Lead and Tin Tetraphenyls in the Preparation of Organo-metallic Compounds. ARCHIBALD EDWIN GODDARD, JULIUS NICHOLSON ASHLEY, and RICHARD BROMLEY EVANS (T., 1922, **121**, 978—982).

Physiological Chemistry.

Free and Bound Water in the Blood. BENJAMIN S. NEUHAUSEN (*J. Biol. Chem.*, 1922, **51**, 435—438).—Water imbibed by the serum proteins retains dissolved salts in practically unchanged concentration. Hence it is impossible to prove or disprove theories of bound and free water by physico-chemical methods based on colligative properties. E. S.

The Interactions of Oxygen, Acid, and Carbon Dioxide in Blood. A. V. HILL (*J. Biol. Chem.*, 1922, **51**, 359—365).—Mainly a re-statement of the author's theory (this vol., i, 193). E. S.

Active Hyperæmia. D. T. HARRIS (*Proc. Roy. Soc.*, 1922, [B], **93**, 384—405).—The increased blood supply to an organ during muscular activity is independent of alterations in vaso-motor or vaso-constrictor tone, but it is due to the products of metabolism. Of these products, carbon dioxide and α -hydroxy-acids are found to be increased. C. R. H.

The Distribution of Sugar between Corpuscles and Plasma. W. FALTA and M. RICHTER-QUITTNER (*Biochem. Z.*, 1922, **129**, 576—581).—Using exact methods of analysis, corpuscles are found to be free from dextrose if clotting is completely avoided, or if clotting is complete. H. K.

Influence of Optical Activity on Cell Permeability. I. YASHIRO KOTAKE and M. OKAGAWA (*J. Biochem. [Japan]*, 1922, **1**, 159—164).—Colorimetric estimations of *d*-, *l*-, and *dl*-hydroxy-phenyl-lactic acid left unabsorbed after incubation with blood

corpuscles in normal saline solution show that only the *l*-compound penetrates the cell-wall to any appreciable extent.

CHEMICAL ABSTRACTS.

Sensitiveness of Cells to Poison as a Function of their Colloid-chemical Conditions. HANS HANDOVSKY (*Kolloid Z.*, 1922, **30**, 336—341).—A theoretical paper in which the sensitiveness of cells to poison is discussed in connexion with the colloid-chemical condition of the cells. It is shown that the sensitiveness to poisons and poisoning is of necessity closely connected with the stability and variability of the colloid-chemical condition of the protoplasm colloids. The difference of the sensitiveness of red blood corpuscles to poisoning in solutions of sucrose and in solutions of salts is explained as follows. The sucrose brings about in the continuously changing sol \rightleftharpoons gel system of the protoplasm a more gelatinised condition, which is accompanied by a decrease in the degree of dispersion, and this makes the blood less sensitive toward the surface active poisons. Solutions of salts act in the opposite sense; they make the blood in sucrose solution sensitive again, and in those cases where the salt has no hæmolytic action of its own it increases the sensitiveness according to the laws which govern the increase in adsorption brought about by the salts. This fact may be regarded as a confirmation of the above quoted hypothesis.

J. F. S.

Glycolytic Action of Leucocytes. I. KANSHI FUKUSHIMA (*J. Biochem. [Japan]*, 1922, **1**, 151—158).—The leucocytes, obtained from the peritoneal cavity of rabbits previously injected with bouillon, are suspended in Rona and Michaelis's citrate mixture of p_H 7.765, washed with the aid of a centrifuge, incubated with isotonic glucose solutions for definite periods, and the sugar estimated by Bertrand's method. The reducing power diminishes gradually within forty-eight hours, and then remains constant, but after seventy-two hours it begins to increase again. Neither pancreatic juice nor pancreatic tissue has any effect on the glycolytic action of leucocytes.

CHEMICAL ABSTRACTS.

The Action of the Phosphatides on the Coagulation of Blood. E. ZUNZ and J. LA BARRE (*Arch. int. physiol.*, 1921, **18**, 116—127).—A study of the effect of cytozymin, cephalin, and lecithin on blood coagulation in vitro. Cytozymin and lecithin show the solubility characters of the cytozyme of Bordet and Delange (*Ann. inst. Pasteur*, **26**, 657, 737). Cytozymin only contains aminated nitrogen; lecithin contains no nitrogen in this form. The addition of small amounts of either of these two compounds to clear serum in the presence of calcium makes such serum induce coagulation in diluted oxalated plasma. An excess of lecithin or cytozymin inhibits coagulation. Cytozyme contains most of its nitrogen in the amino-form. It is probably a mixture of cytozymin and lecithin. Cephalin is to be considered as a thromboplastic agent.

CHEMICAL ABSTRACTS.

Regeneration of Diastase and its Dependence on Oxygen. W. BIEDERMANN (*Biochem. Z.*, 1922, **129**, 582—593).—If an active filtered saliva be heated just to 100°, it becomes turbid. The diastatic activity of this solution is small but is regenerated to a considerable extent by vigorous shaking with air. If, however, the heated saliva be again filtered, the filtrate, free from oxygen, is practically inactive, but is slightly activated by shaking with air. This activation is attributed to oxygen, although the finely divided coagulated protein plays a part. H. K.

Gastric Juice. III. Juice from the Empty Stomach. MAKI TAKATA (*J. Biochem. [Japan]*, 1922, **1**, 107—121).—One hundred c.c. of the juice, *d* 1.006—1.007, yield 1.4873 grams of dry residue, of which 0.5035 gram is ash, and contains pepsin, pepsinogen, rennet, lipase, nuclease, amylase, and maltase, but not sucrase. The mucus content of the juice secreted in unit time does not appear to be influenced either by previous feeding or by the presence of 0.5% hydrochloric acid. The amount of reducing sugar produced by hydrolysis under standard conditions is a measure of the mucus, which exists in the juice in the form of mucotinsulphuric acid. CHEMICAL ABSTRACTS.

Disappearance of Nitrogen during Digestion. A. GOUIN and P. ANDOUARD (*Bull. soc. hyg.*, 1921, **9**, 381—387).—The digested nitrogen is equal to the dietary nitrogen less the nitrogen of fæces, brushings, hair, etc. In cattle, it is assumed that for each kilo increase in weight, 180 grams of protein containing 28.8 grams of nitrogen are retained as growth-nitrogen, whilst in the case of pigs it is assumed that 19.2 grams of nitrogen are retained for each kilo increase in weight. The results of experiments on calves, adult cattle, and pigs are given. CHEMICAL ABSTRACTS.

The Relative Activities of the Secretins of the Digestive Tract. KATSUMI HARAMAKI (*Biochem. Z.*, 1922, **129**, 503—506).—Experiments on the dog show that all sections of the mucous membrane of the intestines except the jejunum are equally active as regards secretin content. The jejunum is slightly less active. H. K.

Purine Metabolism. Fate of Ingested Purines. MITSUGI KIKUCHI (*J. Biochem. [Japan]*, 1922, **1**, 83—106).—Feeding experiments were carried out for seventeen days with a diet containing only 0.00269 gram of purine-nitrogen; these were followed by three meat periods of six days each with an intake of purine-nitrogen ranging from 0.1—0.3 gram, and finally by three periods of three days each with an intake of purine-nitrogen of 0.22, 0.44, and 0.66 gram respectively. Daily analysis showed that endogenous purine-nitrogen elimination in urine remains about 0.18 gram. Purine-nitrogen in the fæces is about 0.05 gram per day, whether the diet is rich or poor in purine; neither are purine bases in the urine markedly increased on a purine-rich diet. With increase in the intake of purine-nitrogen, its output in the urine likewise increases, but the purine-nitrogen balance shifts con-

tinually. With intakes of 0.00257 to 0.04422 gram of purine-nitrogen, there was a negative balance of -0.1794 to -0.0415 gram per day; with an intake of 0.6623 gram, the balance was $+0.1048$ gram. The amount of purine-nitrogen in urine can be calculated from the formula $Y = (E_0 + aX)(1 + bX)$, where X is the purine-nitrogen intake, Y the amount in the urine, E_0 the endogenous purine-nitrogen, a the kidney coefficient, and b the tissue coefficient. The value of b is usually 0.4—0.5, whilst that of a varies according to the diet, being greater in those living on low purine-nitrogen diets, and is especially small in gouty individuals.

CHEMICAL ABSTRACTS.

Determination of the Carbohydrate Assimilative Power of Man. KOZO SAKAGUCHI, OSAMU ASAKAWA, and TOSHITANE MATSUYAMA (*J. Biochem. [Japan]*, 1922, **1**, 139—149).—Samples of blood are taken immediately before a test-meal is eaten, and then every half-hour for two hours. Alimentary hyperglycæmia does not exceed 0.14% and the sugar level has returned to the original in one to one and a half hours in normal persons. When the blood sugar rises to 0.15% and hyperglycæmia lasts for two hours, the assimilative power for carbohydrate is impaired.

CHEMICAL ABSTRACTS.

Nutritive Value of Fats and Lipoids. I. KATSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1922, **43**, 201—242).—The results are summarised as follows: The lipoids, such as cholesterol, lecithin, kephalin, and protagon, or triglycerides have no action like that of fat-soluble vitamin-*A*; the former have also no action like water-soluble vitamin-*B*. The lipoids have not only a bad effect on the nutrition of animals, but also a tendency to prevent growth: cholesterol has the worst effect, preventing the growth of young animals and diminishing the resistance to disease. The physiological action of fat-soluble vitamin-*A* stands in close relation to the metabolism of fats. The greater the molecular weight of a fat, the more fat-soluble vitamin-*A* is needed. When the quantity of fat is increased, the quantity of fat-soluble-*A* has to be increased to obtain good nutritive value. Similarly, vegetable fat needs much fat-soluble-*A*, and fats containing large quantities of sterols have always poor nutritive values in spite of the quantity of vitamin. When triglycerides of different fatty acids are given to animals with food poor in fat-soluble-*A*, the physiological value of each fat is different. The difference is related to the molecular weights of the fats and is not to be attributed to their relative fusibilities. The nutritive value of fats derived from non-volatile acids decreases with increase in molecular weight, whilst with fats derived from volatile acids the reverse is the case. In general, the nutritive value of fats decreases with diminution of the saponification value; that of fats having a large Reichert-Meissl value is not always bad. When the saponification value is small, the presence of "iodine value" in a fat increases the nutritive value.

K. K.

Phosphatides of Fish Sperm. MINORU SANO (*J. Biochem. [Japan]*, 1922, **1**, 1—16).—Porgy, salmon, and cod sperm were

extracted successively with acetone, ethyl ether, and hot ethyl alcohol, the extracted substances dissolved in chloroform, washed repeatedly with 1% sodium chloride solution, the residue after removal of the chloroform taken up with ether and poured into acetone. The phosphatides thus obtained were free from nitrogenous impurities. The acetone extract contained cholesterol and cholesterol esters; the combined cholesterol formed 7.3% (porgy), 8% (salmon), 4.1% (cod) of the total cholesterol. Lecithin also was present. The fraction insoluble in acetone was chiefly lecithin; one-twentieth to one-thirtieth of the total residue not dissolved by hot ethyl alcohol was probably kephalin and perhaps also sphingomyelin. The portion of the ether extract insoluble in acetone appeared to be curin. The alcohol extract contained (1) cholesterol (80% uncombined) and phosphatides of unknown composition, soluble in cold alcohol and acetone (2) lecithin (from cod) or a mixture of lecithin and kephalin (from salmon), soluble in cold alcohol, but not in acetone. The substance precipitated from the alcoholic extract by cooling consists mainly of cerebroside; sphingomyelin could also be identified. From 55 to 65% of the total lipid content of fish sperm is phosphatides, 15 to 18% cholesterol, 20 to 30% fats, and 1 to 2% cerebroside. CHEMICAL ABSTRACTS.

Constitution of the Ovarian Egg of the Carp (*Cyprinus carpio*). E. FAURÉ-FREMIET and (MLLE) H. GARRAULT (*Compt. rend.*, 1922, **174**, 1495—1498).—The ovaries of the carp taken two months before spawning had the following composition: water 66.3%, protein 25.7%, fat 6.2%, cholesterol 0.45%, carbohydrates 0.0%, ash 2.0%. The hyaline globules are constituted by phosphoproteins, and the "ichtidine" by a mixture of a vitellin and a lecithin. The ether extract contains phosphatides 12.33%, glycerides 6.08%, cholesterol 1.34%, unsaponifiable matter 0.8%. W. G.

Fatty Matter in "Herring Roe." KATSUMI TAKAHASHI (*J. Chem. Soc. Japan*, 1922, **43**, 257—268).—Analysis of "*Kazunoko*," herring roe, gave 8.32% water and 91.68% dried substance; the latter contained total nitrogen 11.22%, fatty matter 14.22%, crude ash 6.03%, and total phosphorus 0.54%. Fat-soluble vitamin-A was present. The fatty matter contained lecithin 48.95%, kephalin 5.62%, cholesterol 7.59%, and oil 37.84%. The oil yielded 24.67% of saturated acids (palmitic and stearic) and 75.13% of unsaturated acids (oleic and other higher acids). The lecithin and kephalin agree in properties and composition with those of the hen's egg. K. K.

Constitution of the Egg of the Trout (*Trutta fario*). E. FAURÉ-FREMIET and (MLLE) H. GARRAULT (*Compt. rend.*, 1922, **174**, 1375—1377).—Ripe trout's eggs at the time of laying contain water 58.5%, protein 29.81%, ether extract 9.16% sugars 0.34%, and ash 1.25%. The vitellin, ichtulin, was isolated and found to contain nitrogen 14.28%, phosphorus 0.57%, and ash 2.17%. The ether extract contained glycerides 10%, phosphatides 8.2%,

at least, and cholesterol 1.37%. The glycerides on hydrolysis yielded oleic and myristic acids. There was a small amount of a reducing sugar, but glycogen could not be detected. W. G.

Optical Properties of Sphingomyelin. MINORU SANO (*J. Biochem. [Japan]*, 1922, **1**, 17—20).—Sphingomyelin, prepared from cat's brain, has m. p. 196—198° and contains 3.78% of phosphorus. Its solution in pyridine shows changes in rotatory power with fall of temperature. CHEMICAL ABSTRACTS.

The Liberation of Phosphoric Acid by the Retina in the Presence of Light. HERMANN LANGE and MAX SIMON (*Z. physiol. Chem.*, 1922, **120**, 1—29).—The isolated retina of the frog or carp liberates more phosphoric acid in the presence of light than in the dark. In the case of retinae containing pigment epithelium, the liberation of phosphoric acid ceases more quickly when the illumination is stopped than in the case of the isolated neuro-epithelium. When the illumination is renewed the retina with the pigment epithelium shows an increase in the liberation of phosphoric acid. This is not the case when isolated neuro-epithelium is employed. The liberation of phosphoric acid by the isolated pigment epithelium is not influenced by light, and it is found that it contains only small quantities of organic and inorganic phosphorus. It is assumed that the action of the light degrades an organic phosphorus-containing compound with the formation of free phosphoric acid. The latter raises the permeability of the limiting membrane of the retinal epithelium. It is shown that the retina contains a substance which at 45° liberates phosphoric acid rapidly in the presence of sodium hydrogen carbonate. This acidogen which is the source of the phosphoric acid formed by the action of light is not considered to be identical with lactacidogen of transversely striated muscle. S. S. Z.

Oil from the Heads of Sea Animals of the Family *Delphinidæ*. SHŪICHI NAKATOGAWA and SHŪMEI KOBAYASHI (*J. Chem. Ind. Japan*, 1922, **25**, 158—168).—The authors have determined the specific gravities, solidifying points, refractive indices, acid, saponification, iodine, Hehner, and Reichert-Wollny values and percentages of unsaponifiable matters (and iodine value of the latter) of oils from the jaw, head, and interior of head of six sea animals belonging to the family *Delphinidæ*. [See *J. Soc. Chem. Ind.*, 1922, July.] K. K.

Anticoagulating Substances in the Mucous Membrane of the Uterus. JESSIE L. KING (*Amer. J. Physiol.*, 1921, **57**, 444—453).—Pressure juice from the mucous membrane of the non-pregnant uterus of the pig frequently yields antithrombin. The pregnant uterus seldom yields any. Heparin (Howell and Holt, *Amer. J. Physiol.*, 1918, **47**, 328) appears to be present sometimes in both the pregnant and non-pregnant pig's uterus, but neither antithrombin nor heparin is obtained with regularity and their presence may be masked by an excess of thromboplastic substance. The presence of fibrinogen, thrombin, and antithrombin

was not demonstrated in menstrual blood. There is reason to believe that it clots as normal blood as it passes the uterine mucosa and that the discharge consists of serum and small particles of clot. There is some evidence that the thrombin of the serum has combined with antithrombin forming metathrombin.

CHEMICAL ABSTRACTS.

The Glycogen of the Embryonic Liver. The Factor determining its Formation. MAX ARON (*Bull. Soc. Chim. Biol.*, 1922, **4**, 209—222).—In mammals, the glycogenic function of the liver commences at a period of the foetal life which is constant for the same species, and, in each case investigated, was found to coincide with the appearance of the islets of Langerhans in the pancreas. E. S.

Action of Hydrochloric Acid on the Fat Exchange in the Surviving Liver. U. LOMBROSO (*Arch. int. physiol.*, 1921, **18**, 484—494).—When hydrochloric acid (0.5—1.0%) is given either by the mouth or directly into the duodenum of a fasting dog, and the liver is then isolated and perfused it is found that this organ can destroy fats to a degree equal to or greater than that exhibited by the liver taken from animals during the period of digestion. When the same procedure is carried out on a depancreatized dog no noticeable fat destruction is obtained. These results are interpreted as signifying that the modification of the functional activity of the liver in the fat exchange is not due to an absorption of special products of digestion, but to hydrochloric acid in the duodenum. The pancreas is a necessary factor. CHEMICAL ABSTRACTS.

The Retention and Distribution of Amino-acids with Especial Reference to the Urea Formation. OTTO FOLIN and HILDING BERGLUND (*J. Biol. Chem.*, 1922, **51**, 395—418).—Following a protein meal, the rise in the amino-acid content of the blood precedes that of the urea. The production of urea is not, therefore, a special function of the liver (cf. Van Slyke and Meyer, A., 1914, i, 104). It follows, also, that the excretion of amino-acids is not a test for liver function, although, since the liver is capable of absorbing large quantities of amino-acids, it may serve in cases of cirrhosis as an indication of the extent to which the liver has disappeared. E. S.

A Basic Peptone-like Substance in the Thymus. K. FELIX (*Z. physiol. Chem.*, 1922, **120**, 91—93).—The basic peptone-like substance previously described by the author (this vol., i, 295) gave the following nitrogen distribution according to Kossel and Kutscher's method: total nitrogen in the hydrolysed substance 0.927 gram, arginine nitrogen 0.579 gram, monoamino-acid nitrogen 0.289 gram. No histidine or lysine could be established. S. S. Z.

Animal Hides as Amphoteric and Colloidal Protein. Theory of Dyeing, Tanning, Disinfection, and Preservation of Leather and the Physiological Action of Tanning Material. M. A. RAKUSIN (*Koll. Chem. Beihefte*, 1922, **15**, 103—184).—A paper which is mainly theoretical and in which the author dis-

cusses (1) the theory of the dyeing of animal hides, (2) the tanning of animal hides and gelatin by tannin, (3) the theory of tanning by formaldehyde, aldoses, phenols, picric acid, naphthols, quinone, and "neradol," alum, aluminium, iron, and chromium salts. The part played by water and acid in tanning is discussed and the disinfection and conservation of leather in connexion with the physiological properties of tanning materials are considered. The literature of the subject is considered in connexion with all the above-named points.

J. F. S.

Urea Content of Cow's Milk. Estimation of Urea. YOSHIO MORIMOTO (*J. Biochem. [Japan]*, 1922, **1**, 69—81).—A fairly permanent urease preparation is obtained when 1 gram of finely ground jack-bean is shaken for three hours with a mixture of glycerol and water (8:2) at 40°, 6—7 c.c. of 0.1N-hydrochloric acid are added, the mixture is shaken for one hour, and filtered through paper pulp. Three to five c.c. of urine diluted with 50 c.c. of water, 3 c.c. of urease preparation, and 1 c.c. of indicator (3% calcium caseinate) are incubated for three hours at 38° in a flask closed with a caoutchouc stopper provided with a stoppered funnel, a measured quantity (usually 40 c.c.) of 0.1N-hydrochloric acid is added, and after gentle shaking the excess of acid is titrated with 0.02N-sodium hydroxide solution. Precipitation of casein serves as indicator of the end-point. For the estimation of urea in milk, 10 c.c. are diluted with 40 c.c. of water, 3 c.c. of urease preparation added, and the above procedure carried out. Cow's milk contains 0.025—0.03 gram of urea per 100 c.c., but for a few weeks following calving there is an increase up to a maximum of 0.075 gram, with a rapid fall to normal. Goat's milk contains 0.08 gram of urea per 100 c.c.

CHEMICAL ABSTRACTS.

The Synovial Fluid. F. MALMÉJAC (*Bull. Soc. Chim. Biol.*, 1922, **4**, 190—191).—Results are given of analyses of two different specimens of synovial fluid. Both contained an albumin and an alkali-albumin.

E. S.

Theobromine Excretion and Theobromine Diuresis. LUDWIG GÜNZBERG (*Biochem. Z.*, 1922, **129**, 549—562).—For the estimation of theobromine, the urine is evaporated to dryness with gypsum, extracted with chloroform, and the theobromine removed by precipitation in weakly ammoniacal solution by addition of excess of silver nitrate. The excess of silver is estimated by Volhard's process. Using this method for following the excretion of theobromine in man, a characteristic curve is obtained, showing rapid rise to a maximum after two to three hours and moderately rapid fall. Persons inured to caffeine do not respond so easily to theobromine.

H. K.

Caffeine Excretion in Urine after Tea and Coffee Drinking in Man. KWANICHIRO OKUSHIMA (*Biochem. Z.*, 1922, **129**, 563—569).—The excretion of caffeine after tea and coffee drinking has been followed by Friedberg's method (this vol., i, 88). There is no difference in the excretion after tea or coffee. In the first hour

very little is excreted, more in the second, and most in the third and fourth hours.

H. K.

Composition of the Urine of Whales. S. SCHMIDT-NIELSEN and J. HOLMSEN (*Arch. Int. Physiol.*, 1921, **18**, 128—132).—The urine of five whales was examined and the amounts of the following constituents are tabulated: total nitrogen, urea, uric acid, ammonia, creatinine, protein, ash; potassium, sodium, calcium, and magnesium oxides, chlorine, phosphoric oxide, total sulphur, sulphate, and ethereal sulphates. A relatively large amount of proteinogenous material, partly mucin, was found. Sugar, acetone, and oxalic acid were not found, whilst indican was present. Urobilin tests were positive.

CHEMICAL ABSTRACTS.

Chronic Nephritis with an Unusual Degree of Nitrogen Retention. E. WEISS and V. C. GARNER (*J. Lab. Clin. Med.*, 1922, **7**, 229—232).—The serum of a patient with chronic nephritis had a non-protein nitrogen content of 401 mg. per 100 c.c. twelve hours before death. The urea nitrogen was 304 mg. and the creatinine 13 mg. At an earlier stage when the urea nitrogen of the blood was 246 mg., that of the spinal fluid was 252 mg. At necropsy the following values for tissues and body fluids were found: pericardial effusion 374 mg., muscle 335 mg., liver 352 mg.

CHEMICAL ABSTRACTS.

The Introduction of the Iodine Ion by Electrolysis in a Human Being, and its Elimination by the Urine. GEORGES BOURGUIGNON and CONDUCHÉ (*Compt. rend.*, 1922, **174**, 1437—1440).—Of the iodine introduced into the human system by electrolysis 70—80% is recovered in the urine. During the course of a series of administrations the elimination increases at first for about two days and then remains steady until the administrations are stopped, when it slowly falls and ceases after three or four days. The iodine is better incorporated into the system when introduced electrolytically than when given by the mouth.

W. G.

Toxicity of Neoarsphenamine [Neosalvarsan]. MERRILL C. HART and WILBUR B. PAYNE (*J. Amer. Chem. Soc.*, 1922, **44**, 1150—1160).—The toxicity of commercial samples of neosalvarsan was found to range from 200 to 360 mg. per kilo of body weight for rats. In making such tests, the variability of the test rats is of importance, as it was found that, in some cases, 40—100 mg. difference per kilo was obtained by the same test made on different animals. An apparatus is described for preparing standard solutions of neosalvarsan, and it is suggested that test rats should tolerate doses of 320 mg. per kilo in the form of such a standard solution.

The toxicity of the salvarsan is shown to have a negligible effect on the toxicity of the neosalvarsan prepared from it. The influence of solvents, dilution, time, and temperature on the toxicity of the product as well as the introduction of the methylenesulphinate group and the sulphur distribution have been examined. A curve is given showing the lethal activity of a freshly prepared

solution of neosalvarsan. The introduction of a methylene-sulphinic acid group in the salvarsan increases the tolerated dose of the material from 110 to 320 mg. per kilo (20% of arsenic), but the introduction of the second group was complicated by side reactions giving a higher toxicity. W. G.

Chemotherapy of Antimony. Comparison of the Antimonyl Tartrates with the Organic Compounds of Antimony.

R. G. FARGHER and WM. H. GRAY (*J. Pharm. Expt. Ther.*, 1921, **18**, 341—360).—The following salts of antimonyl tartaric acid are described: *barium* ($3\text{H}_2\text{O}$), hexagonal plates or flattened prisms; *ammonium* ($1\cdot5\text{H}_2\text{O}$), large flattened prisms; *lithium* ($2\cdot5\text{H}_2\text{O}$), glistening octahedra; *ethylenediamine* (H_2O), flattened prisms, does not melt at 300° ; *butylamine* ($0\cdot75\text{H}_2\text{O}$), hexagonal prisms, m. p. 40° , anhydrous m. p. 155° ; *glyoxaline* ($2\text{H}_2\text{O}$), flattened prisms, does not melt at 300° ; *aniline* (H_2O), elongated, rhombic prisms; *p-phenetidine* (H_2O), felted mass of needles, m. p. 148° , anhydrous m. p. 245° ; *quinine* (H_2O), slender, glistening needles; *quinidine* ($4\text{H}_2\text{O}$), slender, glistening needles; *cinchonine* ($0\cdot5\text{H}_2\text{O}$), rectangular plates; *cinchonidine* ($2\cdot5\text{H}_2\text{O}$), large, rectangular plates, m. p. 192° ; *hydroquinine* ($5\text{H}_2\text{O}$). The solubility, viscosity, and surface tension of the solution and the minimum lethal dose per kilo of body weight were determined for each salt.

CHEMICAL ABSTRACTS.

The Action of Different Groups of Local Anæsthetics.

KONRAD FROMHERZ (*Arch. expt. Path. Pharm.*, 1922, **93**, 34—91).—The anæsthetic effects of cocaine, novocaine, various mixed carbonic acid esters, and a substituted ester of β -hydroxybutyric acid were contrasted when the drugs were applied to nerve fibres and directly to nerve-endings (as in the cornea). From the results it was concluded that the group of substances which includes novocaine and the carbonic acid esters, which are easily diffusible, and readily broken down in the body to non-toxic substances, act by means of the nerve-fibres; whereas cocaine and the hydroxybutyric acid ester, which are indeed more toxic but are less readily absorbed, act directly on the nerve-endings and are to be characterised pharmacologically as superficial anæsthetics. C. R. H.

Caffeine Concentration of the Blood and Urine of Rabbits after Parenteral Administration.

L. FARMER LOEB (*Biochem. Z.*, 1922, **129**, 570—575).—Intravenously injected caffeine disappears from the rabbit's blood-stream for the most part in a few minutes, the remainder being recognisable for a considerable time during which there is caffeine in the urine and diuresis. H. K.

Chemistry of Vegetable Physiology and Agriculture.

The Attack of Minerals by Bacteria. Oxidation of Blende. ANDRÉ HELBRONNER and W. RUDOLFS (*Compt. rend.*, 1922, **174**, 1378—1380).—Certain bacteria have been found capable of converting blende into zinc sulphate, and the zinc rendered soluble in this manner does not prevent the further action of the bacteria. The oxidation is favoured by the presence of sulphur. These bacteria in the presence of sulphur are capable of producing sufficient sulphuric acid to dissolve the natural silicates and carbonates of zinc. In minerals containing both zinc and lead sulphides, the zinc is converted into soluble sulphate to the exclusion of the lead, and hence this furnishes a means of separating these two metals.

W. G.

Physical Chemistry of Alexin-fixation Reaction. JULIUS KISS (*Biochem. Z.*, 1922, **129**, 487—502).—The adsorption formula is obeyed by the various forms of alexin fixation, both specific and non-specific.

H. K.

Micro-organisms Concerned in the Oxidation of Sulphur in the Soil. III. Media used for the Isolation of Sulphur Bacteria from the Soil. SELMAN A. WAKSMAN (*Soil Sci.*, 1922, **13**, 329—336).—The literature concerning the various sulphur-oxidising soil bacteria is reviewed. A classification of the organisms on the basis of their physiological and morphological characteristics is preferred to that adopted by Omelianski. The various media used in the study of the different types of bacteria are detailed.

A. G. P.

***Saccharomyces Marxianus* and Top Fermentation Yeast *R*.** H. VON EULER and K. JOSEPHSON (*Z. physiol. Chem.*, 1922, **120**, 42—60).—*Saccharomyces Marxianus* failed to ferment maltose even on the addition of an excess of co-enzyme. It also does not ferment this sugar at a higher temperature, namely, 40°. Its fermenting capacity is diminished on drying, and increases again as the cells imbibe. It ferments sucrose and dextrose with the same velocity. The development of the yeast in dextrose and in maltose solutions is of approximately the same order and follows the ordinary exponential law. Its inverting capacity is about one hundredth of that of culture yeasts. In the case of the top fermentation yeast *R* both treatment with alcohol and drying diminish its activity. The inverting capacity of yeast *R* is greater than that of the top fermentation yeast *SB*.

S. S. Z.

The Energy Yield in the Growth of *Aspergillus niger*. ÉMILE E. TERROINE and RENÉ WURMSER (*Compt. rend.*, 1922, **174**, 1435—1437).—The energy yield in the growth of *Aspergillus niger*, after making allowance for the maintenance requirements, is 66—70% of that of the dextrose consumed.

W. G.

Formation of Oxalic Acid and Ammonia in Cultures of *Aspergillus niger* on Peptone. WL. BUTKEWITSCH (*Biochem. Z.*, 1922, **129**, 445—454).—The proportion of ammonia and oxalic acid formed from cultures of *Aspergillus niger* on peptone corresponds with ammonium oxalate with about 10% excess of ammonia. Of the ammonia formed over a period of ten days, 90% appeared in the first ten days during the vigorous growth of the mould.

H. K.

Utilisation of Peptone as Source of Carbon by *Citromyces* Species. WL. BUTKEWITSCH (*Biochem. Z.*, 1922, **129**, 455—463).—*Citromyces glaber* and *C. citricus* grown on peptone media produce ammonia and oxalic acid (not citric acid), the proportion of ammonia being 12 to 20% greater than that required for ammonium oxalate. As in the case of *Aspergillus niger* (previous abstract), the major portion of the ammonia is produced in the first period of growth and the ratio of the yield of mould to ammonia nitrogen falls off with the age of the culture. H. K.

Formation and Accumulation of Oxalic Acid in *Citromyces* Cultures on Salts of Organic Acids. WL. BUTKEWITSCH (*Biochem. Z.*, 1922, **129**, 464—476).—Salts of organic acids are utilised by species of *Citromyces* with production of oxalic acid, the sodium salts being more conducive to growth than the ammonium salt. *Aspergillus niger* converts tartaric acid rapidly into oxalic acid; *Citromyces* are unable to do this, but can do so on salts of citric, succinic, and quinic acids with production of considerable quantities of oxalic acid.

H. K.

Action of Selenium, Sulphur, and Tellurium Salts on Plants. BOŽO TURINA (*Biochem. Z.*, 1922, **129**, 507—533).—The author has examined the action of selenites, selenates, sulphites, sulphates, tellurites, and tellurates on the germination of plants and on the mature plant. From the deposition of selenium and tellurium by reduction in the tissues, it is concluded that neither selenium nor tellurium salts enter the system in appreciable quantities by way of the root hairs, but that the root-cap plays the important rôle of point of entry and filtration for nutritive salts.

H. K.

Vegetation in Media Poor in Oxygen. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1922, **174**, 1387—1392).—Seeds are not the only organs of a plant which can live for a long time after they have been separated from the plant which produces them. In certain species leaves are capable of preserving their vitality in the absence of air for a relatively long time, which may exceed that required by annual plants to pass through their entire cycle of evolution. It has been shown that small seeds immersed in water may germinate and use up their reserves simply on the small amount of oxygen which aerated water contains.

W. G.

Clay as an Ampholyte. OLOF ARRHENIUS (*J. Amer. Chem. Soc.*, 1922, **44**, 521—524).—It is shown that clays of different origin

and different reaction have the same isoelectric point and the curve obtained by plotting the rate of settling against the hydrogen-ion concentration has the same course as that of gelatin. The clay acts as an amphoteric electrolyte and can therefore combine with either acid or base. This is also shown by the buffer action of clays. J. F. S.

The Effect of Drying Soils on the Water-soluble Constituents. A. F. GUSTAFSON (*Soil Sci.*, 1922, **13**, 173—213).— $\frac{1}{2}$ Comparison is made of the water extracts of a number of soils dried in air, in an oven, and in an autoclave. In general, drying increased the amount of water-soluble material in the soils, but heating above 100° caused a loss in nitrates. Storage of soils at the ordinary temperature for nine weeks had little effect on the quantity of soluble constituents provided the moisture content was maintained, but kept below saturation point. In view of the results obtained, it is noted that in pot culture work it is highly important that soils should be kept under strictly comparable conditions of moisture, temperature, and aeration. A. G. P.

Relation of Hydrogen-ion Concentration in Soils to their "Lime Requirement." HARLAN W. JOHNSON (*Soil Sci.*, 1922, **13**, 7—22).—In the great majority of soils there appears to be no relation between the lime requirement as estimated by the Veitch method (A., 1903, ii, 400) and the hydrogen-ion concentration; the Truog method (A., 1916, ii, 404), however, yields results which are a combination of the Veitch lime requirement and the hydrogen-ion concentration. In soils of similar type, there is a relation between the apparent quantity of acids and the strength of the acids. Acidity in mineral soils appears to be due to weathering and leaching rather than to accumulation of organic acids, and clay particles and organic substances act as "buffers" to lower the hydrogen-ion concentration. W. P. S.

Origin of Soil Colloids. MILTON WHITNEY (*Science*, 1921, **54**, 653—656).—Microscopical examination during the mechanical analysis of soil shows that the clay particles range in diameter from 0.005 to 0.0001 mm. It is assumed that towards the lower limit of size, the particles contain relatively few molecules, and that the bombardment of the water molecules in which the particle is immersed causes disintegration. The atoms of calcium, magnesium, potassium, and sodium in the molecule of the silicate would go for the most part into true solution, whilst the atoms of silicon, aluminium, and iron would go chiefly into colloidal solution, forming the basis of the colloidal matter or ultra clay of the soil. The only known means of changing the colloidal nature of the absorptive soil colloids is to heat the material at 1000° in order to secure complete dehydration. A. A. E.

Organic Chemistry.

Catalytic Transformation of Vegetable and Animal Oils into Petrol. ALPHONSE MAILHE (*Ann. Chim.*, 1922, [ix], 17, 304—332).—A more detailed account of work already published (*A.*, 1921, i, 706, 841; this vol., i, 424). W. G.

The Catalytic Oxidation of Saturated Paraffin Hydrocarbons and Fatty Acids. ARTHUR HENRY SALWAY and PERCY NOEL WILLIAMS (*T.*, 1922, 121, 1343—1348).

Densities and Refractive Indices at 15° of Mixtures of Water, Alcohol, and Ether. A. SANFOURCHE and A. M. BOUTIN (*Bull. Soc. chim.*, 1922, [iv], 31, 546—551).—The densities and refractive indices at 15° of a large number of mixtures of water, ethyl alcohol, and ethylether in varying proportions are tabulated, and the results are also shown in triangular diagrams. W. G.

Catalysis. II. Dehydration and Addition Reactions of Ethyl Alcohol: the Formation of Acetal and Mercaptans. FRANÇOIS A. GILFILLAN (*J. Amer. Chem. Soc.*, 1922, 44, 1323—1333; cf. *A.*, 1921, i, 806).—A comparison of the activity of the oxides of silicon, thorium, titanium, and tungsten in inducing certain catalytic dehydration and esterification reactions with ethyl alcohol vapour.

Ethyl alcohol vapour, alone or in the presence of carbon dioxide, is not decomposed when passed over pumice even at 500°. Thorium oxide is not exclusively a dehydrating catalyst, as, under certain conditions, a considerable amount of acetaldehyde is produced by dehydrogenation. In the presence of carbon dioxide, a quantity of acetal is obtained from the alcohol. The oxide is inactivated for dehydration of the alcohol if it is strongly calcined or heated for a long time at a lower temperature before use. Up to about 340°, the blue oxide of tungsten is a more effective dehydrating agent for ethyl alcohol than is thorium oxide, but above this temperature the two oxides are practically of equal efficiency. Titanium oxide has no dehydrating action up to 355°. In no case was any ether produced from the alcohol.

In the presence of any of the three metallic oxides as catalysts at 300—400° a mixture of absolute alcohol and carbon disulphide produced considerable quantities of ethyl mercaptan, titanium oxide being the most active catalyst for this reaction. At the same time, small amounts of unidentified liquids with high boiling points were obtained.

Pure, dry carbon disulphide, when vaporised over pumice or the

blue oxide of tungsten, was not decomposed at temperatures up to 400°, but in the presence of a trace of moisture hydrogen sulphide was obtained.

W. G.

The Preparation of Dialkylvinylcarbinols. R. LOCQUIN and SUNG WOUSENG (*Compt. rend.*, 1922, **174**, 1551—1553).—Dialkyl-ethinylcarbinols of the type $\text{HO}\cdot\text{CRR}'\cdot\text{C}\equiv\text{CH}$ (this vol., i, 617), when hydrogenated in the presence of reduced nickel under controlled conditions, give dialkylvinylcarbinols, $\text{HO}\cdot\text{CRR}'\cdot\text{CH}\cdot\text{CH}_2$, which have a great tendency to retain water, with which they form more or less stable hydrates. These new carbinols are easily dehydrated, giving hydrocarbons, and they react with magnesium methyl iodide, giving a theoretical evolution of methane. They are not converted into esters under normal conditions, but they give crystalline allophanates. The compounds described are, *methylisohexylvinylcarbinol*, b. p. 89—91°/15 mm.; *dipropylvinylcarbinol*, b. p. 75—76°/12 mm., and its *allophanate*, m. p. 112°, and *methyl-ψ-butylvinylcarbinol*, b. p. 146—147°, d_4^{20} 0.8576, n_D^{20} 1.4432, and its *allophanate*, m. p. 167—168° (decomp.).

W. G.

Δ^α-Butene-γ-ol. [**α-Methylallyl Alcohol**]. J. BAUDRENGHIEN (*Bull. Soc. chim. Belg.*, 1922, **31**, 160—170; cf. Wohl and Losanitsch, A., 1908, i, 934).—If this alcohol is prepared from distilled acetaldehyde which has been stabilised with quinol (Moreu, Dufraisse, Robin, and Pougnet, A., 1920, i, 144), the yield is increased from 25% to 52%. The pure alcohol has d_4^{20} 0.8318, n_D^{20} 1.412746, n_{H_A} 1.40944, n_{H_B} 1.41848, n_s 1.42385. The measurement of viscosity of mixtures of α-methylallyl alcohol and water show that a maximum figure is reached for a mixture corresponding with the hydrate $\text{OH}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot 4\text{H}_2\text{O}$. The haloid esters are easily transformed into their isomerides so that the series of transformations $\text{OH}\cdot\text{CHMe}\cdot\text{CH}\cdot\text{CH}_2 \xrightarrow{\text{HCl}} \text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\text{Cl} \xrightarrow{\text{KOAc}} \text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OAc} \xrightarrow{\text{KOH}} \text{CHMe}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$ can be carried out; the series may be reversed, but the yields obtained are smaller. It is pointed out that this reverse series is more frequently met with in the case of these haloid esters. The following substances have been prepared: γ-chloro-Δ^α-butylene, b. p. 64°/766 mm., d_4^{20} 0.8978, n_D^{20} 1.41493; α-chloro-Δ^β-butylene, b. p. 84°/766 mm., d_4^{20} 0.9282, n_D^{20} 1.43503; α-bromo-Δ^β-butylene, b. p. 104—107°, d_4^{20} 1.333, n_D^{20} 1.47716, γ-acetyl-Δ^α-butylene, b. p. 111—112°/752 mm., d_4^{20} 0.90235, n_D^{20} 1.40386; α-acetyl-Δ^β-butylene, b. p. 132.5—133.5°/752 mm., d_4^{20} 0.91915, n_D^{20} 1.41806; α-chloro-β-bromobutane, b. p. 146—147°/755 mm., d_4^{20} 1.468, n_D^{20} 1.4800.

H. J. E.

Transformation of Tertiary Ethylenic Alcohols (Linalol Type) into Primary Ethylenic Alcohols (Geraniol Type). R. LOCQUIN and SUNG WOUSENG (*Compt. rend.*, 1922, **174**, 1711—1713).—Dialkylvinylcarbinols of the type $\text{HO}\cdot\text{CRR}'\cdot\text{CH}\cdot\text{CH}_2$ readily undergo isomerisation when heated with glacial acetic acid at 110—115° for fifteen hours, giving γγ-dialkylallyl alcohols

of the type $\text{CRR}'\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, which by controlled oxidation give the corresponding $\beta\beta$ -dialkylacraldehydes and on further oxidation the ketones, CORR' . Thus methylisohexylvinylcarbinol gives γ -methyl- γ -isohexylallyl alcohol, b. p. $110^\circ/12$ mm., yielding on oxidation β -methyl- β -isohexylacraldehyde, b. p. $95\text{--}105^\circ/12$ mm., giving a semicarbazone, m. p. 164° . Dipropylvinylcarbinol yields $\gamma\gamma$ -dipropylallyl alcohol, b. p. $99\text{--}101^\circ/12$ mm., giving an allophanate, m. p. $147\text{--}148^\circ$, and on oxidation $\beta\beta$ -dipropylacraldehyde, which gives the semicarbazone, m. p. $171\text{--}173^\circ$. Methyltert.-butylvinylcarbinol yields γ -methyl- γ -tert.-butylallyl alcohol, b. p. $84^\circ/12$ mm., and its allophanate, m. p. 77° . β -Methyl- β -tert.-butylacraldehyde, b. p. $75\text{--}78^\circ/15$ mm., gives a semicarbazone, m. p. $204\text{--}205^\circ$, and on oxidation β -methyl- β -tert.-butylacrylic acid, m. p. 85° .
W. G.

Composition of the Residue on Distillation of Crude Glycerol. ARCHIBALD RAYNER (*J. Soc. Chem. Ind.*, 1922, **41**, 224—225T).—A criticism of a paper by Lewis on the above subject (this vol., i, 419). The author considers that the organic impurities in glycerol residues generally amount to 40% of the inorganic salts, and not to only 7% as stated, and that no polyglycerols are present in commercial crude glycerol, even when made by the autoclave process. The composition of the residues cannot be estimated in terms of glycerol and diglycerol from determinations of their hydroxyl value, as not only are other hydroxy-compounds present, but some of the polymerisation products are of the glycide type with low hydroxyl values, or possibly no hydroxyl value at all. Of this class of compounds the glycides of glycerol, diglycerol, and triglycerol are known. They are liquids of low viscosity and lower boiling points than the parent glycerols. Attempted polymerisation of glycerol by 0.05% of iodine failed to give an 85% yield as stated, very little polymerisation at all being obtained under the conditions described. G. F. M.

Physico-chemical Properties of Phospholipin. I. Precipitation of Lecithin Hydrosol by Electrolytes. SAMURO KAKIUCHI. (*J. Biochem. [Japan]*, 1922, **1**, 165—174).—Lecithin particles have a negative charge in aqueous solution. Addition of salts with univalent kations does not cause precipitation, but salts with bi- or ter-valent kations cause precipitation within a certain range of their concentration. The range of precipitation concentrations is broad in the former case, but narrow in the latter case, and in the former a greater concentration is required. Contrary to Hardy and Schulze's law, the ion of an electrolyte of similar charge to the colloid has an effect on the precipitation of the colloid, this becoming more marked when the valency of the similarly charged ion becomes higher. Further, the validity of antagonistic action between uni- and bi-valent kations is questioned; it is maintained that the antagonism is between anions and kations.

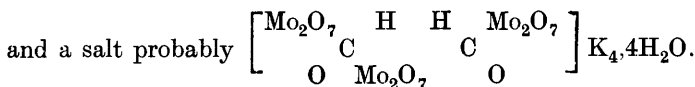
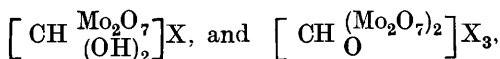
CHEMICAL ABSTRACTS.

Triethylene Tri- and Tetra-sulphides. II. SIR PRAFULLA CHANDRA RÂY (T., 1922, **121**, 1279—1283).

Preparation of Anhydrous Formic Acid. M. C. BOSWELL and H. E. CORMAN (*Can. Chem. Met.*, 1922, **6**, 63—65).—When molecular proportions of sodium formate and 100% sulphuric acid are mixed, allowed to remain for seventeen hours, and then distilled on a water-bath under 15—20 mm. pressure, an 85% yield of 95% formic acid is obtained, whereas by distillation at atmospheric pressure only a 25% yield of 90% formic acid is obtained. Distillation of a mixture of sodium formate and sodium hydrogen sulphate (D.R.-P. 209418) gives a 56% yield of 82.7% formic acid. Fractional crystallisation, in a freezing mixture, of 88% acid yields crystals of 95% acid, whilst from 97% acid, crystals of 99.6% purity can be obtained.

CHEMICAL ABSTRACTS.

Researches on the Photochemically Sensitive Compounds of Molybdic and Formic Acids. W. F. JAKÓB (*Roczniki Chemji*, 1921, **1**, 411—423).—The salts of molybdeno-orthoformic acids are prepared and investigated. From six possible types of acids, the author succeeds in preparing only the sodium, potassium, and ammonium salts of the types:



All the salts prepared are photochemically sensitive, becoming green, yellow, or brown on exposure to light. They are obtained as crystalline precipitates from solutions of the respective molybdates, strongly acidified with formic acid. They cannot be recrystallised, as they decompose in solution.

R. T.

Catalytic Decomposition of Arachis Oil. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1922, [iv], **31**, 567—570).—When arachis oil is passed over an alumina-copper catalyst at 600° and the product freed from acids and then hydrogenated over nickel at 180—200° hydrocarbons of the methane and benzene series are obtained. Amongst the aromatic hydrocarbons, benzene, toluene, and *m*-xylene were identified.

W. G.

Lignoceric Acid and its Derivatives. PERCY BRIGL and EDGAR FUCHS (*Z. physiol. Chem.*, 1922, **119**, 280—311).—The so-called lignoceric acid, m. p. 78—91°, from beechwood tar is a mixture from which can be separated an acid, m. p. 85°, identical with tetracosic acid, $\text{CH}_3 \cdot [\text{CH}_2]_{22} \cdot \text{CO}_2\text{H}$ (*methyl* ester, m. p. 60°, *phenyl* ester, m. p. 70.5°), prepared synthetically from behenic acid (cf. Myer, Brod, and Soyka, A., 1913, i, 1151, and Brigl, A., 1916,

i, 463). The other component of crude lignoceric acid has the same empirical formula and appears to be also a normal tetracosic acid. It melts at 74° , and it is suggested that this may be a case of a peculiar kind of isomerism, due to the possibility of the carbon chain of a fatty acid existing as a right- or left-handed spiral.

Lignocerin, the wax associated with lignoceric acid, after repeated recrystallisation melts at 79° , and has the formula $C_{48}H_{96}O_2$. On hydrolysis with alcoholic potash, it gives (1) an acid identical with crude lignoceric acid, m. p. 79° , from which pure lignoceric acid, m. p. 85° , can be separated, and (2) *lignoceryl alcohol*, $C_{24}H_{50}O$, m. p. 76° (*acetate*, fine, felted needles, m. p. 57°). On fusion with potash, lignoceryl alcohol yields the above-mentioned tetracosic acid of m. p. 74° , and thus is not pure *n*-tetracosyl alcohol. To verify this, *n*-tetracosyl alcohol has been prepared by the reduction of the phenyl ester of *n*-tetracosic acid by sodium in alcohol and is found to melt at 77.5° and give an *acetate*, concentric needles, m. p. 57° , and a *benzoate*, m. p. 61.5° . In the preparation of tetracosic acid the methods previously employed are used (Brigl, *loc. cit.*) except that in the reduction of behenic acid to docosyl alcohol by sodium and alcohol the *phenyl* ester, fine needles, m. p. 66° , is used instead of an alkyl ester.

The preparation of the following waxes from the corresponding alcohols and acid chlorides (in chloroform solution in the presence of quinoline) are described; *cetyl palmitate*, m. p. 53° ; *docosyl behenate*, white, lustrous scales, m. p. 75° ; and *n*-tetracosyl *tetracosate*, m. p. 80.5° .

W. O. K.

The Actual State of the Chemistry of the Fats. ÉMILE ANDRÉ (*Bull. Soc. chim.*, 1922, [iv], **31**, 459—525).—A useful summary of the present state of knowledge of the chemistry of the fats, including an outline of analytical methods, separation and identification of glycerides, and a discussion of the constitutions of the fats.

W. G.

Erucic Acid and Erucic Anhydride. III. D. HOLDE and C. WILKE (*Z. angew. Chem.*, 1922, **35**, 289—291; cf. this vol., i, 317, 519).—A detailed account is given of the methods tried and that finally adopted for the preparation of pure erucic acid from rape oil. The fractional distillation of the esters obtained by the methylation of the oil gave a methyl erucate, b. p. $243\text{--}248^{\circ}/33\text{ mm.}$, $216\text{--}225^{\circ}/4\text{ mm.}$, from which on hydrolysis an erucic acid was obtained which, although having a sharp m. p. 34° , and the correct molecular weight of titration, showed a low iodine value, 71—72, indicating the presence of about 5% of saturated acids. Attempts to separate these by extraction of the lead salts with organic solvents such as ether, light petroleum, or chloroform failed, as the saturated acid salts also dissolved in presence of the large excess of lead erucate, nor could the iodine value of the impure acid be raised by fractional precipitation with lead or magnesium acetate of a preparation which had previously been

partly purified through the methyl ester and recrystallisation from alcohol. The pure acid with an iodine value of 75.02 was eventually obtained by recrystallising the crude acid from alcohol first at temperatures below 0° to remove liquid unsaturated acids, and then at above 0° to remove the greater part of the saturated acids, and finally fractionally precipitating this product with a saturated alcoholic solution of lithium acetate whereby the saturated acids were thrown down first. The pure acid melts at 33.5° . Erucic anhydride was prepared by heating the acid with acetic anhydride in a sealed tube at 170° for seven hours. After purification, it formed microscopic, white prisms, m. p. 46° . It is decomposed by boiling water, boiling alcohol, and cold alcoholic hydroxide solutions, but it is stable towards cold dilute hydrochloric acid and aqueous alkali hydroxides.

G. F. M.

Humoceric Acid. OSSIAN ASCHAN (*Finska Kem. samfundets Meddel.*, 1921, **30**, 37—38).—A new substance was isolated from peat and designated *humoceric acid*. It has the composition $C_{19}H_{34}O_2$, m. p. $72-73^{\circ}$, separates in colourless crystals from light petroleum and methyl alcohol, does not give the cholesterol colour reactions, and reacts instantly with Baeyer's reagent. It is not identical with lignoceric acid, $C_{24}H_{48}O_2$, m. p. 80° .

CHEMICAL ABSTRACTS.

Synthesis of α -Hydroxyisopentacosic Acid and its Bearing on the Structure of Cerebronic Acid. P. A. LEVENE and F. A. TAYLOR (*J. Biol. Chem.*, 1922, **52**, 227—240).—It has been shown that cerebronic acid is an α -hydroxypentacosic acid (Levene and Jacobs, A., 1912, i, 936) and is converted on oxidation into a tetracosic acid (Levene and West, A., 1913, i, 587) which is identical with lignoceric acid. According to Meyer, Brod, and Soyka (A., 1913, i, 1151), and to Levene and West (A., 1914, i, 1123), lignoceric acid differs from *n*-tetracosic acid, a result which indicates that cerebronic acid is not a normal fatty acid. Brigl (A., 1916, i, 463), however, from a comparison with the synthetic acid, considers that cerebronic acid is normal α -hydroxypentacosic acid. The present authors attribute this result to imperfect racemisation, with consequent incorrect melting point, of the natural acid, and advance the following further proof of the identity of tetracosic acid (from cerebronic acid) and lignoceric acid (cf. Brigl, this vol., i, 712). Tetracosic acid, obtained from cerebronic acid, and lignoceric acid, from peanut oil, were converted by the same series of reactions into α -hydroxypentacosic acid. Two series of compounds were thus obtained of which the corresponding members were found to be identical, thus establishing the identity of the first two acids and showing, therefore, that cerebronic acid does not contain a normal chain and is, consequently, α -hydroxy-lignoceropentacosic acid.

Lignoceric acid and tetracosic acid (from cerebronic acid) were converted into lignoceryl iodide. The latter, when boiled in

alcoholic solution with potassium cyanide, gave *lignoceryl cyanide*, $C_{24}H_{49}ON$, m. p. $56\cdot5^\circ$, which on hydrolysis with alcoholic sodium hydroxide yielded *isopentacosic acid*, $C_{24}H_{49}\cdot CO_2H$, m. p. $78\cdot5^\circ$. By bromination, α -*bromoisopentacosic acid*, $C_{24}H_{48}Br\cdot CO_2H$, m. p. 70° , was obtained, from which *dl-cerebronic acid*, $OH\cdot C_{24}H_{48}\cdot CO_2H$, m. p. $92\cdot5^\circ$, was produced by boiling with aqueous sodium hydroxide. *Ethyl isopentacosate*, $C_{24}H_{49}\cdot CO_2Et$, m. p. 57° , was reduced by sodium and alcohol to *isopentacosyl alcohol*, $C_{24}H_{49}\cdot CH_2\cdot OH$, m. p. 75° , and the alcohol converted into *isopentacosyl iodide*, $C_{24}H_{49}\cdot CH_2I$, m. p. $51\cdot5^\circ$, by means of iodine and red phosphorus. The latter, on reduction with zinc and hydrochloric acid, gave *isopentacosane*, $C_{25}H_{52}$, m. p. 56° .

Lignoceric acid was also converted into *isopentacosic acid* by the following reactions: α -hydroxylignoceric acid (cf. Meyer, Brod, and Soyka, *loc. cit.*) was first prepared. This was then oxidised by potassium permanganate in acetone solution to *isotricosic acid*, $C_{22}H_{45}\cdot CO_2H$, m. p. $73\cdot5^\circ$. Reduction of *ethyl isotricosate*, $C_{22}H_{45}\cdot CO_2Et$, m. p. $55\cdot5^\circ$, with sodium and alcohol gave *isotricosyl alcohol*, $C_{22}H_{45}\cdot CH_2\cdot OH$, m. p. 69° , which when heated with iodine and red phosphorus yielded *isotricosyl iodide*, $C_{22}H_{45}\cdot CH_2I$, m. p. 48° . By condensation with diethyl malonate this was converted into *diethyl isotricosylmalonate*, $C_{22}H_{45}\cdot CH_2\cdot CH(CO_2Et)_2$, m. p. $52\cdot5^\circ$, which was then hydrolysed with alcoholic sodium hydroxide to *isotricosylmalonic acid*, $C_{22}H_{45}\cdot CH_2\cdot CH(CO_2H)_2$, m. p. 111° . The latter lost carbon dioxide at 180° , yielding *isopentacosic acid* identical with that obtained above. E. S.

Action of Thionyl Chloride on α -Hydroxy-acids. E. E. BLAISE and (MLLE) MONTAGNE (*Compt. rend.*, 1922, **174**, 1553—1555; cf. this vol., i, 520).—Thionyl chloride reacts with lactic acid and with α -hydroxyisobutyric acid to give, not the chlorosulphite of the acid chloride, but a new type of compound, which the authors call anhydrosulphites of hydroxy-acids, the compound obtained

from α -hydroxyisobutyric acid having the constitution

$$\begin{array}{c} \text{CO-O} \\ | \\ \text{CMe}_2\cdot\text{O} \end{array} \text{SO.}$$

The compound from lactic acid has b. p. $72-74^\circ/19$ mm., and the compound from hydroxyisobutyric acid has b. p. $63^\circ/21$ mm. Both these compounds are decomposed at $120-125^\circ$ at atmospheric pressure, giving off sulphur dioxide and yielding polylactides which with alkalis give the corresponding hydroxy-acids. In contact with moist air, the anhydrosulphites revert to the original acid, and in the case of that from lactic acid an intermediate compound, m. p. 90° , having the constitution $SO_2H\cdot O\cdot CHMe\cdot CO_2H$ or $HO\cdot CHMe\cdot CO\cdot O\cdot SO_2H$ was isolated. With alcohols the anhydrosulphites react readily, giving the esters of the hydroxy-acids, and with arylamines they yield the amides of these acids. With phenylhydrazine, on the other hand, they give thionylphenylhydrazine and the hydroxy-acid.

In the original action of the thionyl chloride on lactic acid there is obtained, in addition to the anhydrosulphite, some *a-chloropropionylpropionyl chloride*, $\text{CHMeCl}\cdot\text{CO}_2\cdot\text{CHMe}\cdot\text{COCl}$, b. p. $100\text{--}103^\circ/19\text{ mm.}$, giving an *anilide*, m. p. $116\text{--}5^\circ$. Similarly, *a-hydroxyisobutyric acid* yields *a-chloroisobutyryloxyisobutyryl chloride*, $\text{CMe}_2\text{Cl}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{COCl}$, b. p. $99\text{--}101^\circ/17\text{ mm.}$, giving an *anilide*, m. p. 115° , and at the same time there is obtained some *a-chloroisobutyryl chloride*, b. p. $113\text{--}114^\circ$, and its *anilide*, m. p. $69\text{--}70^\circ$.
W. G.

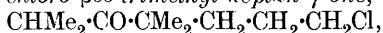
Succinic Acid. UMETARÔ SUZUKI and YOSHIHIKO MATSUYAMA (Japan Pat. 39210).—Ten grams of glutamic acid are gradually heated with 50 grams of concentrated nitric acid and 0.005 gram of vanadium oxide. When the evolution of gas has ceased, the solution is concentrated by evaporation. Succinic acid crystallises out as colourless prisms or plates, the yield being 5–6 grams. Sodium glutamate or gluten and metallic vanadium or vanadates can also be used for the purpose.
K. K.

Crystallographic – optical Properties of Calcium Fumarate and Maleate. EDGAR T. WHERRY and RAYMOND M. HANN (*J. Washington Acad. Sci.*, 1922, **12**, 288–296).—Calcium fumarate, $\text{C}_4\text{H}_2\text{O}_4\text{Ca}\cdot 2\text{H}_2\text{O}$, crystallises from water in blade-like crystals belonging to the orthorhombic system, $a:b:c = 0.3970:1:0.3772$; $d\ 1.71 \pm 0.01$. They are optically negative with extreme double refraction; the mean refractive index is 1.539. Calcium maleate, $\text{C}_4\text{H}_2\text{O}_4\text{Ca}\cdot\text{H}_2\text{O}$, forms groups of interlacing needles, orthorhombic prisms the end faces of which are not well developed; $a:b:c = 0.779:1:0.643$; $d\ 1.84 \pm 0.01$. The double refraction is negative and weaker than in the case of the fumarate; the mean value of n is 1.571. There is no simple space relation between the two salts. The molecular refractions R , calculated from the formula $R = V(n^2 - 1)/(n^2 + 1)$, where V is the molecular volume, are, for the fumarate 34.8, maleate, 30.8, the corresponding values calculated from the atomic constituents being 31.5 and 27.8. The refractivities due to structure are therefore 3.3 and 3.0, respectively, the higher value in the case of the fumarate being due to the fact that the ring system formed by the calcium atom bridging the two acid groups in the molecule is more complex in the fumarate than in the maleate.
E. H. R.

Conditions Underlying the Formation of Unsaturated and Cyclic Compounds from Halogenated Open-chain Derivatives. IV. Products Formed from Halogen Derivatives of Muconic Acid. The Constitution of Muconic Acid. JUAN PEDIGE CHARLES CHANDRASENA and CHRISTOPHER KELK INGOLD (*T.*, 1922, **121**, 1306–1319).

Synthesis of the Polyacetic Acids of Methane. VI. Methanetriacetic Acid and its Unstable Esters. CHRISTOPHER KELK INGOLD and EDWARD ARTHUR PERREN (*T.*, 1922, **121**, 1414–1420).

The Action of Trimethylene Chlorobromide on some Aliphatic Ketones. (MILLE) HÉLÈNE BILLON (*Compt. rend.*, 1922, **174**, 1708—1711).—Haller and Bauer have shown that the sodium derivatives of dialkylacetophenones react with trimethylene chlorobromide to give δ -chloro-ketones (cf. A., 1911, i, 651). This is now shown to be true of aliphatic ketones. The resulting chloro-compounds react with dimethyl- or diethyl-amine to give dimethyl-amino- and diethyl-amino-compounds respectively. The compounds described are η -chloro- $\beta\delta\delta$ -trimethylheptan- γ -one,



b.p. 120—122°/20 mm.; ϵ -dimethylamino- $\beta\delta\delta$ -trimethylheptan- α -one, b. p. 120°/22 mm.; ϵ -diethylamino- $\beta\delta\delta$ -trimethylheptan- α -one, b. p. 126—128°/20 mm.; η -chloro- $\beta\beta\delta\delta$ -tetramethylheptan- γ -one, b. p. 110—112°/12 mm.; ϵ -dimethylamino- $\beta\beta\delta\delta$ -tetramethylheptan- α -one, b. p. 126—138°/20 mm.; η -chloro- $\gamma\gamma\epsilon\epsilon$ -tetramethyl-octan- δ -one, b. p. 124°/16 mm., η -dimethylamino- $\gamma\gamma\epsilon\epsilon$ -tetramethyloctan- δ -one, b. p. 138—140°/20 mm. Under similar conditions, pinacolins does not give a chloro-compound but a ketone which is apparently

pivaloylcyclobutane, $\text{CH}_2 \begin{array}{c} \text{CH}_2 \\ \diagup \quad \diagdown \\ \text{CH}_2 \end{array} \text{CH} \cdot \text{CO} \cdot \text{CMe}_3$, b. p. 97°/17 mm.
W. G.

The Chlorohydrin of Mesityl Oxide and its Transformation into the Chlorohydrin of Tetramethylglycerol. PASTURFAU and HENRI BERNARD (*Compt. rend.*, 1922, **174**, 1555—1557).—Mesityl oxide reacts with a mixture of calcium hypochlorite and boric acid to give its chlorohydrin [α -chloro- β -hydroxyisobutyl methyl ketone), $\text{HO} \cdot \text{CMe}_2 \cdot \text{CHCl} \cdot \text{COMe}$, b. p. 81°/10 mm., and this with magnesium methyl iodide gives a compound which on decomposition with water yields tetramethylglycerol chlorohydrin (γ -chloro- $\beta\delta$ -dihydroxy- $\beta\delta$ -dimethylpentane), $\text{HO} \cdot \text{CMe}_2 \cdot \text{CHCl} \cdot \text{CMe}_2 \cdot \text{OH}$, m. p. 60°.
W. G.

2 : 3 : 6-Trimethyl Glucose. JAMES COLQUHOUN IRVINE and EDMUND LANGLEY HIRST (*T.*, 1922, **121**, 1213—1223).

The Constitution and Rotatory Powers of Mannitol and Fructose Complexes Formed in Solutions Containing Boric Acid and Sodium Hydroxide. GEORGE VAN BARNEVELD GILMOUR (*T.*, 1922, **121**, 1333—1340).

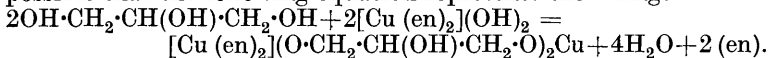
The Action of Ozone on Pure Solutions of Lactose. C. W. SCHONEBAUM (*Rec. trav. chim.*, 1922, **41**, 422—424 ; cf. *Annalen*, 1859, **110**, 86).—It has been stated that lactose is not decomposed by ozone. The author finds that this is only true of neutral and acid solutions at both ordinary temperatures and 70°. In alkaline solution of 0.1*N* concentration, 30% of the lactose is decomposed after three hours' ozonisation, whilst at 70° rapid neutralisation of the alkali takes place. This is due to the formation of formic

c c*

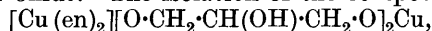
acid, the primary decomposition product. In 4*N*-alkali, carbon dioxide is formed after one hour; this and water are the final products of ozonisation. Ozone of low concentration was used. H. J. E.

The Colloidal Nature of Saccharated Iron. C. MANNICH and C. A. ROJAHN (*Ber. deut. Pharm. Ges.*, 1922, **32**, 158—166).—“Saccharated” iron contains the metal as colloidal ferric hydroxide, and is in no sense a compound of sugar and iron. It gives a colloidal solution in water in consequence of the sugar and the alkali which also must be present. That none of the sugar is chemically combined with the metal appears certain from the fact that the colloid isolated by dialysis, by ultra-filtration, or by kataphoresis contains an amount of sugar varying according to the method adopted from 16.6 to 25.5%. An average value would require 16 atoms of iron to 1 mol. of sugar, which is a remotely improbable combination. It is concluded, therefore, that the iron is present entirely as colloidal hydroxide, which absorbs a certain amount of both sugar and alkali. The solution differs from dialysed solution of iron (*Liquor Ferri Dialysatus*) in that the particles are negatively charged in the former and positively in the latter, and the addition of 4—8 drops of this to 5 c.c. of 5% solutions of saccharated iron results in complete flocculation. A similar precipitation of the iron is caused by neutralising the alkali with, for example, acetic acid or carbon dioxide; like many other colloids it is absorbed by relatively small quantities of charcoal, and a colourless filtrate may be obtained in which iron is undetectable. G. F. M.

Alkaline Copper Oxide Solutions and Copper Oxide-Ammine-Cellulose Solutions. II. WILHELM TRAUBE (*Ber.*, 1922, **55**, [B], 1899—1912).—In a previous communication (this vol., i, 115), the action between copper ethylenediamine hydroxide and glycerol has been considered to take place in accordance with the equations: $2\text{C}_2\text{H}_5\text{O}_2\cdot\text{CH}_2\cdot\text{OH} + [\text{Cu}(\text{en})_2](\text{OH})_2 \rightleftharpoons 2\text{H}_2\text{O} + [\text{Cu}(\text{en})_2](\text{O}\cdot\text{CH}_2\cdot\text{C}_2\text{H}_5\text{O}_2)_2$ and $[\text{Cu}(\text{en})_2](\text{O}\cdot\text{CH}_2\cdot\text{C}_2\text{H}_5\text{O}_2)_2 + \text{Cu}(\text{OH})_2 = [\text{Cu}(\text{en})_2][\text{O}\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{O}]_2\text{Cu} + 2\text{H}_2\text{O}$. It is also possible that the following equation represents the change:



The second possibility is now shown to be the more probable, since the reaction occurs with liberation of considerable amounts of ethylenediamine as is proved by the ability of the solution to dissolve silver oxide. The isolation of the compound



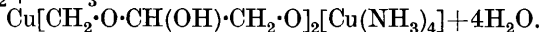
in an almost homogeneous condition is now described.

The conclusions thus drawn in the studies with glycerol can be extended to other polyhydroxy-substances, notably cellulose. The ability of copper oxide-ethylenediamine-cellulose solutions to dissolve further quantities of copper oxide depends on the liberation of ethylenediamine, and the behaviour of Schweizer's solution may

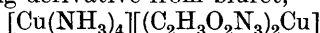
be explained similarly. The difference between the behaviour of the copper bases towards polyhydroxy-compounds and those of the metals silver, cobalt, nickel, zinc, and cadmium is accounted for, since only the former is able to form complexes in which the metallic atom is fixed directly to the hydroxy-group of the polyhydroxy-compound. An uncertainty, however, appears to exist in the case of cobalt, since, according to the literature, the precipitation of this metal from its solutions as hydroxide by means of alkali is hindered by the presence of glycerol in the same manner as is the precipitation of copper hydroxide from copper solutions; the exception is only apparent, however, since the cobalt hydroxide is present in the colloidal state (and not as the glycerate) and can be precipitated completely by barium sulphate.

Confirmation of the results obtained with copper ammine hydroxides and polyhydroxy-compounds is afforded by the behaviour of the former towards biuret. Copper ethylenediamine hydroxide and biuret give the compound $C_8H_{22}O_4N_{10}Cu_2 \cdot H_2O$, lustrous needles, m. p. 198° (decomp.), which is formed in accordance with the scheme: $2C_2H_5O_2N_3 + 2[Cu(en)_2](OH)_2 = [Cu(en)_2](C_2H_3O_2N_3)_2Cu + 4H_2O + 2(en)$.

It has been assumed that the solution of copper hydroxide in ammoniacal glycerol occurs in accordance with the equation: $2C_3H_8O_3 + 2Cu(OH)_2 + 4NH_3 =$



The corresponding derivative from biuret,



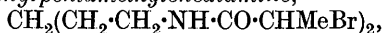
has been analysed.

H. W.

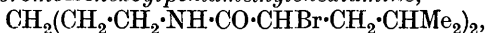
Oxycellulose. EMIL HEUSER AND FRITZ STÖCKIGT (*Cellulosechemie*, 1922, **3**, 61—74).—The formation of furfuraldehyde-yielding groups is one of the constitutional characteristics of oxycellulose. The quantity of furfuraldehyde obtained is not large. Whilst well-purified cotton yielded 0.3%, oxycellulose preparations generally yielded less than 1.0%. Higher yields of furfuraldehyde were recorded when the oxidation was carried out by chromic acid in such quantities that substantial losses of cellulose were incurred. For instance, an oxycellulose prepared by chromic acid with a yield of 66% gave 2.14% of furfuraldehyde, and, in an extreme case, 12.5% of oxycellulose was obtained having a furfuraldehyde value of 3.89%. The presence of carboxylic groups in oxycellulose has often been suggested, but definite proof is now afforded by the observation that on distillation with 12% hydrochloric acid, oxycellulose yields small quantities of carbon dioxide. The carboxyl value of oxycellulose has been estimated by Lefèvre's method for the estimation of glycuronic acid; the values obtained were generally less than 1.0%, but in the case of highly oxidised chromic acid oxycellulose values up to 1.32% were obtained. On hydrolysis with 1% sulphuric acid under pressure, oxycellulose gave a residue of hydrocellulose with low furfuralde-

hyde and carboxyl values, and a solution containing the characteristic oxidised component. This substance yielded a *barium* salt having many of the characteristic properties of barium glycuronate, but differing from that salt in its barium content. On complete hydrolysis by Willstätter's method, oxycellulose yielded a solution having a dextrose value about 10% lower than that obtained from cellulose and hydrocellulose; the residue from the digestion of oxycellulose with dilute sulphuric acid gave the normal dextrose value of hydrocellulose. Hence it is concluded that oxycellulose, prepared as a residue from the action of oxidising agents on cellulose, consists for the major part of cellulose in which there exists, either as a mixture or in combination, a small quantity of an intermediate complex, formed of a combination of cellulose with an oxidation product. This oxidation product has the characters of an aldehyde-carboxylic acid, and is probably derived either from a terminal alcoholic group of a cellobiose residue or from an aldehyde group developed by hydrolysis. J. F. B.

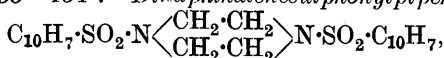
New Diamine Compounds. PETER BERGELL (*Z. physiol. Chem.*, 1922, **120**, 220—226).—The following compounds were prepared by the interaction of the respective bases and acid chlorides: *Di-α-bromopropionylpentamethylenediamine*,



crystallises in radiating needles arranged spherically, m. p. 135—136°. *Di-α-bromoisohexoylpentamethylenediamine*,



crystallises in leaflets, m. p. 127—128°. *Di-β-naphthalenesulphonylpentamethylenediamine*, $\text{CH}_2(\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{SO}_2\cdot\text{C}_{11}\text{H}_7)_2$, crystallises in lustrous leaflets, m. p. 147—149°. *β-Naphthalenesulphonylpiperidine*, $\text{C}_{10}\text{H}_7\cdot\text{SO}_2\cdot\text{N}\langle\text{CH}_2\cdot\text{CH}_2\rangle\text{CH}_2$, is a silky white precipitate, m. p. 133—134°. *Dinaphthalenesulphonylpiperazine*,



is an indistinctly microcrystalline precipitate.

S. S. Z.

Betaines. I. Theory of Betaines. PAUL P. PFEIFFER (*Ber.*, 1922, **55**, [B], 1762—1769).—It is customary to ascribe a cyclic structure to the betaines, which, however, do not obey the usual stereochemical laws of ring closure. This is particularly noticeable with the betaines of the aromatic series in which compounds derived from *p*- and *m*- as well as those derived from *o*-aminobenzoic acid are known. Since, however, the entire chemical behaviour of the betaines causes them to be regarded as intramolecular quaternary ammonium salts, it is reasonable to apply to them the recent ideas on the constitution of salts as deduced by Debye and Scherrer, and to consider that positive and negative ionic charges are located in the molecule which may be formulated,

$-\text{O}\cdot\text{OC}-\text{R}-\text{NMe}_3^+$. The sole difference in the structure of sodium chloride and betaine is that the ions are separated in the former and united by a chain of atoms in the latter. The formation of a betaine has, in principle, no connexion with ring closure; the electric polar charges attract one another, but the extent to which they actually approach one another depends on the configuration of the molecule. With para-betaines the *trans*-configuration of the molecule inhibits the approach of the groups, COO^- and NMe_3^+ , and ring closure does not occur. This is true also of the meta-compounds. With the ortho-products, on the other hand, ring closure is possible. The views thus put forward for the betaines are applicable to the amino-acids.

The crystals of amino-acids or betaines are not exactly similar to those of salts or organic compounds. It must be assumed that in them, as in ordinary organic substances, the molecular lattice structure is pronounced, but between the single molecules, in accordance with their bipolar nature, strong electrostatic forces are operative such as only occur otherwise in ionic lattices. It may therefore be stated that the amino-acids and betaines form molecular lattices with the general character of ionic lattices. An explanation is thereby afforded of the extremely high melting or decomposition points of these substances which are otherwise not related to their molecular complexity. The sparing solubility in organic media likewise receives an explanation.

Similar stereochemical difficulties arise in the elucidation of the constitution of salts of dibasic organic acids with bivalent metals. The co-ordination formulæ, for example, $\left[\overset{\text{O}}{\underset{\text{O}}{\text{C}}} - \text{R} - \overset{\text{O}}{\underset{\text{O}}{\text{C}}} \right]^{--} \text{Ca}^{++}$, are probably to be assigned to them, a normal ring not being present.

H. W.

Transformation of Alkylated Malonic Acids into α -Amino-acids. II. Syntheses of β -Phenyl- α -alanine and of α -Amino-*n*-butyric Acid. THEODOR CURTIUS and WILHELM SIEBER (*Ber.*, 1922, **55**, [B], 1543—1558; cf. Curtius and Sieber, *A.*, 1921, i, 653).—It has been shown previously that potassium hydrazido-malonate is convertible into glycine in accordance with the scheme: $\text{CO}_2\text{K}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{NH}_2 \rightarrow \text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{N}_3 \xrightarrow{-\text{N}_2} [\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{N}\cdot\text{CO}] \xrightarrow{+\text{H}_2\text{O}} \text{NH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H} + \text{CO}_2$. Since also it was found that the yield of α -alanine from methylmalonazidic acid is better than that of glycine from the lower homologue, the possibility of the peculiar applicability of the process to the more highly substituted acids has been examined. In this respect, the results are somewhat disappointing, since ethylmalonazidic acid is extensively hydrolysed by boiling water to hydrazoic acid and ethylmalonic acid whereas benzylmalonazidic acid is insoluble in water and remains unaffected. In boiling ethereal solution, ethyl- and benzylmalonazidic acids are converted into the corresponding carboxylic

anhydrides, $\text{CH}_2\text{R}\cdot\text{CH}\begin{matrix} \text{CO}\cdot\text{O} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}$ (R=Ph or Me), diketopiperazines,

$\text{CHR}\begin{matrix} \text{CO}\cdot\text{NH} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}\text{CHR}$, and complex anhydrides, $\left(\text{R}\cdot\text{CH}\begin{matrix} \text{CO} \\ | \\ \text{NH} \end{matrix}\right)_x$,

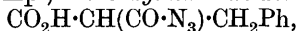
all of which are hydrolysed by concentrated hydrochloric acid under pressure with quantitative production of the hydrochlorides of the simple amino-acids.

When solutions of the azidic acids in indifferent media are boiled, explosions occasionally take place without any apparent cause, as, for example, in dilute ethereal solutions from which solid has not separated. The conversion of the acids into the corresponding urethanes is therefore effected by the addition of absolute ethyl alcohol to the dry ethereal solution and subsequent slow distillation of the ether. The urethanes are thus obtained as oily liquids which generally contain small amounts of the corresponding polymolecular anhydride, and, less frequently, of the diketopiperazine derivative. The crude product is directly converted into the amino-acid hydrochloride by treatment with hydrochloric acid in sealed tubes. The success of these methods of synthesising amino-acids depends greatly on the purity of the initial materials and the reagents.

The conditions have been established under which ethyl benzylmalonate is transformed almost quantitatively by alcoholic potassium hydroxide solution into potassium ethyl benzylmalonate. The latter is converted by anhydrous hydrazine in absolute alcoholic solution into *potassium benzylmalonhydrazidate*,



anisotropic platelets; the corresponding *acid* crystallises in small prisms, m. p. 163° , and gives the *benzylidene* derivative, $\text{CO}_2\text{H}\cdot\text{CH}(\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHPh})\cdot\text{CH}_2\text{Ph}$, rectangular, anisotropic platelets, m. p. 152° (decomp.). *Benzylmalonazidic acid*,



is a heavy, yellow liquid which could not be caused to solidify. It is converted in boiling ethereal solution into phenylalanine-*N*-carboxylic anhydride, m. p. $127\text{--}128^\circ$ (decomp.) [the constitution of which is established by the observation that it is converted by cold aniline into carbon dioxide and *phenylalanineanilide*, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}_2)\cdot\text{CO}\cdot\text{NHPh}$, small, thin, feebly anisotropic prisms, m. p. $160\text{--}161^\circ$], polymolecular phenylalanine anhydride and 2:5-diketo-3:6-dibenzylpiperazine. *Phenylalanine hydrochloride* crystallises in anisotropic prisms, m. p. $234\text{--}235^\circ$. *Benzylmalonazidic acid* decomposes in boiling chloroform with the production of somewhat ill-defined products which are convertible into phenylalanine hydrochloride.

Ethylcarbonatophenylalanine and *methylcarbonatophenylalanine* could only be obtained as liquids which could not be caused to solidify or distilled without decomposition.

Potassium ethyl ethylmalonate is transformed into *potassium*

ethyl malonhydrazidate, a very hygroscopic, crystalline mass; the *benzylidene* compound of the corresponding free acid, $\text{CHEt}(\text{CO}\cdot\text{NH}\cdot\text{N}:\text{CHPh})\cdot\text{CO}_2\text{H}$, prisms, m. p. 144° (decomp.), is described. Diazotisation of the hydrazidic acid leads to the formation of a *substance*, colourless, slender needles, m. p. $82\text{--}83^\circ$, which has not been investigated completely and *ethylmalonazidic acid*, a pale yellow liquid. Decomposition of the latter in boiling ethereal solution leads to the production of ethylmalonic acid and the

carboxylic anhydride, $\text{CHEt}\begin{matrix} \text{CO}\cdot\text{O} \\ | \\ \text{NH}\cdot\text{CO} \end{matrix}$, m. p. 113° (decomp.), which

is converted by warm alcohol into *polymolecular α -amino-*n*-butyric anhydride*, $\left[\text{CHEt}\begin{matrix} \text{CO} \\ | \\ \text{NH} \end{matrix}\right]_x$, m. p. above 300° after becoming brown

at about 250° . *α -Aminobutyric acid hydrochloride* crystallises in coarse, anisotropic prisms, m. p. 182° .

*Methylcarbonato- α -amino-*n*-butyric acid*, $\text{CO}_2\text{Me}\cdot\text{NH}\cdot\text{CHEt}\cdot\text{CO}_2\text{H}$, is obtained as a liquid which cannot be caused to solidify or distilled without decomposition by the action of a mixture of methyl alcohol and ether on ethylmalonazidic acid; it is transformed by concentrated hydrochloric acid into *α -aminobutyric acid hydrochloride*.

Ethyl *α -amino-*n*-butyrate hydrochloride* has m. p. 142° . H. W.

The Synthetic Preparation of Carbamide from Ammonia.

C. MATIGNON and M. FRÉJACQUES (*Ann. Chim.*, 1922, [ix], **17**, 257—304).—A more detailed account of work already published (A., 1920, ii, 250; 1921, ii, 33; this vol., ii, 272, 445). W. G.

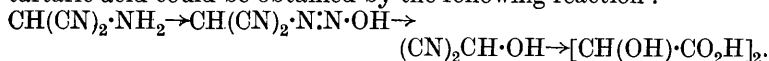
Semicarbazide Hydrochloride. HIDEO OCHI (Japan Pat., 39219).—Semicarbazide hydrochloride is prepared from nitro-carbamide by electrolytic reduction. As catholyte a mixture of nitro-carbamide and ten times the quantity of 10% hydrochloric acid is used and as anodal solution, 25% sulphuric acid. As a cathode, a lead cylinder is used and a spiral of lead tube as an anode, separated by means of a porous cell. The reaction is conducted at $0\text{--}5^\circ$, using a current of 1 ampere per sq. decm. and 4 volts. The product is obtained by evaporation of the catholyte in a vacuum. K. K.

Products of Polymerisation of Hydrocyanic Acid.

E. GRISZKIEWICZ-TROCHIMOWSKI (*Roczniki Chemji*, 1921, **1**, 468—478).—The constitution $\text{NH}_2\cdot\text{CH}(\text{CN})_2$ has been suggested for the trimeride of hydrocyanic acid. In order to verify the presence of the amino-group, two reactions were investigated, namely, condensation with aldehydes and the action of nitrous acid. The first reaction followed the course expected, and the following compounds were obtained. With salicylaldehyde, the *salicylidene* derivative, $\text{CH}(\text{CN})_2\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, yellowish-green needles, m. p. about 235° (decomp.). With anisaldehyde, the *anisylidene* derivative, $\text{CH}(\text{CN})_2\cdot\text{N}:\text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{OMe}$. With benzalde-

hyde, the *benzylidene* derivative, $\text{CH}(\text{CN})_2 \cdot \text{N} : \text{CHPh}$, brown plates, m. p. 190° (decomp.). A *benzoyl* derivative of the trimeride was also prepared, brown plates, m. p. 220° (decomp.), together with its unstable *hydrochloride*.

The results with nitrous acid were not those expected; it was thought that a diazo-compound would be formed, from which tartaric acid could be obtained by the following reaction:—



The product of the reaction does not, however, decompose on boiling; it is obtained from the solution in orange prisms, m. p. about 145° , and is shown to be 4 : 5-dicyano-1 : 2 : 3-triazole. On sublimation at 140° , this is obtained in a colourless modification,

for which the constitution $\text{NH} \begin{array}{c} \text{N} : \text{C} \cdot \text{CN} \\ \text{N} : \text{C} \cdot \text{CN} \end{array}$ is suggested.

The silver, copper, barium, potassium, and ammonium salts of the dicyanotriazole were prepared, also its 1-methyl derivative, m. p. $57.5-58.5^\circ$.

On hydrolysis with hydrochloric acid, the 4-amide of 1 : 2 : 3-triazole-4 : 5-dicarboxylic acid is produced, m. p. 275° . By passing hydrogen chloride through an ethereal solution of the substance, the ethyl ester of 4-cyano-1 : 2 : 3-triazole-5-carboxylic acid is obtained, m. p. $114-115^\circ$, whence the acid, m. p. $225-226^\circ$, is obtained, and from this by hydrolysis with sulphuric acid the 4 : 5-dicarboxylic acid, m. p. $195-196^\circ$, is produced.

It is suggested that the dicyanotriazole may be produced from the nitrous acid by condensation of a diazotised molecule of it with an undiazotised one. The results both with aldehydes and with nitrous acid, therefore, support the view that the trimeride of hydrocyanic acid is $\text{CH}(\text{CN})_2 \cdot \text{NH}_2$. R. T.

Equilibrium in the System Ammonia-Mercuric Cyanide.

S. R. BRINKLEY (*J. Amer. Chem. Soc.*, 1922, **44**, 1210-1216).—The vapour pressures of ammonia in the binary system ammonia-mercuric cyanide have been determined at 0° over a range from 370 mm. to 1600 mm., and in the ternary system, ammonia-water-mercury cyanide the solubility curve has been determined at the same temperature. It is shown that the vapour pressures of the solutions are far below those required by Raoult's law. The solid products, $\text{Hg}(\text{CN})_2 \cdot \text{NH}_3$ and $\text{Hg}(\text{CN})_2 \cdot 2\text{NH}_3$, have been isolated and have been shown to be the only additive compounds between these two components at 0° . J. F. S.

The Solubility of Potassium Ferrocyanide. REECE H. VALLANCE (*Chem. News*, 1922, **125**, 7).—The solubility of potassium ferrocyanide at temperatures up to 30° has been determined with the following results expressed in grams per 100 grams of saturated solution: 10.4° , 17.541; 13.8° , 19.067; 16.9° , 20.862; 20.4° , 21.953; 23.1° , 23.074; 25.0° , 23.971. Determinations by previous

workers have given widely varying results. Evidence was obtained of a transition point in the neighbourhood of 18° . G. F. M.

Thermochemical Researches on Oximes. II. The Stereoisomeric Ethyl Esters of Oximinoacetoacetic Acid. ALICJA DORABIALSKA (*Roczniki Chemji*, 1921, **1**, 448—467).—Ethyl oximinoacetoacetate has been described by Jovitschitsch (A., 1896, i, 82), who states that it may exist in two forms, both oils. The β -form, according to him, differs from the α -, in that its sodium hydroxide solution on acidification evolves carbon dioxide. The conversion is stated by him to be effected by the action of nitrous and sulphuric acids on the ester. Bouveault and Wahl (A., 1905, i, 506), however, only obtained one form, m. p. 56° , and the author finds that no conversion is effected by their method. The α -isomeride is prepared in various ways, including a hitherto undescribed method, whereby it is obtained from nitrosyl chloride and acetoacetic acid ester. The purest form has m. p. $56\cdot7^{\circ}$. A *monohydrate*, m. p. 45° , is obtained in rhombic plates, and from analyses of the compound m. p. $56\cdot7^{\circ}$ it is concluded that it contains at least 28·7% of the hydrate, which can be isomorphous with it, and has the same space structure. It is found that if the α -isomeride be left in strongly acid solution, and this is extracted with ether, a new modification is obtained, m. p. 49° . This is the β -ester, mixed with, at the very least, 19% of the α -form. On solution in alkalis and reprecipitation, the α -form is regenerated. Attempts to produce a hydrochloride failed. Both forms were examined thermochemically. The reactions studied were the formation of the sodium salt of both forms, from solutions and from the solid esters. Further, the heat of reaction with hydrochloric acid in ether solution, q_{HCl} , was measured, and that of the solution of the oximes in water (S). The following values were obtained for the α -ester: q 8·85, q_{HCl} 2·86, Q 4·83, and S -3·77, and for the mixed $\alpha\beta$ -ester: q_{HCl} 4·96, Q 6·14, and S -3·70. The heat of formation of the sodium salt is, for solutions of the esters, given by q , and with solid esters by Q , all figures being given in calories per millimole.

For the β -ester, q is calculated to be 6·72, whilst for the monohydrate it is 8·77. The degree of hydrolysis of the sodium salt is found to be zero. The heat of reaction of the ester with a solution of nitrosyl chloride in toluene is 31·77 cal. per millimole.

R. T.

The Variation of Refractive Index and Density of Benzene with Temperature. WILLIAM BAYLEY PARKER and GARTHA THOMPSON (T., 1922, **121**, 1341—1343).

Equilibrium in Liquid Mixtures of Ammonia and Xylene. CHARLES A. KRAUS and EDWARD H. ZEITFUCHS (*J. Amer. Chem. Soc.*, 1922, **44**, 1249—1260).—The total vapour pressure of liquid mixtures of ammonia and *m*-xylene has been determined for the entire range of compositions at 8° , 10° , 12° , 14° , 15° , 17° , and 20° . Mixtures of liquid ammonia and *m*-xylene

exhibit a critical end-point at 14.7° at a pressure of 6.85 atm. and a composition of 81.4 mol. % of ammonia. The composition of the liquid phases in equilibrium with each other in the three-phase system has been determined at all the temperatures mentioned above and at -33.5° . At lower temperatures, the percentage of ammonia in the phase rich in xylene decreases very rapidly with the temperature.

J. F. S.

The Chlorination of Benzyl Chloride. S. C. J. OLIVIER (*Rec. trav. chim.*, 1922, **41**, 419—421; cf. Beilstein and Kuhlberg, *Annalen*, 1868, **146**, 320).—The preparation of *p*-chlorobenzyl chloride by chlorination of benzyl chloride in presence of iodine is unsatisfactory, as, in addition to iodine derivatives which are difficult to separate, considerable quantities of the ortho- and traces of the meta-isomeride are also obtained. The product is not identical, as stated, with that obtained by chlorination of boiling *p*-chlorotoluene.

H. J. E.

Nitrotoluenes. VIII. Binary Systems of *m*-Nitrotoluene with another Nitrotoluene. JAMES M. BELL and JOSEPH L. McEWEN. (*J. Ind. Eng. Chem.*, 1922, **14**, 536—537; cf. A., 1921, i, 234, 330).—Freezing-point curves have been constructed for binary mixtures of *m*-nitrotoluene with *o*- and *p*-nitrotoluene, respectively. In the system *m*-nitrotoluene-*p*-nitrotoluene a single eutectic exists at -2.8° corresponding with 37% of the para-constituent, whilst in the system *m*-nitrotoluene-*o*-nitrotoluene the eutectic lies at -31.65° and corresponds with 48% of the meta-constituent. In the latter case, a metastable curve is indicated which would have a eutectic at about -39° , corresponding with about 46% of the meta-constituent.

J. F. S.

Organic Radicles with Quadrivalent Nitrogen. III. HEINRICH WIELAND and FRITZ KÖGL (*Ber.*, 1922, **55**, [B], 1798—1803).—An extension of the work of Wieland and Roth (A., 1920, i, 304).

Di-*p*-tolylnitric oxide has been shown to yield a pale yellow, unstable, crystalline, additive compound with nitric oxide; this is now identified as di-*p*-tolylnitroamine, $(C_6H_4Me)_2N \cdot NO$, since it is converted by hydrogen in the presence of palladium black into ammonia and di-*p*-tolylamine.

Diphenyl-nitrogen oxide reacts with tetra-*p*-anisylhydrazine in absolute ethereal solution, with the formation of di-*p*-anisylnitrogen oxide, m. p. 161° . The reaction probably occurs in accordance with the scheme: $O \cdot NPh_2 \cdot N(C_6H_4 \cdot OMe)_2 \longrightarrow NPh_2 \cdot N(O)(C_6H_4 \cdot OMe)_2 \longrightarrow NPh_2 + O \cdot N(C_6H_4 \cdot OMe)_2$.

Attempts to prepare the hydroxylamine, $NMe_2 \cdot C_6H_4 \cdot NPh \cdot OH$, did not lead to the desired result, since the bulk of the *p*-nitrosodimethylaniline was recovered unchanged after the action of magnesium phenyl bromide on this substance; *pp'*-azodimethylaniline, m. p. 263° , was also produced in small amount.

N-Phenyl-*N*-*p*-tolylhydroxylamine, $C_6H_4Me \cdot NPh \cdot OH$, colourless, lustrous needles, m. p. $65-66^\circ$ (decomp.), is prepared by the action of magnesium phenyl bromide on nitrosotoluene. It is reduced by tin and hydrochloric acid to phenyl-*p*-tolylamine. Phenyl-*p*-tolyl-nitrogen oxide appears to be formed when an absolute ethereal solution of the hydroxylamine is treated with silver oxide and ignited sodium sulphate at -5° ; the garnet-red crystals are, however, so unstable that they could not be analysed.

Attempts have been made to apply the reactions characteristic of diarylnitrogen oxides to sodium nitrosodisulphonate (Fremy's salt), $(SO_3Na)_2N:O$, which appears to contain quadrivalent nitrogen. Its solution in water is rapidly decolorised by nitric oxide with formation of nitrous acid: $O:N(SO_3Na)_2 \cdot N:O \longrightarrow N(SO_3Na)_2 \cdot OH + HO \cdot NO$, but reaction only occurs in the presence of a trace of acid. Fremy's salt is reduced by phenylhydrazine to nitrogen (evolved from the hydrazine) and hydroxylamine disulphonate.

p-Nitroso-*N*-diphenylhydroxylamine cannot be dehydrogenated to the corresponding diarylnitrogen oxide; since inhibition is not caused by the presence of the nitroso-group, it is probable that the substance has the constitution $OH \cdot N:C_6H_4:NPh \cdot O$ instead of the usually accepted $NO \cdot C_6H_4 \cdot NPh \cdot OH$. H. W.

Naphthalenesulphonic Acids. IV. Solubilities of some Amine Salts of Naphthalenesulphonic Acids. H. WALES (*J. Ind. Eng. Chem.*, 1922, **14**, 317—318).—The solubilities of salts formed by different naphthalenesulphonic acids with α - and β -naphthylamine were investigated. As hydrolysis occurs in some cases with water, *N*/100-hydrochloric acid was used as solvent, the acid of this strength having no influence on the solubility. Of the disulphonates, the 1 : 5- α -naphthylamine salt, and the 2 : 6- β -naphthylamine salt are least soluble. As a general rule, the more symmetrical a salt, the lower is its solubility. The solubility curve of α -naphthylamine naphthalene- β -sulphonate shows an allotropic change at 54° , and that of the corresponding α -sulphonate at 66° . A complete series of solubilities as determined between 25° and 98° is tabulated. C. I.

Catalytic Hydrogenations under Pressure in the Presence of Nickel Salts. I. Indene and Acenaphthene. JULIUS VON BRAUN and GEORG KIRSCHBAUM (*Ber.*, 1922, **55**, [B], 1680—1686).—The method adopted is essentially that due to Schroeter (this vol., i, 122), hydrogenation being effected under a pressure of 10—15 atmospheres at a suitable temperature in an autoclave provided with stirring gear and in the presence of a nickel catalyst. At 200° , indene is very readily transformed into hydrindene, b. p. 176° , the yields being theoretical. At 210° , technical acenaphthene which has been purified by a single crystallisation from alcohol is rapidly and quantitatively reduced to tetrahydroacenaphthene [tetraphthene], b. p. $115^\circ/12$ mm. The latter hydrocarbon is dis-

tinguished from hydrindene and tetrahydronaphthalene by its ready susceptibility to oxidising agents. Whereas it is stable when preserved in closed vessels and becomes coloured merely pale yellow by exposure to air, it behaves towards permanganate as an unsaturated compound. For this reason, its smooth nitration has not yet been accomplished. Tetrahydroacenaphthene is converted by acetyl chloride and aluminium chloride in the presence of carbon disulphide into *5-acetyltetrahydroacenaphthene*, a colourless liquid, b. p. 180—181°/13 mm., which is oxidised by dilute nitric acid to benzene-1 : 2 : 3 : 4-tetracarboxylic acid. The conclusive proof that the acetyl group enters the molecule in position 5 is deduced from a study of its dehydrogenation (von Braun, Hahn, and Seemann, following abstract). The compound gives a *semicarbazone*, m. p. 240—241°, and an *oxime*, m. p. 148°.

The treatment of tetrahydroacenaphthene with sulphuric acid at temperatures between 0° and 80° or higher leads mainly to the production of *tetrahydroacenaphthene-4-sulphonic acid*, leaflets, m. p. 104—105°; the *sodium*, *calcium*, and *lead* salts are described. The corresponding *chloride*, glassy needles, m. p. 69—70°, *amide*, m. p. 154°, and *anilide*, m. p. 170°, are described. Reduction of the sulphonyl chloride by zinc dust in the presence of ether leads to the formation of *tetrahydroacenaphthene-4-sulphinic acid*, cubes, m. p. 102—103°. Zinc dust and sulphuric acid reduce the sulphonyl chloride to *4-thioltetrahydroacenaphthene*, b. p. 167—169°/12 mm.; the corresponding *methyl ether*, b. p. 180—182°/10 mm., and *disulphide*, m. p. 129°, are described. Sodium tetrahydroacenaphthene-4-sulphonate is transformed with some difficulty and in poor yield by molten potassium hydroxide into *4-hydroxytetrahydroacenaphthene*, m. p. 98—99°. H. W.

Benzopolymethylene Compounds. III. Dehydrogenation of Tetrahydronaphthalene, Hydrindene and Tetrahydroacenaphthene [Tetraphthene] Derivatives. JULIUS VON BRAUN, ERICH HAHN and JON SEEMANN (*Ber.*, 1922, **55**, [B], 1687—1700).—The processes of substitution in the aromatic portion of tetrahydronaphthalene and of naphthalene follow different laws. In the former case, nitration, bromination, chlorination, etc., lead to a mixture of ar- α - and ar- β -derivatives which frequently are readily separable from one another, whereas α -derivatives are formed from naphthalene, and the corresponding β -compounds can often only be prepared by circuitous methods. Since, however, tetrahydronaphthalene is readily re-converted into naphthalene, it appeared possible that a ready method of preparing otherwise difficultly accessible naphthalene compounds might be opened up through the tetrahydro-compounds. In a number of cases it is now shown that the dehydrogenation of the tetrahydronaphthalene derivatives can be effected smoothly. Unfortunately, a similar process does not appear to be applicable to hydrindene and its derivatives, since these substances are unaffected by mild treatment and the

molecule is extensively decomposed in circumstances which are sufficiently drastic to induce reaction. On the other hand, tetrahydroacenaphthene is readily dehydrogenated, yielding, according to circumstances, acenaphthene or acenaphthylene.

β -Ethyltetrahydronaphthalene is decomposed when distilled in an atmosphere of carbon dioxide through a tube (empty or filled with pumice coated with lead oxide) at 650° into β -ethyl-naphthalene, b. p. 251 — 252° /atmospheric pressure; at 600° very little action occurs, whereas at 700° the ethyl group is also eliminated and naphthalene is formed. Similar observations are made with β -tetrahydronaphthyl methyl ketone, the optimum temperature for the conversion of which into β -naphthyl methyl ketone is 680 — 700° . The pure ketone has m. p. 53 — 54° and gives an *oxime*, m. p. 143 — 144° , a *semicarbazone*, m. p. 230° , and a *phenylhydrazone*, m. p. 176 — 177° .

Tetrahydronaphthyl methyl ketone condenses with isation in boiling aqueous alcoholic, alkaline solution with the formation of 2- β -tetrahydronaphthylcinchoninic acid, m. p. 198 — 199° (decomp.) [the *sodium* and *copper* salts and the *ethyl* ester, needles, m. p. 86° , are described]. When heated until carbon dioxide ceases to be evolved, the acid is converted into 2- β -tetrahydronaphthylquinoline, needles, m. p. 75° (*picrate*, m. p. 191° ; *hydrochloride*, m. p. 227° ; *methiodide*, m. p. 190°). The base is dehydrogenated by lead oxide-pumice at 700° with formation in more than 50 % yield of 2- β -naphthylquinoline, m. p. 161° (*methiodide*, orange-coloured prisms, m. p. 188°).

Tetrahydroacenaphthene is almost quantitatively transformed by sulphur at 180° into acenaphthene; under similar conditions, the acetyl group of acetyltetrahydroacenaphthene is also affected. If, however, the latter is heated at 700° , a large amount of acenaphthylene is produced together with smaller quantities of incompletely dehydrogenated acetyltetrahydroacenaphthene from which 5-acetylacenaphthene can be isolated in the form of its *semicarbazone*.

β -Nitrotetrahydronaphthalene suffers a complicated decomposition when heated at a high temperature. On the other hand, it reacts readily with bromine at 100° , giving a *dibromonitrotetrahydronaphthalene* which could not be caused to crystallise; the latter substance evolves hydrogen bromide at a somewhat higher temperature, giving β -nitronaphthalene, m. p. 79° , the yield being 96—98% of that theoretically possible. The process appears to be the best method favourable at present for the preparation of β -nitronaphthalene when the pure tetrahydro-derivative is available. Unfortunately, although the nitration of tetrahydronaphthalene is a simple operation, the separation of the α - and β -isomerides is somewhat tedious. α -Nitrotetrahydronaphthalene is smoothly dehydrogenated in the same manner as the β -compound. If, however, the process is applied to the mixed tetrahydro-compounds a mixture of nitronaphthalenes is produced which cannot be separated by distillation or by crystallisation from alcohol.

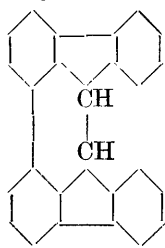
β -Nitronaphthalene is readily brominated with the formation of 5 (or 8)-bromo-2-nitronaphthalene, needles, m. p. 131° , which is reduced by stannous chloride to 5 (or 8)-bromo-2-aminonaphthalene, colourless crystals, m. p. 35° , b. p. $207\text{--}210^\circ/16\text{ mm.}$; the corresponding *picrate*, needles, m. p. 216° ; *hydrochloride*, m. p. 265° after darkening at 230° ; *acetyl* compound, m. p. 158° ; *benzoyl* compound, m. p. 109° , and *benzylidene* derivative, m. p. 63° , are described. The amine is converted in the usual manner into 5 (or 8)-bromo-2-hydroxynaphthalene, colourless needles, m. p. 105° , but the yields are only moderate owing to the simultaneous production of the compound, $\text{C}_{10}\text{H}_6\text{Br}\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_5\text{Br}\cdot\text{NH}_2$, cinnabar red needles, m. p. 115° . The naphthol is oxidised by permanganate to 3-bromophthalic acid.

H. W.

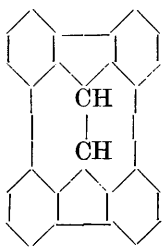
The Pyrogenic Transformation of Fluorene. K. DZIEWOŃSKI and J. SUSZKO (*Roczniki Chemji*, 1921, **1**, 387—410).—Fluorene vapour is passed under reduced pressure, through a quartz tube, heated to redness, and containing a coil of iron wire. The vapours condense to an oily solid, mainly unchanged fluorene, but containing three other hydrocarbons, of the empirical formulæ $\text{C}_{26}\text{H}_{16}$, $\text{C}_{26}\text{H}_{14}$, and $\text{C}_{26}\text{H}_{12}$. Graeber (A., 1893, i, 38) obtained a substance, $\text{C}_{26}\text{H}_{16}$, by passing fluorene vapours over heated lead oxide, but this substance, bidiphenylene-ethylene, is shown to be different from the substance of the same empirical formula obtained by the author.

This hydrocarbon, *difluorenylene* (formula I) forms colourless prisms, m. p. 218° , and is identical with the hydrocarbon, $\text{C}_{26}\text{H}_{16}$, obtained by Klinges and Lonnes (A., 1896, i, 691) from tetraphenylene-pinacolin, to which an asymmetrical structure was wrongly assigned. The *picrate*, reddish-brown needles, m. p. $202\text{--}203^\circ$, the *dinitro*-derivative, m. p. $360\text{--}365^\circ$ (decomposition), and *dihydroxy*-derivative, colourless, rhombic plates, m. p. 269° , were prepared.

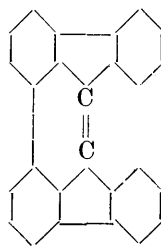
The second hydrocarbon, *dihydorrubicene*, $\text{C}_{26}\text{H}_{14}$ (formula II), forming colourless needles, m. p. 296° , is obtained in small quantity only. The *picrate*, orange needles, m. p. $254\text{--}260^\circ$, is unstable. The



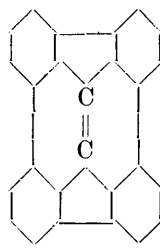
(I.)



(II.)



(III.)



(IV.)

third product, rubicene, $\text{C}_{26}\text{H}_{12}$, forms deep red needles, m. p. 305° , and seems to be best prepared by this method. Pummerer (A., 1912, i, 182), who prepared it from phenanthraquinone, assigned to it the empirical formula $\text{C}_{26}\text{H}_{14}$ and the structure III; this is shown to be incorrect, and the structure IV is assigned to it. The *picrate*,

reddish-brown needles, m. p. 258° , is unstable; the *dinitro*-derivative, brick-red needles, m. p. 440 — 442° (decomp.), and the *dibromo*-derivative, brownish-red needles, m. p. 378° (decomp.), were prepared, also a *rubicenedisulphonic acid*, which is found to act as an acid dye. Attempts to reduce the hydrocarbon did not lead to any definite results, whilst oxidation with chromic acid mixture gives a yield of only 5% yellow plates, m. p. 203° , and of a feebly acid nature.
R. T.

Aniline Arsenates. E. PATERNÒ (*Atti R. Accad. Lincei*, 1922, [v], 31, i, 165—169).—According to Béchamp, aniline forms a dianiline arsenate, m. p. 140° , which loses aniline at 180° , giving a monoaniline arsenate. The author finds that the former salt, which forms trimetric crystals, is always obtained when aniline is treated in the cold with aqueous arsenic acid. When distilled either in a vacuum at 60° or in a current of steam, or when left in a desiccator over sulphuric acid, the dianiline salt loses aniline, giving the monoaniline salt, which forms vitreous prisms, m. p. 154° , belonging to the triclinic system; if the fused salt is allowed to solidify, it then melts at a somewhat lower temperature. The melting point of the dianiline salt varies for different samples and different modes of heating, from about 140° to about 150° , and cannot be determined exactly owing to the readiness with which the salt undergoes change. Cryoscopic measurements show that the monoaniline salt is hydrolysed into two, and the dianiline salt into three molecules.

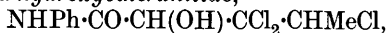
Solutions of aniline in water and of water in aniline have also been investigated cryoscopically. The maximum solubility of aniline in water is about 3.7% at -0.6° and that of water in aniline about 2.8% at -5.4° ; Alexéev (A., 1877, ii, 472) gave for these solubilities at the ordinary temperature 3.11% and 4.58%, respectively, the latter being evidently too high.
T. H. P.

The Hydroferrocyanides and Hydroferricyanides of the Organic Bases. I. WILLIAM MURDOCH CUMMING (T., 1922, 121, 1287—1298).

isoNitriles. III. Reactions with the Hydrates of Halogenated Aldehydes. M. PASSERINI (*Gazzetta*, 1922, 52, i, 432—435).—The results previously obtained (A., 1921, i, 895) suggest that, in the reaction of an *isonitrile* with an aldehyde or a ketone in presence of an organic acid, the aldehyde or ketone first forms with the organic compound a labile additive compound of the structure, $\text{OH}\cdot\text{CR}_2\cdot\text{O}\cdot\text{CO}\cdot\text{R}$, capable of reacting with *isonitrile* groups. The accuracy of this suggestion is supported by the fact that the analogous compounds formed by halogenated aldehydes with water, $\text{OH}\cdot\text{CHR}\cdot\text{OH}$, react with phenylcarbylamines yielding anilides of halogenated α -hydroxy-acids, $\text{R}\cdot\text{N}:\text{C}+\text{OH}\cdot\text{CHR}\cdot\text{OH}=\text{NHR}\cdot\text{CO}\cdot\text{CHR}\cdot\text{OH}$. Thus, chloral hydrate and phenylcarbylamine yield β -trichloro- α -lactanilide, and butylchloral hydrate and phenylcarbylamine, $\beta\beta\gamma$ -trichloro- α -valeranilide,

β -Trichloro- α -lactanilide, $\text{NHPh}\cdot\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CCl}_3$, crystallises in colourless, elongated plates or flat needles, m. p. 147° , and is readily decomposed by alkali hydroxide or carbonate with quantitative loss of the chlorine. It is highly resistant towards the action of acids, but is converted into trichlorolactic acid when heated with excess of hydrochloric acid in a sealed tube at 80 — 100° . The compound, m. p. 164 — 165° (decomp.), described as trichlorolactanilide and obtained by Anschütz and Haslam (A., 1890, 27) from aniline and tetrachloroethylidene trichlorolactate, may be an isomeride of the above compound.

$\beta\beta\gamma$ -Trichloro- α -hydroxyvaleranilide,



forms colourless, highly refractive plates, m. p. 156 — 158° , and yields aniline and $\beta\beta\gamma$ -trichloro- α -hydroxyvaleric acid when heated in a sealed tube with hydrochloric acid.

T. H. P.

Akylation of Amines with Sulphonic Esters. ZOLTAN FÖLDI (*Ber.*, 1922, **55**, [B], 1535—1543).—The reaction between sulphonic esters and amines does not proceed more uniformly than that between amines and alkyl haloids. Quaternary salts are, however, obtained smoothly and quantitatively as the sole final product of the action of sulphonic esters on tertiary amines. Primary and secondary amines, on the other hand, give more or less uniform results. The process does not stop at the stage indicated by the equation $\text{Ph}\cdot\text{SO}_3\text{Me} + \text{NH}_2\text{Ph} = \text{NHMePh}, \text{Ph}\cdot\text{SO}_3\text{H}$, since the secondary base is partly displaced from its salt by unchanged primary amine (even when the latter is the relatively weaker) and then suffers further alkylation. The process is explained by the reversibility of the change $\text{NHMePh}, \text{SO}_3\text{HPh} + \text{NH}_2\text{Ph} \rightleftharpoons \text{NH}_2\text{Ph}, \text{SO}_3\text{HPh} + \text{NHMePh}$. This disadvantage can be remedied to some extent by using an excess of the initial amine, but this procedure suffers from the defect that it causes a displacement of the equilibrium in an unfavourable sense. The reactivity of phenols towards sulphonic esters has been found to diminish with increasing acidity of the phenolic hydroxy-groups. A definite relationship between reactivity and basicity, however, does not appear to exist in the case of amines, since the feebly basic and usually slightly reactive diphenylamine is attacked by sulphonic esters with the same vigour as methylaniline or aniline.

The following substances do not appear to have been described previously: *allyl-p-toluidine*, b. p. 122 — $125^\circ/12$ mm.; *diallylanthr-anilic acid*, transparent rhombohedra, m. p. 86° ; *phenyltrimethyl-ammonium toluene-p-sulphonate*, colourless, very hygroscopic crystals, m. p. 159° ; *diphenylmethylaniline ferrocyanide*, $\text{C}_{13}\text{H}_{13}\text{N}_2\cdot 2\text{H}_4\text{FeC}_6\text{N}_6$, colourless, somewhat unstable needles; *diphenylallylamine*, a colourless liquid which rapidly becomes purplish-red, b. p. 185 — $190^\circ/12$ mm., about 320 — 325° (decomp.)/atmospheric pressure; *1-methyl-pyridinium toluene-p-sulphonate*, unusually hygroscopic crystals, m. p. 136 — 137° ; *1-allylpyridinium benzenesulphonate*, very hygroscopic crystals; *N-methylpapaverinium toluene-p-sulphonate*, m. p.

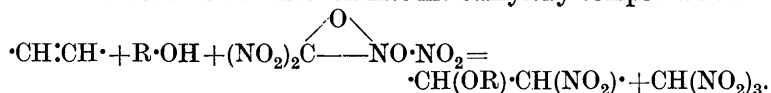
171°; N-allylpapaverinium benzenesulphonate, m. p. 174—175°, pale yellow needles (+2H₂O), lemon-yellow rods (anhydrous); N-allylbrucinium benzenesulphonate (anhydrous and trihydrate), m. p. 148—150°, slight decomp. 150—160° and m. p. 238° after re-solidification; benzenesulphonyldiallylamine, a pale yellow, viscous liquid, b. p. 180—190°/11 mm., d_4^{25} 1.086.

Sulphonic esters can be used for the preparation of nitriles, since they react as easily as the alkyl sulphates with potassium cyanide.

H. W.

Reciprocal Induced Polarity Effects in Cresols and their Derivatives. Properties of the Isomeric Methoxybenzyl Bromides. ARTHUR LAPWORTH and JOHN BALDWIN SHOESMITH (T., 1922, **121**, 1391—1400).

Tetranitromethane. V. Tetranitromethane as Nitrating Agent. II. ERICH SCHMIDT, RICHARD SCHUMACHER, WILLY BÄJEN, and ADALBERT WAGNER (*Ber.*, 1922, **55**, [B], 1751—1759; cf. Schmidt and Fischer, A., 1920, i, 726, 727).—It has been shown previously (*loc. cit.*) that tetranitromethane in the presence of pyridine can effect the replacement of hydrogen attached to carbon atoms united by an olefinic double bond by the nitro-group. The entrance of the nitro-group, however, depends on the position of the double bond relatively to the aromatic nucleus. Allyl compounds (*o*-esdragole, safrole, eugenyl methyl ether, myristicin, and apiole) are unaffected, whereas the isomeric propenyl derivatives are transformed into the corresponding β -nitro-compounds. Unsaturated compounds which are nitrated by tetranitromethane and pyridine with retention of the double bond are converted by tetranitromethane and alcohols into nitroalkyloxy-compounds thus :



The following individual substances are described: β -nitro-*o*-anethole, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$, m. p. 52—53°, b. p. 127—128°/0.5 mm.; β -nitroisoeugenyl methyl ether, m. p. 72°; β -nitroascarone, $\text{C}_6\text{H}_2(\text{OMe})_3\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$, m. p. 98—99°; β -nitroisomyristarin, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_2(\text{OMe})\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$, m. p. 111—112°; β -nitroisopaprole, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}(\text{OMe})_2\cdot\text{CH}\cdot\text{CMe}\cdot\text{NO}_2$, yellow needles, m. p. 110—111°.

The following compounds are obtained by the gradual addition of an alcoholic solution of tetranitromethane to a boiling solution of the unsaturated substance in alcohol; the solution is poured into water and extracted with ether. The ethereal solution is decolorised and treated for some time with an aqueous suspension of magnesium oxide: β -nitro- α -methoxydihydro-*p*-anethole, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CHMe}\cdot\text{NO}_2$, m. p. 49–50°, b. p. 133–135°/0.5 mm.; β -nitro- α -methoxydihydro-*o*-anethole, needles, m. p. 63–64°, b. p. 127–128°/0.5 mm.; β -nitro- α -ethoxydihydro-*p*-anethole, a pale yellow liquid, b. p. 137°/0.5 mm.; β -nitro- α -ethoxydihydro-*o*-anethole, a pale yellow liquid, b. p. 125°/0.5 mm.; β -nitro- α -methoxydihydro-

isosafole, $\text{CH}_2\text{O}_2\cdot\text{C}_6\text{H}_3\cdot\text{CH}(\text{OMe})\cdot\text{CHMe}\cdot\text{NO}_2$, colourless crystals, m. p. 67—68°, b. p. 138—140°/0.5 mm.

p-Nitrodimethylaniline is converted by tetranitromethane, glacial acetic acid, and alcohol into methyl-*p*-nitrophenylnitrosoamine, m. p. 100—101°. Similarly, *p*-dimethylaminobenzonitrile gives *p*-methylnitrosoaminobenzonitrile, colourless crystals, m. p. 125°, and 2:4-dinitrodiethylaniline is transformed into 2:4-dinitroethylaniline, m. p. 113—114°.

H. W.

Decomposition of Benzyl Disulphoxide. JOHN ARMSTRONG SMYTHE (T., 1922, **121**, 1400—1405).

Organomagnesium Derivatives. A. GARCÍA BANÚS and J. PASCUAL VILA (*Anal. Fís. Quím.*, 1921, **19**, 326—346; cf. Smidlin and García Banús, A., 1913, i, 50).—The reaction of Grignard reagents with certain aldehydes and ketones and in particular with benzaldehyde, is discussed with reference to the possibility that these organomagnesium compounds exist in two tautomeric forms, one of which is supposed to possess two active radicles and to be able to condense with two molecules of an aldehyde or ketone. Magnesium benzyl chloride, however, reacts normally with benzophenone and benzil; In the experimental portion, the reaction of magnesium benzyl chloride with benzil is studied. Equimolecular proportions of these compounds in ethereal solution give *benzoylphenylbenzylcarbinol* (benzylbenzoin), $\text{CH}_2\text{Ph}\cdot\text{CPhBz}\cdot\text{OH}$, obtained after recrystallisation in white needles, m. p. 120—121°. The crystals are triclinic. It gives a *syn-oxime*, m. p. 175—176°. The *phenylhydrazone* forms colourless crystals m. p. 115—116°, after softening at 61—62°. From the products of the reaction of one molecule of benzil with two molecules of magnesium benzyl chloride α - and β -*deoxybenzoinpinacones*, $\text{CH}_2\text{Ph}\cdot\text{CPh}(\text{OH})\cdot\text{CPh}(\text{OH})\cdot\text{CH}_2\text{Ph}$, are obtained. The α -pinacone forms white prisms, m. p. 215—216°. They are rhombic tetragonaloid; $a:b:c = 0.8746:1:0.7514$ (?). The β -pinacone has m. p. 172—173° and forms white, monoclinic needles; $a:c = 1:0.2475$; $\beta = 92^\circ 7'$. By varying the conditions of reaction dibenzyl may be obtained.

G. W. R.

Condensations of *p*-Nitrobenzyl Chloride with Cinnamaldehyde and Furfuraldehydes. ERNST KLEUCKER (*Ber.*, 1922, **55**, [B], 1634—1654).—A solution of *p*-nitrobenzyl chloride in methyl alcohol is converted by cinnamaldehyde and potassium carbonate at 35—40° into a mixture of *cis*- and *trans*- α -*phenyl*-

δ -*p*-nitrophenyl- $\Delta^{\alpha\gamma}$ -butadiene oxide, $\text{O} \begin{cases} \text{CH}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2 \\ | \\ \text{CH}\cdot\text{CH}\cdot\text{CHPh} \end{cases}$, which are

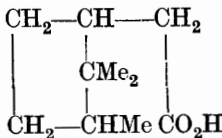
separated by taking advantage of the readiness with which the *cis*-variety forms supersaturated solutions in alcohol. The *cis*- and *trans*-modifications have m. p. 115° and 148°, respectively. [*p*-Nitrobenzyl chloride is converted by potassium carbonate and methyl alcohol into 4:4'-dinitrostilbene and *p*-nitrobenzyl methyl

ether, m. p. 26—27°]. The *trans*-variety is oxidised by potassium permanganate in the presence of acetone to benzoic acid and *p*-nitrophenylglycidic acid, m. p. 186—188° (decomp.), the identity of the latter being confirmed by converting it by means of concentrated hydrochloric acid into β -chloro-*p*-nitrophenylpropionic acid, m. p. 167—168°. The similar oxidation of the *cis*-acid gives benzoic and *cis*-*p*-nitrophenylglycidic acid, m. p. 124—125°, which is converted by concentrated hydrochloric acid into *cis*- β (?)-chloro-*p*-nitrophenylpropionic acid, m. p. 125—126°. Either of the α -phenyl- δ -*p*-nitrophenyl- $\Delta^{\alpha\gamma}$ -butadiene oxides, when suspended in anhydrous ether and treated with dry hydrogen chloride, yields a mixture of *cis*- and *trans*- α -phenyl- δ -*p*-nitrophenyl- $\Delta^{\alpha\gamma}$ -butadiene- $\gamma\alpha$ -chlorohydrins, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CHCl}\cdot\text{CH}(\text{OH})\cdot\text{CH}\cdot\text{CHPh}$, m. p. 105—110°, which is converted by boiling glacial acetic acid into (?) *p*-nitrobenzyl styryl ketone, m. p. 144° (the corresponding *oxime*, m. p. 121—122°, could not be obtained in a perfectly homogeneous condition).

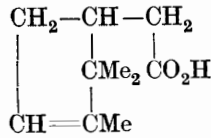
In a similar manner, *p*-nitrobenzyl chloride and furfuraldehyde give *trans*-*p*-nitrophenyl-2-furylethylene oxide, colourless crystals, m. p. 117°, and *cis*-*p*-nitrophenyl- α -furylethylene oxide, colourless needles, m. p. about 85°. Either variety is converted by hydrogen chloride and ethyl alcohol into ethyl δ -*p*-nitrobenzylidenelævulate, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CH}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, m. p. 107°. The corresponding methyl ester has m. p. 150°. Hydrolysis of the ester by boiling glacial acetic acid containing a little concentrated sulphuric acid leads to the production of δ -*p*-nitrobenzylidenelævulic acid, m. p. 169°, which is oxidised by potassium permanganate to *p*-nitrobenzoic and succinic acids. The acid may also be prepared by the condensation of *p*-nitrobenzaldehyde with lævulic acid; the corresponding semicarbazone has m. p. about 210°. Ethyl δ -*p*-nitrobenzylidenelævulate gives two semicarbazones, $\text{C}_{15}\text{H}_{18}\text{O}_5\text{N}_4$, m. p. 207—209° and 175—180°, respectively. If a solution of *cis*- or *trans*-*p*-nitrobenzyl- α -furylethylene oxide in hot ethyl or methyl alcohol is poured into boiling water, *p*-nitrobenzyl α -furyl ketone (?), pale yellow, prismatic crystals, m. p. 158—159°, is produced (the corresponding *oxime*, m. p. 136—138°, could not be obtained in the homogeneous condition). The ketone is oxidised by hydrogen peroxide in alcoholic alkaline solution to *p*-nitrobenzoic and pyromucic acids.

H. W.

Comparison of α -Campholanic Acid with Mahla and Tiemann's Dihydrocampholenic Acid and with *iso*-Campholic Acid. P. LIPP (*Ber.*, 1922, 55, [B], 1883—1892).—Dihydrocampholenic acid (formula I) has been isolated by Mahla and Tiemann (*A.*, 1900, i, 507) by a peculiar transformation of camphorimine, and its constitution has been deduced from its oxidative degradation. If the formula assigned to it is correct, it must be produced by the hydrogenation



I.



II.

tion of α -campholenic acid (formula II), but according to van Kregten (*Diss.*, Gröningen, 1910), this does not appear to be the case when the Sabatier-Senderens method is used. The author considers that the question can only be elucidated satisfactorily by a study of the optically inactive compound. He has therefore converted *dl*-camphor into *dl*-dihydrocampholenic acid on the one hand and into *dl*- α -campholenic acid on the other; the latter acid is hydrogenated by Skita's method in acid and alkaline or neutral medium, thereby yielding *trans*- and *cis*- α -campholanic acids, the former of which is identical with the *dl*-acid prepared according to Mahla and Tiemann.

Fission of the camphor ring with alkali leads to the formation of campholic acid, together with a small proportion of *isocampholic* acid. It has been suggested, without experimental evidence being adduced, that the latter acid is identical with α -campholanic acid (Mahla and Tiemann, *loc. cit.*). A comparison of *dl*-*isocampholic* and *dl*- α -campholanic acids shows that the substances are closely similar to, but certainly not identical with, one another. The supposed marked difference in strength between campholic and *isocampholic* acids does not exist.

dl-Camphoroxime is converted, according to Tiemann's method (*loc. cit.*), into *dl*- α -campholenic acid, b. p. 148.2—149.2° (corr.)/15 mm. (amide, m. p. 115—116°), which is hydrogenated in ethereal solution in the presence of spongy platinum to *dl*-*cis*- α -campholanic acid, b. p. 150.9—151.2° (corr.)/14 mm. [*chloride*, b. p. 102—104°/16 mm., *amide*, lustrous leaflets, m. p. 129—130° (corr.); *anilide*, prismatic crystals, m. p. 140—141°]. The *cis*-acid is also obtained by the catalytic hydrogenation of α -campholenic acid, according to Sabatier-Senderens, in the presence of nickel as catalyst at 200°. On the other hand, treatment of α -campholenamide in ethereal methyl alcoholic solution with hydrogen in the presence of spongy platinum gives *trans*- α -campholanamide, rectangular leaflets, m. p. 124.5—125° (corr.). *dl*-Camphoroxime is converted successively in accordance with the procedure of Mahla and Tiemann (*loc. cit.*), into *dl*-camphorimine nitrite, decomp. 160°, *dl*-dihydrocampholenonitrile, b. p. 112—117°/16 mm., and *dl*-dihydrocampholenic acid, which is identified with *trans*- α -campholanic acid [*anilide*, m. p. 136—137° (corr.)].

The following derivatives of *dl*-*isocampholic* acid are described: *chloride*, b. p. 88—89° (corr.)/10 mm.; *amide*, m. p. 109—110° (corr.); *anilide*, m. p. 137—139° after previous softening.

H. W.

The Spontaneous Decomposition of Imino-ethers.

TREAT B. JOHNSON and LAWRENCE W. BASS (*J. Amer. Chem. Soc.*, 1922, **44**, 1341—1343).—Samples of carefully purified benzonitrile, benziminomethyl ether, benziminoethyl ether, benziminoisobutyl ether, and *p*-toluiminomethyl ether were kept for twenty-two years in sealed glass vessels and then examined. In every case, with the exception of benzonitrile, heavy, crystalline deposits of cyapherine

combinations and also unaltered nitrile were found, the amount of dissociation and polymerisation varying with the ether. The pure benzonitrile showed no evidence of polymerisation. W. G.

The Formation of Salts from Aromatic Nitro-compounds. I. LIFSCHITZ (*Ber.*, 1922, **55**, [B], 1631—1634).—Isomeric salts and esters from *p*-nitrophenylacetonitrile have been described by Jenner and Lifschitz (*A.*, 1916, i, 45), who have ascribed to them a paraquinonoid structure. Their observations have been confirmed by Opolski, Kowalski, and Pilewski (*A.*, 1917, i, 25), who also claim to have isolated similar compounds from *m*-nitrophenylacetonitrile, which they regard as having a meta-quinonoid structure. Repetition of the latter work with carefully purified *m*-nitrophenylacetonitrile has not given evidence of the formation of such compounds. The spectrum of an absolute alcoholic solution of *m*-nitrophenylacetonitrile which has been treated with sodium ethoxide does not contain any characteristic bands and is not in any way analogous to that of the para-salts. These solutions are very unstable, so that even with rapid work distinct changes in absorption occur during the exposures. Recovery of the paranitrile from such solutions appears to be impossible. The preparation of the solid salts by means of ethereal sodium ethoxide could not be effected. H. W.

The Addition of Bromine to the *trans*-Substituted Cinnamic Acids. C. F. VAN DUIN (*Rec. trav. chim.*, 1922, **41**, 402—418).—Measurements of the velocity of the reaction, in presence of different concentrations of hydrochloric acid, between bromine and the $\text{R} \begin{smallmatrix} \diagup \text{CO}\cdot\text{OH} \\ \diagdown \text{SO}_3 \end{smallmatrix}$ and $\text{R} \begin{smallmatrix} \diagup \text{CO}\cdot\text{O}' \\ \diagdown \text{SO}_3 \end{smallmatrix}$ ions have been made, the latter being derived from the normal and acid sodium salts of the three sulphocinnamic acids. The results show that the reaction is of the bimolecular type and that the differences in the constants depend entirely on differences in the speed of reaction of the ions. Negative catalysis due to the presence of hydrogen ions does not occur. The small variations which are found in the constant for the reaction are attributed to the comparatively large changes in the concentration of the hydrochloric acid. The reaction velocities in the case of the normal sodium salts are so great that it is only towards the end of the reaction that measurements are practicable; this involves considerable experimental error, so that the resulting figures are of value only from a comparative point of view. The rate at which the addition of bromine takes place, in the case of both ions, is greatest for the meta- and least for the para-compound; but the influence of the position of the sulphonic group is only of secondary importance compared with the retarding action exerted by that group. This is shown by comparing the results obtained by Barrett and Lapworth (*T.*, 1908, **93**, 85) for cinnamic acid, $K > 1000$, with the values (29 to 52) obtained for the sulphocinnamic acids. H. J. E.

Betaines. II. Betaines of the Cinnamic Acid Series.

PAUL PFEIFFER and GERHARD HAEFELIN (*Ber.*, 1922, **55**, [B], 1769—1788).—Theoretical considerations have led the author (this vol., i, 720) to advance the formula, ${}^+\text{NMe}_3\text{—R—CO—O}^-$, for the betaines. An opportunity of testing its validity lies in the preparation of betaines of the *trans*-cinnamic acid series, since, according to the older methods of formulation (annexed formula) these substances cannot be conceived as capable of existence. Such betaines are found to be readily prepared.

Methyl trans-p-dimethylaminocinnamate, pale yellow, lustrous leaflets, m. p. 135—136°, is prepared by the condensation of *p*-dimethylaminobenzaldehyde with methyl acetate in the presence of sodium. It gives a *perchlorate*, colourless, prismatic crystals, m. p. 169—170°. It is hydrolysed by concentrated hydrochloric acid to *trans-p*-dimethylaminocinnamic acid, m. p. 220° (*perchlorate*, colourless prisms, m. p. 196—197°). *Ethyl trans-p-dimethylaminocinnamate*, prepared by esterification of the acid with ethyl alcohol and hydrogen chloride but apparently not obtainable from *p*-dimethylaminobenzaldehyde and ethyl acetate, crystallises in pale yellow leaflets, m. p. 76—78°. The methyl ester is converted by methyl iodide into *methyl trans-p-dimethylaminocinnamate methiodide*, pale yellow leaflets, m. p. 174—176° when slowly, 186° when rapidly, heated. An aqueous solution of the latter is converted by moist silver oxide into *trans-p-aminocinnamic acid trimethylbetaine*.

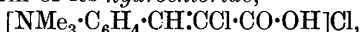
${}^+\text{NMe}_3\text{·C}_6\text{H}_4\text{·C—H}$ (annexed formula), colourless, lustrous leaflets, decomp. 214—220°. The substance contains half a molecular proportion of water of crystallisation which cannot be removed without decomposing the betaine. The *hydrochloride*, $[\text{NMe}_3\text{·C}_6\text{H}_4\text{·CH:CH·CO}_2\text{H}]\text{Cl}$, colourless leaflets, m. p. 240° (decomp.), after darkening at 215° and softening at 210°, the *hydrobromide*, colourless, rhombic crystals, m. p. 225—230° (decomp.) after darkening at 210°, the *iodide* (from *p*-dimethylaminocinnamic acid and methyl iodide or from the betaine and hydriodic acid), pale yellow crystals, m. p. 190—191°, and the *perchlorate*, colourless, lustrous needles, are described.

The stereochemical configuration of the dimethylaminocinnamic acid is established in the following manner. *trans*-Cinnamic acid is nitrated to *trans-p-nitrocinnamic acid*, m. p. 286°, which is also obtained by the condensation of *p*-nitrobenzaldehyde with anhydrous sodium acetate in the presence of acetic anhydride. The nitro-acid is reduced to the amino-acid, which is converted into its methyl ester. The amino-acid is transformed by methyl iodide and sodium hydroxide into *trans-p*-dimethylaminocinnamic acid, m. p. 220°, which is identical with the product obtained from *p*-dimethylaminobenzaldehyde.

The constitution of the betaine just described is somewhat obscured by the presence of water of crystallisation. The following

series of experiments was therefore performed. Methyl *trans*-*p*-dimethylaminocinnamate is converted by bromine into the corresponding dibromide, a viscous, yellow liquid, which is converted by warm glacial acetic acid into methyl *trans*- α -bromo-*p*-dimethylaminocinnamate, m. p. 96°. The ester is converted by hydrochloric acid into *trans*- α -bromo-*p*-dimethylaminocinnamic acid, greenish-yellow leaflets, m. p. 175—176°. The methyl ester, when treated with methyl iodide, gives *methyl trans*- α -bromo-*p*-dimethylaminocinnamate methiodide, pale yellow leaflets, m. p. 171—172°, which is transformed by moist silver oxide into *trans*- α -bromo-*p*-amino-cinnamic acid trimethylbetaine, $\text{NMe}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}^+ \cdot \text{CBr} \cdot \text{CO} \cdot \text{O}$, long, colourless needles, m. p. 222° (decomp.) after softening at 218—219°. The corresponding *hydrochloride*, colourless needles, which darken at 205° but do not melt below 250°, and the *hydrobromide*, small, colourless needles which become brown at 190° but do not melt below 250°, are described.

trans- α -Chlorocinnamic acid, m. p. 139° (cf. Sudborough and James, T., 1906, **89**, 107), is converted by fuming nitric acid into *trans*- α -chloro-*p*-nitrocinnamic acid, pale yellow needles, m. p. 220—221° (*cis*- α -chlorocinnamic acid gives a nitro-acid, m. p. 152—153°), which is reduced by ferrous sulphate and ammonia to *trans*- α -chloro-*p*-aminocinnamic acid, which becomes brown at 219° but does not melt below 250°; the acid is conveniently characterised by conversion into its *methyl* ester, pale yellow needles, m. p. 123°; the *hydrochloride* of the acid was analysed. The acid is converted by methyl iodide and sodium hydroxide into the betaine, which is isolated in the form of its *hydrochloride*,



pale yellow needles, which darken at about 170°, soften at about 200°, but do not melt below 250°. The corresponding *perchlorate*, colourless leaflets, which darken between 230° and 240°, soften at 250—255°, but are not completely melted below 280°, is described. The free *betaine* is prepared by heating an aqueous solution of the purified hydrochloride with silver oxide; it crystallises in colourless needles, m. p. 252—256°, after previous darkening. H. W.

Abietic Acid and certain Metal Abietates. LAWRENCE L. STEELE (*J. Amer. Chem. Soc.*, 1922, **44**, 1333—1341).—Abietic acid may be prepared readily by boiling white rosin with 98% acetic acid under a reflux condenser for two hours and then, after filtering the mixture, leaving it overnight. The acid, when recrystallised from 98% acetic acid, has m. p. 161—165°; n_D^{20} 1.510, n_D^{25} 1.578, n_D^{30} 1.618; $[\alpha]_D^{20}$ —80.0°, iodine value (Wijs) 168.5—171.1, acid value 186. A number of abietates were prepared by adding a neutral solution of sodium abietate to an excess of an aqueous solution of a salt of the metal. All the abietates prepared, with the exception of the basic chromium salt, were soluble in benzene. The abietates described are those of lead, manganese, cobalt, nickel, chromium, and iron. W. G.

A Variety of Wax from Pine Needles and certain Abietic Esters. H. P. KAUFMANN and M. FRIEDEBACH (*Ber.*, 1922, **55**, [B], 1508—1517).—The dried residue left after the distillation of pine needles with steam is extracted with ether, benzene, and carbon disulphide, thereby giving a dark green, viscous mass the weight of which does not exceed 8—10% of that of the crude material and varies greatly with the season of the year. The isolation of the wax, m. p. 64—65°, can be effected by repeated crystallisation of the green mixture from alcohol, but the process is considerably complicated by the presence of relatively large amounts of resin derived from the twigs (the complete separation of needles and twigs does not appear to be practicable). It is preferable to extract the residue with cold acetone in which the wax does not dissolve; the residue is distilled under diminished pressure, and the distillate is crystallised repeatedly from ethyl alcohol or acetic acid. The wax is hydrolysed by alcoholic sodium hydroxide solution with unusual difficulty, giving a mixture of cetyl, ceryl, and myricyl alcohols. Stearic, palmitic, and hydroxypalmitic acids are present.

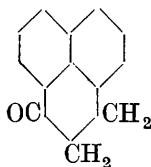
The portion of the crude green wax which is soluble in acetone is a fat-like mass which contains phytosterol, and oleic, stearic, and abietic acids in the form of their esters; the presence of free abietic acid could not be established.

Cetyl abietate, a yellow, waxy mass, m. p. 40°, is prepared by the action of cetyl iodide on silver abietate at 140°. *Myricyl abietate* is a dark brown, brittle substance resembling shellac. H. W.

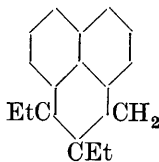
Investigations and Ring Closures in the Series of the Methylnaphthalenes. FRITZ MAYER and ADOLF SIEGLITZ [with E. FISCHER, J. HAGEN, R. JUNG, W. KNIES, C. KOHL, F. LISTMANN, W. NEUGEBAUER and TH. SCHULTE] (*Ber.*, 1922, **55**, [B], 1835—1859).—The bromination of α -methylnaphthalene in carbon disulphide solution in the absence of light gives mainly 4-bromo-1-methylnaphthalene, b. p. 162—164°/12 mm. (picrate, m. p. 123—124°), and 4-bromo-1-bromomethylnaphthalene. The position of the bromine atom in the former is established by its conversion into 1-methylnaphthalene-4-carboxylic acid, colourless crystals, m. p. 175° (*methyl* ester, b. p. 192—194°/12 mm.; *ethyl* ester, b. p. 203°/12 mm.; *chloride*, b. p. 150—160°/12 mm.; *amide*, colourless needles, m. p. 193°; *anilide*, colourless needles, m. p. 179°). The ethyl ester is transformed through the *hydrazide* (colourless needles, m. p. 154°) into the *urethane*, pink needles, m. p. 96°, from which the previously obtained 4-amino-1-methylnaphthalene, m. p. 51°, is derived. 1-Methyl-4-naphthoyl chloride is converted by benzene and aluminium chloride into 4-benzoyl-1-methylnaphthalene, m. p. 174—175°, which is transformed by aluminium chloride at 150° into 4-methylperibenzanthrone, m. p. 115°. 4-Bromo-1-methylnaphthalene is oxidised by dilute nitric acid to 4-bromonaphthalene-1-carboxylic acid, colourless needles, m. p. 212° (*methyl* ester, colourless needles, m. p. 42°, b. p. 195—200°/15 mm.). The oxidation of 4-methylnaphthalene-1-carboxylic acid by permanganate in alkali

line solution gives *naphthalene-1 : 4-dicarboxylic acid*, colourless rods, m. p. 288° (*methyl ester*, m. p. 64°, b. p. 195—197°/12 mm.).

α -Naphthylmethyl bromide yields $\alpha\beta$ -di-1-naphthylethane, m. p. 161—162°, when treated with magnesium and ether and subsequently with acetaldehyde. It is converted by sodium and ethyl acetoacetate into *ethyl α -1-naphthylmethylacetoacetate*, b. p. 204·5—206°/12 mm., which is transformed by aqueous sodium hydroxide into naphthylpropionic acid and *α -1-naphthylbutane- γ -one*, b. p. 186—187°/12 mm. (*semicarbazone*, m. p. 176—177°; *oxime*, needles, m. p. 89—91°). Reduction of the ketone with amalgamated zinc and hydrochloric acid gives *α -1-naphthylbutane*, a colourless, mobile liquid, b. p. 151—152°/14 mm. α -Naphthylmethyl bromide reacts with ethyl malonate and sodium to give *ethyl α -naphthylmethylmalonate*, b. p. 221°/11 mm. [An intermediate fraction contains a nuclear brominated methyl naphthalene, b. p. 161—162°/11 mm. (*picrate*, m. p. 127—128°), which is not identical with 4-bromo-1-methylnaphthalene; on oxidation, it yields small amounts of a *bromonaphthalenecarboxylic acid*, m. p. 215—216°.] The ester is hydrolysed to *α -naphthylmethylmalonic acid*, m. p. 160—163°, which gives β -1-naphthylpropionic acid, m. p. 151°, when heated. The latter acid is converted by thionyl chloride into the corresponding *chloride*, b. p. 187°/12 mm. (*amide*, leaflets, m. p. 85°), which is transformed by aluminium chloride in the presence of light petroleum into 7 : 8-*dihydrophenalene-9** (annexed



formula), yellow leaflets, m. p. 85—86° (*oxime*, m. p. 124—125°). α -Naphthylmethyl bromide and ethyl ethylmalonate yield *ethyl α -naphthylmethylethylmalonate*, b. p. 227°/12 mm., from which *α -naphthylmethylethylmalonic acid*, needles, m. p. 151—153°, is obtained. The latter loses carbon dioxide at 150—160° and passes into *α -1-naphthylmethylbutyric acid*, b. p. 223—227°/15 mm. *α -1-Naphthylmethylbutyryl chloride*, b. p. 188°/12 mm. (corresponding *amide*, m. p. 132°), is transformed by aluminium chloride in the presence of light petroleum into δ -*ethyl-7 : 8-dihydrophenalene-9*, a viscous, yellow liquid, b. p. 195°/15 mm., which is reduced by amalgamated zinc and hydrochloric acid to 8-*ethyl-7 : 8-dihydrophenalene*, b. p. 167—168°/16 mm. The phenalene is transformed by magnesium ethyl bromide and distillation into 7 : 8-*diethylphenalene* (annexed formula), a yellow, odourless liquid, b. p. 185°/13 mm. The latter is oxidised by potassium permanganate to hemimellitic acid.



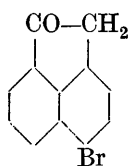
α -Naphthylmethyl bromide and hexamethylenetetramine give an additive *compound*, colourless needles, m. p. 175—179° (indefinite), which is readily transformed into α -naphthaldehyde, b. p. 150—152°/13 mm. The latter is converted by nitromethane into α -1-

* As the name in use, *perinaphthindanone*, is incorrect (cf. Stelzner, *Lit.-Reg. org. Chem.*, 3, 41, 62) the author suggests that the parent hydrocarbon should be termed "*phenalene*," an abbreviation of the structural name *periphenonaphthalene*.

naphthyl-β-nitroethylene, $C_{10}H_7 \cdot CH:CH \cdot NO_2$, yellow needles, m. p. 87.5° , which is reduced by aluminium amalgam in the presence of ether to *α-naphthylacetaldoxime*, $C_{11}H_7 \cdot CH_2 \cdot CH:N \cdot OH$, colourless needles, m. p. 118° . Treatment of the oxime with sodium amalgam, acetic acid, and alcohol gives *α-naphthylethylamine*, $C_{10}H_7 \cdot CH_2 \cdot CH_2 \cdot NH_2$, b. p. $170-173^\circ/16$ mm. (*hydrochloride*, m. p. $243-248^\circ$; *acetyl derivative*, colourless needles, m. p. 91°). The amine is also prepared from *β-1-naphthylpropionic acid* by successive conversion into the corresponding *hydrazide*, needles, m. p. $125-126^\circ$, *azide*, and *urethane*, colourless, lustrous leaflets, m. p. $50-51^\circ$ and hydrolysis of the latter.

4-Bromo-α-naphthylmethyl bromide, needles, m. p. $103-104^\circ$, is converted by alcoholic sodium ethoxide solution into *4-bromo-α-naphthylmethyl ethyl ether*, b. p. $185-187^\circ/17$ mm.

α-4-Bromonaphthylacetonitrile, needles, m. p. 82° , is hydrolysed to *α-4-bromonaphthylacetic acid*, colourless needles, m. p. $149-150^\circ$. The corresponding *chloride*, a yellow liquid, b. p. $110-112^\circ/12$ mm., and *amide*, colourless needles, m. p. 182° , are described. The chloride is transformed by aluminium chloride in the presence of nitrobenzene into *5-bromoacenaphthenone*, colourless needles, m. p. $174-175^\circ$ (*oxime*, needles, m. p. $215-216^\circ$).



4-Bromo-α-naphthylmethyl bromide reacts with ethyl sodiomalonate to give *ethyl 4-bromo-α-naphthylmethylmalonate*, leaflets, m. p. 55° , b. p. $237^\circ/14$ mm., which is transformed by boiling glacial acetic and hydrochloric acids into *β-4-bromo-α-naphthylpropionic acid*, leaflets, m. p. 148° ; the *chloride* of the latter, b. p. $195^\circ/10$ mm., is converted by aluminium chloride into *7:8-dihydrophenalene-9* (see above).

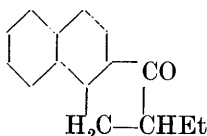
4-Bromo-α-naphthaldehyde, colourless needles, m. p. 85° , is prepared from *4-bromo-α-naphthylmethyl bromide* and hexamethylenetetramine and is converted by sodium acetate and acetic anhydride at $160-165^\circ$ into *β-4-bromo-α-naphthylacrylic acid*, slender, pale yellow needles, m. p. $250-251^\circ$.

β-4-Methoxy-α-naphthylpropionic acid is transformed successively into the *chloride* and *7:8-dihydrophenal-9-one*.

1-Bromo-2-methylnaphthalene, b. p. $165-170^\circ/13$ mm., $290-295^\circ/760$ mm. (*picrate*, m. p. 113°), is converted in the manner described for the *α-series* into *2-methylnaphthalene-1-carboxylic acid*, colourless prisms, m. p. $126-127^\circ$. The acid cannot be esterified with alcohol and hydrogen chloride; its oxidation to a dicarboxylic acid could not be effected. The *chloride*, b. p. $170-172^\circ/20$ mm., *ethyl ester* (from the chloride), b. p. $180-183^\circ/15$ mm., *methyl ester*, b. p. $168-170^\circ/15$ mm., *amide*, m. p. 143° , and *anilide*, m. p. $167-168^\circ$, are described. The ester is transformed by an ethereal solution of hydrazine hydrate into a mixture of *bis-2-methyl-1-naphthoylhydrazine*, m. p. 234° , and the normal *hydrazide*, cubes, m. p. 164° . The latter is converted in the usual manner into the

urethane, m. p. 135°, and 1-amino-2-methylnaphthalene. 1-Benzoyl-2-methylnaphthalene, prisms, m. p. 74°, b. p. 240—245°/15 mm., is prepared from 2-methyl-1-naphthoyl chloride and benzene or from benzoyl chloride and 2-methylnaphthalene in the presence of aluminium chloride; it is transformed by aluminium chloride into 6-methylbenzanthrone, bronze-coloured leaflets, m. p. 195°. 1-Bromo-2-methylnaphthalene is converted by the successive action of magnesium in the presence of ether and methyl sulphate into 1:2-dimethylnaphthalene, b. p. 137°/13 mm., $d_4^{19.0}$ 1.0118 [d_4^{20} 1.011], n_D^{19} 1.60691, n_D^{19} 1.61461, n_D^{19} 1.63613, n_D^{20} 1.6142, (picrate, m. p. 129° after softening at 126°).

β -Naphthylmethyl bromide has b. p. 168—172°/12 mm., Its magnesium compound is converted by acetaldehyde into $\alpha\beta$ -di-2-naphthylethane, m. p. 182°. β -Naphthylmethyl bromide and ethyl sodioacetoacetate give ethyl β -naphthylmethylacetoacetate, b. p. 218—220°/13 mm., which is hydrolysed by methyl alcoholic potassium hydroxide solution to β -2-naphthylpropionic acid and α -2-naphthylbutane- γ -one, m. p. 50°, b. p. 190—200°/13 mm. (oxime, needles, m. p. 115—116°; semicarbazone, needles, m. p. 173°). The ketone is reduced to α -2-naphthylbutane, b. p. 125—130°/13 mm. Ethyl β -naphthylmethylmalonate has b. p. 214—216°/13 mm., and is hydrolysed to β -naphthylmethylmalonic acid, needles, m. p. 94—95°, from which β -2-naphthylpropionic acid, leaflets, m. p. 134—135°, is prepared. The chloride of the latter acid, m. p. 54°, is converted by aluminium chloride in the presence of light petroleum into 4:5-benzoindan-1-one, colourless needles, m. p. 103°. Ethyl β -naphthylmethylethylmalonate, a colourless liquid, b. p. 225—227°/13 mm., is converted successively into β -naphthylethylmalonic acid, colourless crystals, m. p. 150°, α -2-naphthylmethyl-n-butyric acid, b. p. 225—227°/13 mm. (ethyl ester, b. p. 159—196°/13 mm., amide, needles, m. p. 108°), α -2-naphthylmethyl-n-butyryl chloride, a heavy liquid, b. p. 190—195°/13 mm., and 2-ethyl-4:5-benzoindan-1-one (annexed formula), colourless needles, m. p. 54°, b. p. 195—200°/13 mm., the oxime and semicarbazone of which could not be prepared. 2-Ethyl 4:5-benzoindane has b. p. 157—160°/14 mm. 2:3-Diethyl-4:5-benzoindene, b. p. 205—207°/16 mm., is oxidised by nitric acid to mellophanic acid.



β -Naphthylmethyl bromide and hexamethylenetetramine give an additive compound, colourless leaflets, decomp. 160°, from which β -naphthaldehyde, m. p. 61°, b. p. 155—160°/13 mm., is prepared in 70—80% yield. The aldehyde is converted by nitromethane into β -nitro- α -2-naphthylethylene, yellow needles, m. p. 123°, which is reduced to β -naphthylacetaldoxime, colourless, lustrous needles, m. p. 120°, and β -2-naphthylethylamine, b. p. 160—165°/15 mm., [hydrochloride, m. p. 250° (decomp.)]; acetyl derivative, m. p. 109—110°].

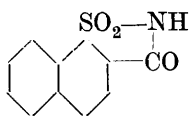
1-Bromo- β -naphthylmethyl bromide, needles, m. p. 107—108°,

prepared by the bromination of 1-bromo-2-methylnaphthalene at 240—245°, is converted successively into 1-bromo- β -naphthylacetonitrile, needles, m. p. 127·5°, and 1-bromo- β -naphthylacetic acid, needles, m. p. 194° (*methyl ester*, b. p. 210—215°/18 mm.). It is transformed by hexamethylenetetramine into 1-bromo-2-naphthaldehyde, needles, m. p. 118° (*oxime*, m. p. 164—166°), which is oxidised to 1-bromo-2-naphthoic acid, needles, m. p. 186°. With ethyl sodiomalonate, the bromide gives *ethyl 1-bromo- β -naphthylmethylmalonate*, leaflets, m. p. 79—80°, b. p. 250—260°/15 mm., which after hydrolysis and loss of carbon dioxide yields β -1-bromo-2-naphthylpropionic acid, leaflets, m. p. 125° (*methyl ester*, m. p. 86—87°, *chloride*, b. p. 210—220°/20 mm., *amide*, needles, m. p. 164°). 4-Bromo-5:6-benzoinstan-1-one, $C_{10}H_5Br \begin{smallmatrix} CH_2 \\ \diagup \quad \diagdown \\ CO \end{smallmatrix} CH_2$, has m. p. 152° [*oxime*, m. p. 222—225° (decomp.)]. Reduction by Clemmensen's method gave a somewhat impure hydrindene, m. p. 92°. H. W.

Isomeric Sulphonimides of Naphthoic Acid, a Contribution to the Theory of Dulcegenic Groups. H. P. KAUFMANN and H. ZOBEL (*Ber.*, 1922, 55, [B], 1499—1508).—A series of substances is described which have a constitution analogous to that of "saccharin" but contain the naphthalene instead of the benzene nucleus. In chemical behaviour they resemble "saccharin" very closely. Unlike the latter, however, they have a pronouncedly bitter taste, which is still more marked in their freely soluble salts with the alkali metals.

β -Naphthylamine-1-sulphonic acid is diazotised and the product is converted by potassium cuprocyanide solution into 2-cyanonaphthalene-1-sulphonic acid, the potassium salt of which is transformed by phosphorus pentachloride and phosphoryl chloride at 140° into 2-cyanonaphthalene-1-sulphonyl chloride, pale yellow needles, m. p. 92°. The latter is converted by an excess of ammonia dissolved in boiling alcohol into 2-cyanonaphthalene-1- ψ -sulphonamide, $C_{10}H_6 \begin{smallmatrix} SO_2 \\ \diagup \quad \diagdown \\ C(NH_2) \end{smallmatrix} N$, large, colourless cubes which do not melt below 300°, and is transformed by hot aqueous sodium hydroxide solution into 2-naphthoic-1-sulphonimide ["naphthasaccharin I"] (annexed formula), m. p. 267° (decomp.); the corresponding sodium salt, cubes (+ 2H₂O) and lead salt, anhydrous needles, are described. The sulphonimide condenses with resorcinol in the presence of concentrated sulphuric acid at 150—180° with the production of the corresponding *sulphurein*, $C_{23}H_{14}O_6S$.

The preparation of 1-naphthoic-2-sulphonimide ["naphthasaccharin II"] has been described independently by Kalcher (cf. Behrend, A., 1918, i, 413). 1-Cyanonaphthalene-2-sulphonamide, colourless crystals, m. p. 294°, is obtained by the action of the calculated quantity of ammonia on 1-cyanonaphthalene-2-sulphonyl



chloride dissolved in benzene (the corresponding compound obtained by Kalcher is regarded as the ψ -amide). 1-Naphthoic-2-sulphonimide is converted by resorcinol and aluminium chloride into the "saccharein," $C_{23}H_{15}O_5NS$, and by resorcinol and concentrated sulphuric acid into the *sulphurein*, $C_{23}H_{14}O_6S$.

3-Amino-2-naphthoic acid is diazotised and the diazonium compound is transformed into the disulphide, which is reduced by powdered iron in boiling alkaline solution to 3-thiol-2-naphthoic acid. Oxidation with potassium permanganates converts the latter into 3-sulpho-2-naphthoic acid which, with phosphorus pentachloride at 140° , gives the corresponding *dichloride*, pale yellow prisms, m. p. 159° . The latter is transformed by ammonium carbonate into the 2-naphthoic-3-sulphonimide, slender, colourless needles, m. p. 288° ; the *sodium* salt, cubes ($+2H_2O$), and *lead* salt, anhydrous, colourless needles, are described.

1-Cyanonaphthalene-8- ψ -sulphonamide, cubes which do not melt below 300° , is prepared from α -naphthylamine-8-sulphonic acid through the cyanosulphonic acid and the corresponding chloride. It is converted by aqueous sodium hydroxide solution into the 1-naphthoic-8-sulphonimide, colourless needles, m. p. 255 – 265° (decomp.); the corresponding *sodium* salt, cubes ($+2H_2O$), and *lead* salt, colourless, anhydrous needles, are described. H. W.

4-Nitrosalicylic Acid. HEISABURÔ KONDÔ, TOMOICHI NAKAJIMA, and GORÔ MURAKAWA (*J. Pharm. Soc. Japan*, 1922, 355–369).—Ullmann and Uzbachian (A., 1903, i, 626) oxidised 4-nitro-2-acetylaminotoluene with potassium permanganate, and regarded the product as 5-nitro-2-acetylaminobenzoic acid (from its m. p. 221° , etc.). The authors have repeated the work and obtained light yellow needles, m. p. 221° , the decomposition of which by boiling with 15% hydrochloric acid gave 4-nitro-2-amino-benzoic acid, yellowish-red needles, m. p. 263 – 264° (decomp.), giving the ethyl ester, yellow plates, m. p. 97 – 98° (Seidel, 89 – 91°). The acid was converted into 4-nitrosalicylic acid, small, yellow needles, m. p. 234 – 235° (Ullmann, 226° ; Borsche, 235°), and its ethyl ester, light yellow needles, m. p. 86 – 87° . It follows that Ullmann and Uzbachian's acid is 4-nitro-2-acetylaminobenzoic acid. The process is recommended for the preparation of 4-nitrosalicylic acid. The latter was reduced electrolytically to 4-amino-salicylic acid, small, slightly coloured plates, m. p. 149 – 151° ; hydrochloride, small, yellow leaves, m. p. 222 – 223° (decomp., Seidel, 220°); it gives a purple-red coloration with ferric chloride.

On the other hand, 4- and 5-nitrosalicylic acids and other compounds were prepared from β -nitrophthalimide according to the directions of Seidel and Bittner (*Monatsh.*, 1891, **23**, 435) for comparison with the compounds above described. Correction of m. p. is given in some cases. Ethyl 5-nitro-2-aminobenzoate has m. p. 150 – 151° (Seidel, 146°). 5-Aminosalicylic acid was prepared electrolytically from 5-nitrosalicylic acid. It is unmelted at 260° ; its acid sulphate, white needles, has m. p. 236 – 237° (Beilstein,

234°); the hydrochloride crystallises in hexagonal plates. Its aqueous solution gives an indigo coloration with ferric chloride, thus differentiating it from the 4-isomerides. K. K.

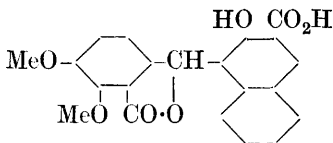
Polysalicylides. V. PAOLINI and S. SCALBA (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 378—380).—Like the acetyl derivative (*Giorn. Chim. Ind. Appl.*, 1921, **3**, 403), other similar derivatives of salicylic acid, such as benzoyl-, propionyl-, and *n*-butyryl-derivatives and the acetyl compound of Boehringer's diplosal or salicylosalicylic acid (A., 1909, i, 803; 1910, i, 386), undergo decomposition when heated at about their melting points, benzoic, propionic, etc., acid being liberated and a colourless or yellow, vitreous, polymerised salicylide or depside, $\left(\text{C}_6\text{H}_4 \begin{array}{c} \text{CO} \\ \diagdown \\ \text{O} \end{array}\right)_n$, formed.

The latter represents a mixture of various polymerides of different complexity, the molecular weight being six to ten times that of salicylide. All these products are converted solely into salicylic acid when hydrolysed by means of alcoholic potassium hydroxide. T. H. P.

Catalytic Racemisation of Optically Active Acid Amides.

ALEX. MCKENZIE and ISOBEL AGNES SMITH (T., 1922, **121**, 1348—1361).

The Condensation of Methyl β -Naphthol-3-carboxylate with Methyl *n*-Opianate. KARL STOSIUS (*Monatsh.*, 1922, **43**, 43—47).—Opianic acid itself does not condense with methyl 2-hydroxy-3-naphthoate, but its methyl ester condenses slowly in ethereal solution in the presence of hydrogen bromide. The condensation is more sluggish than the similar condensation of benzaldehyde with methyl 2-hydroxy-3-naphthoate. The failure of opianic acid itself to condense supports the view that this acid in the free state exists in the pseudo- or lactonic form. The condensation product when the methyl ester is used has a lactonic structure (annexed formula).



2-Carboxy-3:4-dimethoxyphenyl-3-carboxy-2-hydroxy- α -naphthyl-carbinol lactone forms pale yellow crystals, m. p. 193.5°. The disodium salt, $\text{C}_{21}\text{H}_{14}\text{O}_7\text{Na}_2$ crystallises in hygroscopic needles, and the dimethyl ester, $\text{C}_{23}\text{H}_{20}\text{O}_7$, forms pale yellow crystals, m. p. 164°. E. H. R.

The Diphenyleneoxide Series. FRITZ MAYER and WILHELM KRIEGER (*Ber.*, 1922, **55**, [B], 1659—1666).—The constitution of γ -diphenyleneoxide- γ -keto-*n*-butyric and γ -tetrahydrodiphenyleneoxide- γ -keto-*n*-butyric acids has been completely elucidated by the proof that the side chain is attached to the diphenyleneoxide nucleus in position 5.

γ -Diphenyleneoxide- γ -keto-*n*-butyric acid is oxidised by potassium permanganate to diphenyleneoxide-5-carboxylic acid, m. p.

246—247° after softening at 237°. The latter acid is also obtained by the action of bleaching powder on 5-acetyldiphenyleneoxide and from 5-bromodiphenyleneoxide, needles, m. p. 108—109°, b. p. 220°/40 mm., by the successive action of magnesium and carbon dioxide. An acid, m. p. 266°, has been described by Borsche and Bothe as diphenyleneoxide-5-carboxylic acid, but the ultimate proof that the acid, m. p. 246—247°, has this constitution is adduced in the following manner. *p*-Cresol is condensed with *o*-bromonitrobenzene by means of potassium in the presence of naphthalene at 220—230° to 2-nitro-4'-methylidiphenyl ether, $\text{NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{O} \cdot \text{C}_6\text{H}_4\text{Me}$, coarse prisms, m. p. 48—48·5°, b. p. 230—232°/17—18 mm. The latter is reduced by alcoholic ammonium sulphide to 2-amino-4'-methylidiphenyl ether, b. p. 195°/15 mm., which is diazotised and converted into 5-methylidiphenyleneoxide, slender needles, m. p. 45°, b. p. 160°/30 mm.; oxidation of the methyl compound with potassium permanganate gives the acid, m. p. 246—247°.

Ethyl γ -5-diphenyleneoxide- γ -keto-*n*-butyrate, b. p. 260°/2—3 mm., is reduced by amalgamated zinc and hydrochloric acid and the product is re-esterified, thus giving ethyl γ -5-diphenyleneoxide-*n*-butyrate, b. p. 260°/10 mm. Hydrolysis of the latter gives γ -5-diphenyleneoxide-*n*-butyric acid, colourless needles, m. p. 112—113° (chloride, b. p. 170—272°/10—12 mm., amide, colourless leaflets, m. p. 157°). Hydrazine hydrate converts the ester into the corresponding hydrazide, coarse crystals, m. p. 122—123°, which is transformed by sodium nitrite and dilute hydrochloric acid into the azide. The latter is transformed by boiling alcohol into γ -5-diphenyleneoxide-*n*-propylurethane, $\text{C}_{12}\text{H}_7\text{O} \cdot [\text{CH}_2]_3 \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, colourless needles, m. p. 73—74°. Hydrolysis of the urethane with alcoholic potassium hydroxide solution gives γ -5-diphenyleneoxide-*n*-propylamine, b. p. 230—232°/17—18 mm. (hydrochloride, colourless leaflets, m. p. 219—220°, acetyl derivative, colourless needles, m. p. 120°).

γ -5-Diphenyleneoxide- γ -keto-*n*-butyric acid is converted by hydrazine hydrate in boiling alcoholic solution into 3:5-diphenyleneoxidepyridazin-6-one, $\text{C}_{12}\text{H}_7\text{O} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{NH} \\ \diagup \quad \diagdown \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} \text{CO}$, colourless needles, m. p. 199—200°, which is transformed by bromine in hot glacial acetic acid solution into 3:5-diphenyleneoxidepyridazin-6-one, $\text{C}_{12}\text{H}_7\text{O} \cdot \text{C} \begin{smallmatrix} \text{N} - \text{NH} \\ \diagup \quad \diagdown \\ \text{CH} : \text{CH} \end{smallmatrix} \text{CO}$, colourless needles, m. p. 259—260°. 3:5-Diphenyleneoxide-6-chloropyridazine crystallises in leaflets, m. p. 204—205°.

When dissolved in boiling cyclohexanol, diphenyleneoxide is reduced by sodium to tetrahydrodiphenyleneoxide, b. p. 265—270°.

Ethyl γ -5-tetrahydrodiphenyleneoxide- γ -keto-*n*-butyrate, colourless needles, b. p. 277—278°/23 mm., m. p. 68—69°, is reduced by Clemmensen's method to ethyl γ -5-tetrahydrodiphenyleneoxide-*n*-butyrate, b. p. 253—255°/23 mm., and the latter is hydrolysed to

γ-5-tetrahydrodiphenyleneoxide-*n*-butyric acid, silver leaflets, m. p. 119—120°. The ester is converted successively into the corresponding *hydrazide*, colourless needles, m. p. 125·5—126·5°, and *urethane*, colourless needles, m. p. 68—69°. Alkaline hydrolysis of the latter leads to the production of *γ*-5-tetrahydrodiphenyleneoxide-*n*-propylamine, b. p. (about) 220—230°/25 mm. (*hydrochloride*, colourless needles, m. p. 253—254; *acetyl* derivative, leaflets, m. p. 118°). H. W.

Ring-chain Tautomerism. II. The Effect of the *gem*-Diethyl Group on the Carbon Tetrahedral Angle. SHANKAR SHRIDHAR DESHPANDE and JOCELYN FIELD THORPE (T., 1922, **121**, 1430—1442).

amphoric Acid Derivatives. E. S. FAUST (U.S. Pat., 1406547).—Camphoric acid β -diethylaminoethylimide hydrochloride, colourless, lustrous crystals, m. p. 89—90°, is prepared by heating camphoric acid with *as*-diethylethylenediamine at 180—200°, dissolving in ether, and treating with alcoholic hydrogen chloride. Camphoric acid β -piperidylethylimide hydrobromide has m. p. 193·5°, the β -allylaminoethylimide hydrobromide has m. p. 144°, the β -diethylaminoethylimide hydrobromide has m. p. 157°, the β -dimethylaminoethylimide hydrobromide has m. p. 207°, and the β -aminoethylimide hydrobromide has m. p. 135—140° (decomp.). These compounds have therapeutic uses. CHEMICAL ABSTRACTS.

Dyes Derived from Camphoric Anhydride. ANUKUL CHANDRA SIRCAR and SIKHIBHUSAN DUTT (T., 1922, **121**, 1283—1286).

Optically Active Dyes. I. Camphoreins. BAWA KARTAR SINGH, RAGHUNATH RAI, and RATTAN LAL (T., 1922, **121**, 1421—1430).

Vanillin Glyceride. FRANCIS D. DODGE (*J. Amer. Chem. Soc.*, 1922, **44**, 1405—1407).—A crystalline deposit which had formed in a mixture of alcohol, glycerol, and vanillin was shown to be *vanillin glyceride*, m. p. 160—162°, formed by the condensation of 1 molecule of vanillin with 1 molecule of glycerol. The reaction between these two compounds is much accelerated by the presence of mineral acids, but, on the other hand, the resulting glyceride is readily hydrolysed by acids. W. G.

Benzopolymethylene Compounds. IV. The Two *ar*-Aldehydes of Tetrahydronaphthalene [Tetralene]. JULIUS VON BRAUN [with K. MOLDAENKE, H. DIRLAM, and H. GRUBER]. (*Ber.*, 1922, **55**, [B], 1700—1709).—Difficulties are encountered in the conversion of tetrahydronaphthalene into the corresponding aldehydes by the action of carbon monoxide, hydrogen chloride, and aluminium chloride, since the greater part of the hydrocarbon undergoes auto-condensation; the small proportion of alde-

hyde produced appears to consist exclusively of the β -derivative. The α -aldehyde is obtained by the following sequence of changes. *ar*- α -Tetrahydronaphthylamine is diazotised and converted into *ar*- α -tetrahydronaphthonitrile, pale yellow crystals, m. p. 48° , b. p. $153^{\circ}/15$ mm. (cf. Bamberger and Bordt, A., 1889, 715), which is converted by fuming hydrochloric acid at 120° into *ar*- α -tetrahydronaphthoic acid, m. p. 150° . Reduction of the nitrile by sodium and alcohol yields tetrahydronaphthalene and *ar*- α -tetrahydronaphthylmethylamine, a colourless liquid, b. p. 149 — $152^{\circ}/11$ mm.; (the *hydrochloride*, lustrous needles, m. p. 253° , *picrate*, prisms, m. p. 242° , *acetyl* compound, m. p. 125° , *benzoyl* compound, m. p. 144° , *phenylcarbamide*, m. p. 199° , and *phenylthiocarbamide*, m. p. 153° , are described). The amine is converted by sodium nitrite and acetic acid into the corresponding *alcohol*, b. p. 154 — $155^{\circ}/12$ mm., which is oxidised by potassium dichromate and sulphuric acid to *ar*- α -tetrahydronaphthaldehyde, a colourless, almost odourless liquid, b. p. 131 — $133^{\circ}/12$ mm. (*semicarbazone*, m. p. 187°). From the preparative point of view, the difficulty involved in this sequence is due to the poorness of the yields. This has been largely overcome by the subsequent observation that, contrary to the observations of Bamberger and Lotter (A., 1887, 719), α -naphthylmethylamine is directly reducible to *ar*- α -tetrahydronaphthylmethylamine, the process being effected conveniently by sodium and amyl alcohol.

The following derivatives of *ac*- α -tetrahydronaphthylmethylamine are described: *hydrochloride*, m. p. 230° ; *picrate*, m. p. 169 — 170° ; *phenylcarbamide*, m. p. 126° ; *benzoyl* derivative, m. p. 125° . *ar*- β -Tetrahydronaphthonitrile, a colourless liquid, b. p. 151 — $152^{\circ}/11$ mm., m. p. 20 — 21° , is reduced by sodium and ethyl alcohol to *ar*- β -tetrahydronaphthylmethylamine, a colourless liquid, b. p. 146 — $148^{\circ}/11$ mm. (*hydrochloride*, m. p. 248° ; *picrate*, m. p. 215° ; *benzoyl* derivative, long needles, m. p. 165° , b. p. 260 — $265^{\circ}/10$ mm., *p*-nitrobenzoyl compound, m. p. 170° ; *phenylthiocarbamide*, m. p. 130°). The amine is more conveniently prepared by the reduction of β -naphthylmethylamine by sodium and amyl alcohol; the yield is about 90 % of that theoretically possible, but the product appears to be contaminated with very small amounts of the alicyclic derivative. It is converted by sodium nitrite and acetic acid into the corresponding *alcohol*, a pale yellow liquid with a powerful, pleasant odour, b. p. 148 — $152^{\circ}/14$ mm., which is oxidised to *ar*- β -tetrahydronaphthaldehyde, a colourless liquid with an odour of peppermint, b. p. $138^{\circ}/14$ mm. The corresponding *oxime* has little tendency to crystallise; the *semicarbazone* has m. p. 219° . The aldehyde is smoothly oxidised by potassium permanganate to β -tetrahydronaphthoic acid, m. p. 151° . H. W.

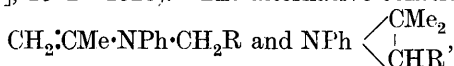
Sulphoacetic Acid as Condensing Agent. IV. iso-Acetovanillone. WILHELM SCHNEIDER and EDGAR KRAFT (Ber., 1922, 55, [B], 1892—1899; cf. A., 1921, 4, 680, 859, 879)—3-Acetoxy-4-methoxyacetophenone [*acetylisoacetovanillone*], colourless
d d *

leaflets or slender needles, m. p. 66° , is prepared by the regulated action of acetic anhydride (350 c.c.) and concentrated sulphuric acid (50 c.c.) on guaiacol (50 grams) at 80° , and is converted by aqueous alkali hydroxide solutions into 3-hydroxy-4-methoxyacetophenone, m. p. (monohydrate) $66-69^{\circ}$, (anhydrous) 91° . The corresponding *oxime*, colourless needles, m. p. 138° , and *semicarbazone*, colourless crystals, m. p. 206° , are described. The constitution of the substance is deduced from its difference from 4-hydroxy-3-methoxyacetophenone [acetovanillone], on the one hand, and from its methylation to 3:4-dimethoxyacetophenone, m. p. $49-50^{\circ}$, and oxidation of the latter to veratric acid, on the other.

Guaiacol is acetylated and anisole is practically unaffected by acetic anhydride containing a trace of concentrated sulphuric acid (2 drops in 40 grams); a perceptible amount of ketone could not be detected in either case.

H. W.

Ketoanils. II. Constitution of the N-Alkylketoanils and Transformation of Aliphatic Ketoanils into Derivatives of Quinoline. E. KNOEVENAGEL and HANS BÄHR (*Ber.*, 1922, 55, [B], 1912—1928).—The alternative constitutions,



have been assigned by Jaeger (*A.*, 1921, i, 785) to the *N*-alkylketoanils obtained by the fission of ketoanil alkylidides with alkali. A decision in favour of the first formula is reached indirectly, since the alkylidides of compounds with the C:N-linking (methiodides of benzylideneaniline, benzophenoneanil and benzophenone-*p*-tolil) are decomposed when distilled in a vacuum into the same products, which do not contain a three-membered ring, as are obtained by the action of water on them. A more direct confirmation of the non-cyclic structure is based on the observation that methylacetone-*p*-tolil ethiodide is identical with ethylacetone-*p*-tolil methiodide.

Acetoneanil is generally converted by methyl iodide into a glassy methiodide which is transformed by sodium hydroxide into isopropenylmethylaniline [as by-products, a *base*, $\text{C}_{22}\text{H}_{30}\text{N}_2$, coarse needles, m. p. 147° , and a *methiodide* (?), m. p. 181° , are isolated]. Acetoneanil is transformed by methyl sulphate into the compound, $\text{C}_{17}\text{H}_{17}\text{O}_4\text{NS}$, silvery leaflets, m. p. 148° , from which methylisopropenylaniline, b. p. $144^{\circ}/14 \text{ mm.}$, is obtained in 88.7% yield by means of sodium hydroxide. The base is transformed by nitrous acid into a compound, m. p. $85-91^{\circ}$; it unites with iodine to form methylisopropenylaniline di-iodide, $\text{NPhMe}\cdot\text{CMeI}\cdot\text{CH}_2\text{I}$, m. p. $138-140^{\circ}$.

Benzophenoneanil methiodide, pale yellow needles, m. p. 120° , is converted by dilute sodium hydroxide into benzophenone and aniline.

Benzophenone-p-tolil methiodide, m. p. 198° , is transformed by boiling methyl alcohol into benzophenonedimethylacetal, $\text{CPh}_2(\text{OMe})_2$,

p-toluidine hydriodide, and methyl alcohol. It is hydrolysed by water to benzophenone and *p*-toluidine.

Acetoneanil methiodide decomposes when distilled in a vacuum into hydrogen iodide and methylisopropenylaniline. Benzophenoneanil methiodide and benzophenone-*p*-tolil methiodide are only decomposed slightly under similar conditions.

The *ethiodide* of methylisopropenylaniline, m. p. 244°, is shown to be identical with the methiodide of ethylisopropenylaniline.

Methylisopropenylaniline is converted by hydrogen chloride at 180–200° into methane, methyl chloride, and 2:4-dimethylquinoline, a pale yellow liquid, b. p. 143°/15 mm. (*hydrochloride*, m. p. 210–215° after darkening at 190°; *picrate*, m. p. 194°, *tartrate*, m. p. 158°); the base is also obtained from acetoneanil by an analogous process.

2:4:6-Trimethylquinoline, m. p. 65·5, b. p. 146–148°/13·5 mm., is prepared from acetone-*p*-tolil; the *hydrochloride*, m. p. 268–272° after darkening at 245°, the *tartrate*, m. p. 172°, and the *methiodide*, pale yellow needles, m. p. 245–247°, are described. The base is also obtained from methylisopropenyl-*p*-toluidine.

2:4-Dimethylquinoline can also be prepared from acetoneanil at 280° by the action of aluminium chloride, or from methylisopropenylaniline, phosphorus, and hydriodic acid at 180–200°.

Methylethylketoanil is converted into 2-methyl-4-ethylquinoline, b. p. 150–153°/14 mm. (*methiodide*, m. p. 246°; *tartrate*, needles, m. p. 149°); the volume of ethane liberated is greater than that calculated, and points to non-uniformity in the base. Methyl-ethylquinoline is oxidised by potassium dichromate and sulphuric acid into 2-methylquinoline-4-carboxylic acid, m. p. 244°.

2:6-Dimethyl-4-ethylquinoline, a pale yellow liquid, b. p. 169–171°/20 mm., is obtained from methylethylketone-*p*-tolil; the *tartrate* has m. p. 173°.

H. W.

Ketoanils. III. Fatty-aromatic Ketoanils. E. KNOEVENAGEL and OSKAR GOOS (*Ber.*, 1922, **55**, [B], 1929–1937).—It has been shown by Knoevenagel and Bähr (preceding abstract) that purely aliphatic ketoanils are convertible into quinoline derivatives; this is also true of the mixed fatty-aromatic compounds.

Acetophenoneanil cannot be prepared by the direct action of aniline and acetophenone (whereby 1:3:5-triphenylbenzene is formed), but is produced from the amine and acetophenoneacetal. It is a pale yellow, crystalline substance, m. p. 41°, which is very readily hydrolysed to acetophenone and aniline; the *hydrochloride* has m. p. 190°. When heated at a temperature just below its boiling point, it yields *dypponanil*, m. p. 98° (2CMePh:NPh = NH₂Ph + CMePh:CH:CPh:NPh, which, when heated further, yields 1:3:5-triphenylbenzene, m. p. 170°. Acetophenoneanil is converted by methyl iodide into *acetophenoneanil methiodide*, colourless rhombohedra, m. p. 209°, and by methyl sulphate into *acetophenoneanil methosulphate*, m. p. 159°; either compound is

decomposed by dilute aqueous alkali hydroxide or carbonate solution into acetophenone and aniline. Acetophenoneanil hydrochloride is converted by hydrogen chloride at 180—190° into benzene, aniline and 4-phenyl-2-methylquinoline, m. p. 97° (tartrate, m. p. 104°).

Deoxybenzoin is converted by ethyl orthoformate in the presence of alcohol and a trace of hydrogen chloride into *deoxybenzoinacetal*, a colourless, highly refractive liquid, b. p. 172°/14 mm. When heated with aniline, it gives *deoxybenzoinanil*, thin, pale yellow prisms, m. p. 74°, b. p. 215°/13 mm.; it is very readily hydrolysed to deoxybenzoin and aniline. The product thus obtained is an isomeric variety (α -form) of the deoxybenzoinanil, m. p. 89° (β -form), prepared by Busch and Falco (A., 1910, i, 747) from benzanilideimide chloride and magnesium benzyl chloride. The α - is converted into the β -variety when it is heated in a vacuum and subsequently distilled. The former is oxidised to α -benzilil, m. p. 96°, whereas the latter gives the isomeric β -benzilil, m. p. 105°. *α -Deoxybenzoinanil hydrochloride* has m. p. 178—179°. *α -Deoxybenzoinanil methosulphate* forms lustrous crystals, m. p. 139°. H. W.

The Intermolecular Condensation of Methyl Ethyl Ketone in the Presence of Calcium Carbide. OSCAR BECKER and JOCELYN FIELD THORPE (T., 1922, **121**, 1303—1306).

Studies in the Anthracene Series. II. EDWARD DE BARRY BARNETT and JAMES WILFRED COOK (T., 1922, **121**, 1376—1391).

Catalytic Reduction of *d*-Camphor. I. SHIGERU KOMATSU and BUNKICHI MASUMOTO (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1922, **5**, 225—232).—*d*-Camphor was hydrogenated over reduced nickel at 175—185°, and the white, crystalline product fractionally distilled. The main fraction, b. p. 164—165°/757 mm., consisted of a hydrocarbon, C₁₀H₁₈; the last fraction, boiling above 175°, was a mixture of *d*-borneol and unchanged camphor, and the intermediate fractions were mixtures of the above substances. The hydrocarbon was a white, crystalline substance with a pleasant odour, having $[\alpha]_D - 1^\circ 35'$, and was apparently *l*-isocamphane identical with that obtained by Lipp by the catalytic hydrogenation of camphene (A., 1911, i, 731). The same substance was also the main product of the catalytic hydrogenation of both *l*-borneol and *d*-borneol, and it is suggested that the transformation of camphor into *isocamphane* occurs through the formation of borneol, which is

dehydrated to an intermediate product, $\begin{array}{c} \text{CH}_2-\text{CH}-\text{CH}_2 \\ | \quad | \\ \text{CH}-\text{CMe}_2-\text{CH} \\ | \\ \text{CMe} \end{array}$, which

isomerises to camphene and is then further hydrogenated to *isocamphane*. G. F. M.

Some Derivatives of Fenchone. T. B. MAXWELL (*Ann. Chim.*, 1922, [ix], **17**, 332—381).—When reduced by sodium in absolute alcohol, dihydrofencholenamide gives an alcohol and an amine. The alcohol is shown to be dihydrofencholenyl alcohol, identical with that obtained by Semmler from methyl fencholate. With thionyl chloride or phosphorus pentachloride, it does not give the normal chloride, but undergoes molecular transposition, giving *tert*-carvomenthyl chloride, $\text{CHMe}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\text{CMeCl}$, b. p. $96^\circ/20$ mm., $d_4^{25.7}$ 0.9368, $n_a^{25.5}$ 1.45971, $n_D^{25.5}$ 1.46202, $n_B^{25.5}$ 1.46811, which was also obtained from carvomenthene by the action of hydrogen chloride. From this chloride by the action of alcoholic ammonia carvomenthene is obtained.

The amine referred to above is shown to be *dihydrofencholenamine*, $\text{CHMe}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{NH}_2 \end{smallmatrix}$, b. p. $90\text{--}91^\circ/16$ mm., and gives a *hydrochloride*, m. p. $171\text{--}173^\circ$ (decomp.); a *sulphate*, m. p. 190° (decomp.); an *acetate*, m. p. 140° (decomp.); an *acetyl* derivative, b. p. $193^\circ/27$ mm., and a *benzylidene* derivative, b. p. $183\text{--}184.5^\circ/21$ mm. The hydrochloride reacts with nitrous acid to give *tert*-carvomenthol, b. p. $100\text{--}102^\circ/13$ mm., $d_4^{24.6}$ 0.91556, $n_a^{24.6}$ 1.45961, $n_D^{24.6}$ 1.46202, $n_B^{24.6}$ 1.46790, and a hydrocarbon which seems to be identical with carvomenthene.

Dihydrofencholenyl alcohol, when distilled over infusorial earth at $400\text{--}450^\circ$ is dehydrated and gives a *hydrocarbon*, $\text{C}_{10}\text{H}_{18}$, b. p. $60\text{--}61^\circ/16$ mm., $d_4^{24.6}$ 0.81550, $n_a^{24.6}$ 1.45211, $n_D^{24.6}$ 1.45474, $n_B^{24.6}$ 1.46146. Its products of oxidation depend on the agent used. With potassium permanganate in acetone solution it gives β -isopropylpentanone. With hydrogen chloride a certain amount of it is converted into a *chloride*, b. p. $96\text{--}99^\circ/21$ mm., $d_4^{21.9}$ 0.91234, $n_a^{21.9}$ 1.45591, $n_D^{21.9}$ 1.45854, $n_B^{21.9}$ 1.46443, whilst the remainder undergoes isomerisation, giving a *hydrocarbon*, b. p. $67\text{--}70^\circ/16$ mm., $d_4^{23.5}$ 0.81220, $n_a^{23.5}$ 1.45521, $n_D^{23.5}$ 1.45804, $n_B^{23.5}$ 1.46503, which gives a *chloride*, b. p. $100\text{--}101^\circ/23$ mm., $d_4^{25.2}$ 0.92814, $n_a^{25.2}$ 1.45721, $n_D^{25.2}$ 1.45964, $n_B^{25.2}$ 1.46582. To the hydrocarbon is assigned the constitution $\text{CHMe}_2\cdot\text{CH}\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ | \\ \text{CH}_2\cdot\text{C}\cdot\text{CHMe} \end{smallmatrix}$ W. G.

The Essential Oil from the Leaves of *Abies Pindrow*, Spach. JOHN LIONEL SIMONSEN (*Indian Forest Rec.*, 1922, **8**, 368—372).—The essential oil was obtained in 2.5% yield by the steam distillation of the leaves of *Abies Pindrow*, a silver fir growing in the western Himalayas. It is a colourless oil with a strong odour of turpentine, and has the following constants:— d_{30}^{20} 0.8558, n_D^{20} 1.4667, $[\alpha]_D^{20}$ -10.38 , saponification number 5.3, do. after acetylation 15.44, acid number 0.3. On distillation, 90% passed over below $120^\circ/100$ mm., and on fractionating this under 699 mm. pressure the following fractions were obtained: $154\text{--}158^\circ$,

55.9% consisting of *d*- α -pinene; 158—160°, 11.9%, and 160—164°, 6.8% consisting of a mixture of α - and β -pinene; 164—167°, 4.2% consisting of *l*- β -pinene; 167—180° 10.3% containing *l*-limonene and possibly dipentene; and above 180° 10.6%, from which and from the fraction boiling above 120°/100 mm., *l*-terpineol, *l*-terpinyl nonoate, and two isomeric sesquiterpene alcohols, $C_{15}H_{24}O$, were isolated. *l*-Terpinyl nonoate boils at 140—145°/50 mm., and the two alcohols were obtained as oils boiling at 155—160°/50 mm., and 180—190°/50 mm., having respectively the constants d_{30}^{30} 0.9076, n_D^{30} 1.4807, $[\alpha]_D^{30}$ - 7.72, and d_{30}^{30} 0.9259, n_D^{30} 1.4915, $[\alpha]_D^{30}$ + 8.1. No crystalline derivatives could be isolated in either case.

G. F. M.

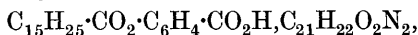
Essential Oil of *Lantana Camara*. K. L. MOUDGILL and P. N. VRIDHACHALAM (*Perf. Essent. Oil Rec.*, 1922, **13**, 173—174).—The essential oil of *Lantana Camara*, a wild shrub growing on waste lands in Southern India, was isolated by steam distillation of the leaves, in a yield of about 0.2%. It is a greenish-yellow, slightly fluorescent oil, having an odour resembling sage. It is soluble in 5 vols. of 97% alcohol, and has the following characters:— d_4^{30} 0.8842, $[\alpha]_D^{30}$ + 14.7, n 1.4899, acid value 1.6, saponification value 4.6, acetyl value 23.4, aldehyde content 2.4%. On distillation, three fractions were obtained: (1) 55—75°/12 mm. 12%, (2) 75—125°/12 mm. 8%, (3) 125—130°/12 mm. 74%. The first fraction proved to be *l*- α -phellandrene, the second contained the odoriferous principles which from the oil constants appear to consist mainly of an aldehyde and an alcohol, the third fraction was mainly a bicyclic sesquiterpene closely resembling, if not identical with, caryophyllene, although the solid caryophyllenic alcohol could not be obtained. On redistilling this fraction under ordinary pressure, the original rotation of +16.1° was changed in the distillate to -2.6°. The change does not appear to be a racemisation, as repeated distillation does not modify or remove the laevorotation.

G. F. M.

Sudan Essential Oils. A. F. JOSEPH and B. W. WHITEFIELD (*J. Soc. Chem. Ind.*, 1922, **41**, 172T).—"Seid" oil is contained to the extent of about 0.5% in the rhizomes of *Cyperus rotundus*, Linn., a glabrous herb growing freely throughout the Sudan. The oil, which has an aromatic, slightly camphoraceous odour, gave the following constants: d_{20}^{20} 0.9548, α^{25} -19.9°, n_D^{25} 1.4967, acid number 1.0, saponification number 6.6, do. after acetylation 105 (corresponding with 45% of alcohol), solubility in 80% alcohol 1 in 4, in 70% alcohol nil.

G. F. M.

Isomeric Amyrols. V. PAOLINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 374—377; cf. von Soden, A., 1900, i, 401; 1901, i, 159).—By means of the double phthalate formed with strychnine, the author has succeeded in separating amyrol into *d*- and *l*-compounds.

Strychnine d-amyryl phthalate,

forms colourless, acicular crystals, m. p. 201° , $[\alpha]_D + 18^\circ 26'$. *d-Amyryl hydrogen phthalate* forms a syrup, and *d-amyrol* a clear, dense, oily liquid of unpleasant odour, b. p. 302° , $d^{15}_4 0.982$, $[\alpha]_D + 74^\circ 16'$.

Silver l-amyryl phthalate forms crystals, m. p. 145° ; *l-amyryl hydrogen phthalate* is oily, and *l-amyrol* is a dense, colourless liquid of unpleasant odour, b. p. 295° , $d^{15}_4 0.980$, $[\alpha]_D - 1^\circ 59'$.

[No analytical results are given for either amyrol.]

T. H. P.

Mercaptothiazoles as Accelerators in Vulcanisation.

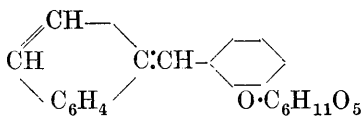
G. BRUNI and E. ROMANI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 86—88; cf. A., 1921, i, 734).—When added to caoutchouc and sulphur in presence of oxide of zinc, lead, magnesium, calcium, mercury, etc., 2-mercapto-5-methylthiazole (cf. Miolati, A., 1893, i, 634), in the proportion of 1—3%, produces ultra-accelerating effects on vulcanisation, which takes place in five minutes at 120° . The zinc, cadmium, lead, mercuric, cobalt, and cuprous salts of this thiazole have been prepared, and the first four of them are found to cause similar accelerating action, which is especially marked with the zinc salt.

5-Methylthiazole sulphide, $(\text{C}_4\text{H}_4\text{NS})_2\text{S}$, prepared by oxidising 2-mercapto-5-methylthiazole by means of potassium ferricyanide, forms crystals, m. p. 64° .

T. H. P.

Syntheses of New Glucosides. REMO DE FAZI (*Gazzetta*, 1922, **52**, i, 429—431; *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 209—212).

—The glucoside of 2-hydroxybenzylideneindene (annexed formula), obtained by the action of sodium ethoxide on indene and helicin in absolute alcoholic solution at the ordinary temperature, crystallises in lustrous, pale yellow needles, m. p. $205\text{--}206^\circ$, and dissolves in concentrated sulphuric acid to a green solution which becomes cherry-red after a few hours.



The glucoside of 2-hydroxybenzylidenefluorene (annexed formula), prepared similarly from fluorene and helicin, forms small, yellow needles, m. p. $198\text{--}200^\circ$, and gives a reddish-brown coloration and then a reddish-violet solution with concentrated sulphuric acid; if the latter is added carefully to a solution of



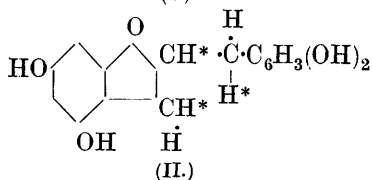
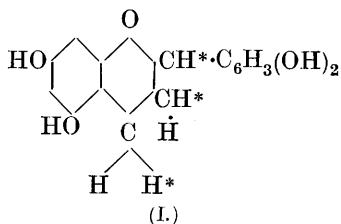
the glucoside in absolute alcohol, a reddish-violet ring appears at the surface of contact of the two liquids.

The *glucoside* of 2-hydroxybenzylideneacenaphthenone (annexed formula), prepared from acenaphthenone and helicin, crystallises in lustrous, pale yellow needles, m.p. 246—248° (decomp.), and dissolves in concentrated sulphuric acid to an orange solution showing green fluorescence. T. H. P.

Benzopyrylium Salts of Distyryl Ketones. JOHANNES SYBRANDT BUCK and ISIDOR MORRIS HEILBRON (T., 1922, **121**, 1198—1212).

Catechin. KARL FREUDENBERG (*Ber.*, 1922, **55**, [B], 1938—1942).—Polemical against Nierenstein (A., 1913, i, 501; T., 1920, **117**, 971, 1151; T., 1921, **119**, 164; T., 1922, **121**, 23).—The author maintains his contention that the tannins are condensation products of catechin-like substances. Attempts to prepare catechin-carboxylic acid according to Nierenstein's directions were unsuccessful, the catechin appearing to be decomposed completely during the action. This is also true of Nierenstein's hydroxycatechin. The catechin-carboxylic acid from *Paullinia* tannin is optically inactive and resolvable: its conversion by loss of carbon dioxide into *d*-catechin (Gambier catechin) is therefore inexplicable. Demethylation of tetramethylcatechin cannot be effected by acetic anhydride and acetyl chloride, and penta-acetylcatechin cannot be hydrolysed to catechin by sulphuric acid as claimed by Nierenstein. The identity of the methylated reduction product of catechin, m. p. 87—88°, with pentamethoxy- $\alpha\gamma$ -diphenylpropane has been confirmed; Nierenstein's synthesis of acacatechin is therefore difficult to understand since his compounds belong to the $\alpha\alpha$ -diphenylpropane group. H. W.

Tannins and Similar Compounds. IX. Stereoisomeric Catechins. II. KARL FREUDENBERG, OTTO BÖHME, and LUDWIG PURRMANN (*Ber.*, 1922, **55**, [B], 1734—1747; cf. A. 1921, i, 576, 799).—It has been shown previously that catechin must be



formulated in accordance with one of the annexed types (I and II), in which one of the hydrogen atoms marked with an asterisk is replaced by the hydroxyl group. If this replacement occurs at the carbon atom united to the oxygen bridge, a single asymmetric carbon atom must be present in catechin, which therefore exists in two active and one racemic form. If, on the other hand, the replacement occurs in a methylene group, two asymmetric carbon atoms are present in catechin,

which therefore exists in two racemic and four active forms.

The latter is shown to be the case, since, under conditions which cause the racemisation of the optically active catechins, *r*-catechin is transformed into *r*-epicatechin, the presence of which is also established in Pegu catechu.

Acacia (Pegu) catechu is exhaustively extracted with ether in a specially designed apparatus which permits the use of large quantities of material and is fully figured and described in the original. The ether is removed from the extract and the residue is crystallised from water whereby mainly *r*- and *l*-catechins are obtained; *l*-epicatechin and *r*-epicatechin are successively obtained from the filtrates, and the fractions are separately purified. *l*-*Epicatechin* crystallises in slender needles and is analysed in the anhydrous condition and as *trihydrate*; the former has decomp. about 228° , $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} - 38.4^{\circ}$ in acetone (50%), $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} - 41.2^{\circ}$ in alcohol (96%). It gives a *penta-acetate*, colourless needles, m. p. $128-129^{\circ}$, $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} - 28.6^{\circ}$ in *s*-tetrachloroethane. *r*-*Epicatechin* crystallises in colourless, thick plates or needles, m. p. 240° (decomp.), and yields a *penta-acetate*, m. p. $169-172^{\circ}$. (The catechin from Chinese rhubarb is shown to be pure *d*-catechin; that from mahogany contains *d*- and *r*-catechin and probably also *d*-epicatechin, but only steamed wood was available for the investigation in which the original catechins had suffered alteration: the catechin from *Paullinia cupana* is similar to that from mahogany.)

d-Catechin *penta-acetate* readily loses four acetyl groups when treated with potassium acetate and boiling alcohol, giving *d-catechin monoacetate*, needles (+2H₂O), m. p. (anhydrous) $120-125^{\circ}$, $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} - 19.9^{\circ}$ in acetone (50%). The fifth acetyl group could only be removed under conditions which caused the complete decomposition of the material. Tetramethyl-*d*-catechin has m. p. $146-147^{\circ}$, $[\alpha]_{\text{D}}^{25} - 12^{\circ}$ in *s*-tetrachloroethane. Exhaustive methylation of *d*-catechin with methyl sulphate gives pentamethyl-*d*-catechin, m. p. $92-93^{\circ}$, $[\alpha]_{\text{D}}^{25} + 8.2^{\circ}$ in *s*-tetrachloroethane. Tetramethyl-*d*-catechin is converted by acetic anhydride and pyridine into tetramethylacetyl-*d*-catechin, m. p. $95-96^{\circ}$, $[\alpha]_{\text{D}}^{25} + 6.8^{\circ}$ in *s*-tetrachloroethane.

d-Catechin generally crystallises with 4H₂O; recrystallisation of a considerable quantity of the substance from water gave a small proportion of the anhydrous *substance*, short, yellow needles, $[\alpha]_{\text{H}_2\text{O}}^{\text{yellow}} + 16.9^{\circ}$ in acetone (50%), $[\alpha] \pm 0^{\circ}$ in alcohol (96%).

The behaviour of *d*-catechin towards gelatin is described; with brucine it gives the additive *compound*, C₁₅H₁₄O₆, C₂₃H₂₆O₄N₂.
H. W.

Reduction of Flavanone. KARL FREUDENBERG and LUDWIG ORTHNER (*Ber.*, 1922, **55**, [B], 1748—1751).—In connexion with their work on the catechins, the authors have prepared flavanol [4-hydroxyflavan], $\text{C}_6\text{H}_4 \begin{array}{l} \text{O} \text{---} \text{CHPh} \\ \diagdown \quad \diagup \\ \text{CH(OH)} \cdot \text{CH}_2 \end{array}$ since the substance possibly represents the parent of catechin (cf. Freudenberg, Böhme, and Purrmann, preceding abstract). It gives a decided, reddish-

pyrrole-3-carboxylate and ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate the nitro-group replaces the acetyl radicle. A similar influence is exerted by the aldehydo-groups. Unexpectedly, the same effect is not produced by the carbethoxy-group since ethyl 2:4-dimethylpyrrole-3:5-dicarboxylate is converted into ethyl 2:4-dinitropyrrole-3:5-dicarboxylate, the methyl groups being replaced by the nitro-residue. Binuclear pyrroles suffer fission at the methylene group uniting the nuclei.

Ethyl 5-acetyl-2:4-dimethylpyrrole-3-carboxylate is converted by nitric acid (*d* 1.4) into *ethyl 5-nitro-2:4-dimethylpyrrole-3-carboxylate*, colourless needles, m. p. 149.5°; it can also be obtained from ethyl 2:4-dimethyl-5-aldehydopyrrole-3-carboxylate, bis-3-carbethoxy-2:4-dimethylpyrrolmethane or bis-3-carbethoxy-2:4-dimethylpyrrolmethene. *5-Nitro-2:4-dimethylpyrrole-3-carboxylic acid*, colourless needles, m. p. 231° (decomp.), is obtained by hydrolysis of the corresponding ethyl ester or by the addition of 5-acetyl-2:4-dimethylpyrrole-3-carboxylic acid to concentrated nitric acid.

Ethyl 3-nitro-2:4-dimethylpyrrole-5-carboxylate, colourless needles, m. p. 204°, is prepared from ethyl 3-acetyl-2:4-dimethylpyrrole-5-carboxylate; *3-nitro-2:4-dimethylpyrrole-5-carboxylic acid* darkens at 240° and becomes carbonised at a higher temperature.

Ethyl 2:4-dinitropyrrole-3:5-dicarboxylate crystallises in pale yellow plates (+H₂O), m. p. 136° (decomp.). When heated above its melting point or at 100° in a vacuum, it loses its water of crystallisation and two molecular proportions of nitric oxide, leaving probably a diketo-pyrrole.

H. W.

Relationships between Constitution and Pharmacological Action in the Cases of the Benzoic and Tropic Esters of Hydroxyalkylamines. JULIUS VON BRAUN, OTTO BRAUNSDORF, and KURT RÄTH (*Ber.*, 1922, **55**, [B], 1666—1680).—A series of hydroxyalkylamines of the types $\text{NR}_2 \cdot (\text{CH}_2)_2 \cdot \text{OH}$, $\text{NR}_2 \cdot [\text{CH}_2]_3 \cdot \text{OH}$, $\text{R} \cdot \text{N} \cdot [\text{CH}_2]_2 \cdot \text{OH}$, and $\text{R} \cdot \text{N} \cdot [\text{CH}_2]_3 \cdot \text{OH}$ have been prepared and the hydroxyl hydrogen atom in them has been replaced by the benzoyl (or *p*-aminobenzoyl) or tropoyl groups. It is found that the benzoates of the γ -alkylamines are generally more active physiologically than those of the β -hydroxy-bases, whereas the reverse is the case with the tropates. With regard to the influence of the number of members in the nitrogen ring, it is shown that the six-membered ring is the most active both with respect to the anæsthetising action of the benzoates and the mydriatic and cardiac action of the tropates. The introduction of carbon chains on the nitrogen ring increases the physiological action, but only to a remarkably slight degree. The introduction of an aromatic ring to the monocyclic nitrogen ring diminishes the physiological action, but exact comparison is very difficult in these cases and, in any case, the effect is not important.

The preparation of the substances follows the general lines. The tertiary β -hydroxyalkylamines are obtained by heating the requisite secondary bases with ethylene oxide in chloroform solution to

which a drop of water had been added at 40—60° during several hours by means of ethylene chlorohydrin. Benzoylation is effected by direct warming with benzoyl chloride in chloroform or by agitation with benzoyl chloride and aqueous alkali. The tropoyl group is introduced by heating the alkylamine hydrochlorides with acetyltropoyl chloride, removal of the acetyl group by cold water, and precipitation of the tropic ester with alkali. The benzoates of the γ -series are prepared by warming the requisite secondary base with γ -bromopropyl benzoate.

The following individual compounds are described. β -Dimethylaminoethyl tropate hydrochloride. γ -Dimethylamino-n-propyl tropate hydrochloride. β -Diethylaminoethyl tropate hydrochloride. γ -Diethylamino-n-propyl tropate hydrochloride (the *platinichlorides*, *hydrobromides*, *picrate*, and *methiodides* of the diethyl compounds are oily). γ -Diethylaminopropyl p-nitrobenzoate, a brown liquid which could not be caused to crystallise (*hydrochloride*, m. p. 185—186°; *platinichloride*, m. p. 181°; *picrate*, needles, m. p. 167°; *methiodide*, m. p. 161°). γ -Diethylaminopropyl p-aminobenzoate, a liquid (*hydrochloride*, a liquid; *picrate*, m. p. 132°; *picrate* of the corresponding *acetyl* derivative, m. p. 164—165°). N- β -Hydroxyethylpyrrolidine, a colourless liquid, b. p. 187—189° (*picrate*, m. p. 96°; *methiodide*) and the *hydrochloride* of the corresponding *benzoate*, m. p. 175° after softening at 170°; the *hydrochloride* of the corresponding *tropate* is a transparent liquid. N- β -Hydroxyethylpiperidine *picrate*, yellow prisms, m. p. 100°, and *methiodide*, colourless leaflets, m. p. 238°; *hydrochloride* of the corresponding *benzoate*, m. p. 171—172°. N- β -Tropoxyethylpiperidine *hydrochloride*, a colourless liquid (*hydrochloride* of the corresponding *acetyl* derivative, m. p. 168°). N- γ -Hydroxypropylpiperidine, a colourless, rather viscous liquid, b. p. 228° (*picrate*, m. p. 63—64°; *methiodide*, m. p. 133°). N- γ -Benzoxypropylpiperidine *hydrochloride*, m. p. 185°. N- γ -Tropoxypropylpiperidine *hydrochloride*, a liquid. Hydroxyethylconiine, a colourless liquid, b. p. 117—118°/13 mm. (the *methiodide* and *picrate* are oily; the unusually hygroscopic *hydrochloride* has m. p. about 150°). β -Benzoxyethylconiine *hydrochloride*, a liquid. N- γ -Hydroxypropylconiine *hydrochloride*, a colourless powder, m. p. 162—163°. N- γ -Benzoxypropylconiine *hydrochloride*, m. p. 181—182°. N- β -Hydroxyethylidihydroisoindeole, $\text{OH}\cdot\text{CH}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{NH}\cdot[\text{CH}]_2\cdot\text{OH}$, a viscous liquid, b. p. 162—164°/12 mm., (*picrate*, m. p. 125°; *methiodide*, m. p. 130°). N- β -Benzoxyethylidihydroisoindeole *hydrochloride*, m. p. 197° (the tropoyl derivative could not be obtained pure). N- γ -Benzoxypropylidihydroisoindeole *hydrochloride*, leaflets, m. p. 178—179° (decomp.); the corresponding *base* is a liquid which cannot be distilled without decomposition. The latter when hydrolysed gives a *base*, $\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$, long prisms, m. p. 63—64°, which contains two atoms of hydrogen and one of oxygen more than the expected γ -hydroxypropylidihydroisoindeole; this is not attributable to the presence of firmly combined water of crystallisation, since the difference persists in the salts (*hydrochloride*, liquid; *platinichloride*, long, yellow

needles, m. p. 123° ; *picrate*, coarse, lustrous crystals, m. p. 84° ; the base, $C_{11}H_{17}O_2N$, gives essentially a *tri-p-nitrobenzoyl* derivative, m. p. $116-118^{\circ}$, which was not obtained in a perfectly homogeneous condition. *N-β-Hydroxyethyltetrahydroisoquinoline*, a colourless, somewhat viscous liquid, b. p. $164-166^{\circ}/12$ mm. (*picrate*, a liquid; *methiodide*, lustrous leaflets, m. p. 147°). *N-β-Benzoxylethyltetrahydroisoquinoline hydrochloride*, m. p. $177-178^{\circ}$. *N-γ-Hydroxypropyltetrahydroisoquinoline*, a transparent, viscous liquid, b. p. $197^{\circ}/13$ mm. (*hydrochloride*, m. p. $151-152^{\circ}$; *picrate*, a liquid; *methiodide*, m. p. 132°). *N-γ-Benzoxylethyltetrahydroisoquinoline hydrochloride*, m. p. 191° ; the *hydrochlorides* of the tropic derivatives of β -hydroxyethyl- and γ -hydroxypropyl-tetrahydroisoquinolines are solid but exceedingly hygroscopic. H. W.

Hexamethyleneimine and its Behaviour on Oxidation.

FRIEDRICH SCHMIDT (*Ber.*, 1922, **55**, [B], 1584—1591).—Attempts are described to convert hexamethyleneimine into hexamethine-

imine, $\begin{array}{c} \text{CH}\cdot\text{CH}\cdot\text{CH} \\ \parallel \\ \text{CH}\cdot\text{CH}\cdot\text{CH} \end{array} \rangle \text{NH}$, the latter being required for the comparison

of its properties with those of ψ -aniline (Schmidt, this vol., i, 777). The isolation of the product has not, however, been effected, α -picoline being obtained in its place. A greatly improved method for the preparation of hexamethyleneimine is described and the substance has been more fully investigated.

Ethyl suberate is converted directly by an excess of hydrazine hydrate into suberdihydrazide, m. p. $185-186^{\circ}$, from which (when perfectly pure material is used) the corresponding di-azide, m. p. 26° , is readily produced. The dry azide is transformed by perfectly dry ethyl alcohol into the ethyl urethane (if somewhat moist azide is employed hexamethylenecarbamide, $[\text{CH}_2]_6 \langle \begin{array}{c} \text{NH} \\ \text{NH} \end{array} \rangle \text{CO}$, and the compound $\text{CO}(\text{NH}\cdot[\text{CH}_2]_6\cdot\text{NH}\cdot\text{CO}_2\text{Et})_2$ are also produced, the latter of which is gelatinous and greatly complicates filtration). The action of concentrated hydrochloric acid on the urethane gives hexamethylenediamine hydrochloride. Alternatively, the azide is decomposed by ebullition of its solution in anhydrous ether into *hexamethylenedicarbimide*, $\text{C}_6\text{H}_{12}(\text{N}\cdot\text{CO})_2$, a colourless liquid, b. p. 255° , which is readily converted by concentrated hydrochloric acid into carbon dioxide and hexamethylenediamine hydrochloride. The conversion of the diamine into the imine takes place with remarkable readiness, and is conveniently effected by heating the diamine hydrochloride in small portions over a free flame until local carbonisation begins to be observed; the product is rendered alkaline and distilled with steam when the imine is volatilised, whereas the unchanged diamine is not volatile. Hexamethyleneimine is a colourless, mobile liquid with a strong odour of piperidine. It has b. p. $126-127^{\circ}$, d^{15}_4 0.829 [the *picrate* (described previously as a liquid) forms pale yellow crystals, m. p. 85° ; the *hydrochloride* is very hygroscopic, the *platinichloride* crystallises in pale yellow platelets, m. p. 191°

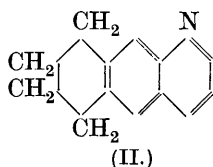
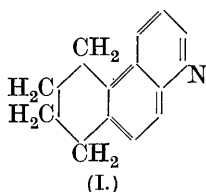
(decomp.), after softening and darkening at about 185° (von Braun has described a monohydrate, m. p. 148°)]. The identity of hexamethyleneimine obtained in this manner with the product described by von Braun is placed beyond doubt by a comparison of the completely methylated products. *Acetylhexamethyleneimine* is a colourless liquid, b. p. 239—241°.

The regulated oxidation of hexamethyleneimine is a problem of considerable difficulty; when dissolved in acetic acid and treated with silver acetate at 180° it gives α -picoline. H. W.

Preparation of *N*-Substituted 3-Dihalogenoxindoles.

ROBERT STOLLÉ (D. R.-P., 341112; from *Chem. Zentr.*, 1922, ii, 35—36; cf. A., 1921, i, 596).—A modification of an earlier patent whereby *N*-trihalogen acetyl derivatives of secondary alkylaryl- or diaryl-amines of the general formula $\text{NRR}'\cdot\text{CO}\cdot\text{CX}_3$ ($\text{R}=\text{alkyl}$ or aryl, $\text{R}'=\text{aryl}$, $\text{X}=\text{halogen}$) are heated with aluminium haloids. Ring formation takes place whereby the *N*-dihalogen oxindole derivative is formed with elimination of the corresponding hydrogen haloid, a halogen atom of the trihalogen acetyl group combining with the hydrogen in the ortho-position to the amino-group. 3-Dichloro-1-phenyloxindole is formed by the action of aluminium chloride on trichloroacetyldiphenylamine (from trichloroacetyl chloride and diphenylamine, m. p. 86°) in carbon disulphide solution at the ordinary temperature. By the action of alkalis on it 1-phenylisatin or sodium 1-phenylisatinate are obtained. Trichloroacetylmethylanilide (Spiegel and Spiegel, A., 1907, i, 507, 508) gives with aluminium chloride, 3-dichloro-1-methyloxindole. It has m. p. 145° after recrystallisation from methyl alcohol. G. W. R.

Benzopolymethylene Compounds. V. Synthesis of α -Anthrapyridine [Naphthazine] from Tetralin [Tetrahydronaphthalene]. JULIUS VON BRAUN and HEINRICH GRUBER (*Ber.*, 1922, 55, [B], 1710—1717).—*ar*- β -Tetrahydronaphthylamine is converted by glycerol, concentrated sulphuric acid, and nitrobenzene into a mixture of 5:6- and 6:7-tetramethylenequinolines [7:8:9:10-tetrahydro- β -naphthaquinoline (I) and 6:7:8:9-tetra-



hydronaphthazine (II)] which can be separated from one another by taking advantage of their widely differing solubilities in hot ethyl alcohol. The former is a colourless crystalline substance,

m. p. 158°, b. p. 183—185°/12 mm., which becomes pink on exposure to air. The hydrochloride, m. p. 236° after darkening at 226°, picrate, m. p. 207°, and methiodide, m. p. 203°, are described. The constitution of the base is established by its dehydrogenation at 700° to β -naphthaquinoline, m. p. 91—92°.

6 : 7 : 8 : 9-Tetrahydronaphthazine is a colourless, crystalline substance, m. p. 71—72°, b. p. 187°/11 mm. It gives a *hydrochloride*, pale yellow needles, m. p. 177°, a *picrate*, m. p. 269·5°, and a *methiodide*, m. p. 187°. The base is dehydrogenated at 720° to naphthazine, colourless crystals, m. p. 114°, b. p. 200—250°/14 mm. The corresponding *hydrochloride*, intensely yellow crystals, m. p. 196—197° after softening at 191°, the *picrate*, m. p. 258° after darkening at 229°, and the *methiodide*, m. p. 225—226°, are described. The base is oxidised by chromic acid in warm glacial acetic acid solution to naphthazinequinone, $C_6H_4 \begin{smallmatrix} \diagup CO \\ \diagdown CO \end{smallmatrix} C_5H_3N$, long, yellow needles, m. p. 280°. Treatment of naphthazine with tin and concentrated hydrochloric acid effects hydrogenation of the pyridine nucleus, thus giving 1 : 2 : 3 : 4-tetrahydronaphthazine, $C_6H_4 \begin{smallmatrix} \diagup CH \\ \diagdown CH \end{smallmatrix} C_5H_7N$, lustrous leaflets, m. p. 149°. The *hydrochloride* has m. p. 229°. The secondary nature of the base is established by its smooth conversion into a *nitroso*-derivative, golden-yellow leaflets, m. p. 129°. H. W.

Iodo-derivatives of Pyrrole. ANTONIO PIERONI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 321—323).—When treated with aqueous potassium hydroxide and iodine, pyrrole-3-carboxylic acid, acetyl- and benzoyl-pyrroles, and indole-2- and indole-3-carboxylic acids undergo iodination, yielding various products in each case. In presence of the required proportion of iodine dissolved in potassium iodide solution and of excess of the alkali, either pyrrole or pyrrole-2-carboxylic acid yields principally tetraiodopyrrole and hepta-

*i*iododipyrryl, $\begin{array}{c} \text{Cl}-\text{Cl} \\ \parallel \\ \text{Cl} \cdot \text{NH} \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} \text{C} \cdot \text{C} \begin{array}{c} \diagdown \\ \diagup \end{array} \begin{array}{c} \text{Cl} : \text{Cl} \\ | \\ \text{N}-\text{Cl}_2 \end{array}$, which crystallises in silvery

needles, has the normal molecular weight in freezing glacial acetic acid, and decomposes with emission of violet vapour at 166—173°. A blackish-blue powder is also formed in the reaction; this is a product of the condensation and de-iodination of tetraiodopyrrole and when washed with ether gives a residual compound, which contains iodine, exhibits physical properties similar to those of indigotin, and is being investigated further. The above formation of hepta*i*iododipyrryl indicates that, in alkaline solution, tetraiodopyrrole exists in

the tautomeric forms, $\text{NH} \begin{array}{c} \diagup \text{Cl} : \text{Cl} \\ \diagdown \text{Cl} : \text{Cl} \end{array}$ and $\text{N} \begin{array}{c} \diagup \text{CH} : \text{Cl} \\ \diagdown \text{Cl}_2 \cdot \text{Cl} \end{array}$

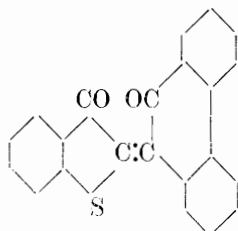
Both the tetra- and the hepta-iodo-compounds react in alkaline solution with diazonium salts and with *p*-bromophenylazoxy-carbonamide, whilst on reduction in either neutral or alkaline media they yield an oily product which gives a vapour capable of reddening a pine splinter moistened with hydrochloric acid and readily loses part of its iodine to form a black powder insoluble in ordinary solvents.

T. H. P.

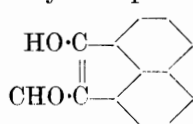
Influence of Substituents on the Formation and Stability of Heterocyclic Compounds. 1. Hydantoin. CHRISTOPHER KELK INGOLD, SHINICHI SAKO, and JOCELYN FIELD THORPE (T., 1922, 121, 1177—1198).

Indigoid Dyes of the Phenanthrene and Indene Series.

P. FRIEDLÄNDER, WALTER HERZOG, and G. VON VOSS (Ber., 1922, 55, [B], 1591—1596).—“2-Thionaphthen-9-phenanthreneindigo” [10-oxy-9-oxythionaphthenyl-6-oxyphenanthrene] (annexed formula), dark violet, almost black crystals,



is readily prepared by the addition of a few drops of concentrated hydrochloric acid to a boiling solution of 3-hydroxythionaphthen and phenanthraquinone in acetic acid. It gives dull violet shades from a yellow vat on the textile fibres. The *diacetyl* compound of the leuco-derivative is described. The dye is remarkable for its stability towards boiling solutions of alkali. For purposes of comparison, the analogously composed 8-oxy-7-oxythionaphthenylacenaphthene (A., 1908, i, 674) has been examined in this



respect; it is found to be decomposed with far greater readiness into thiosalicic acid and *acenaphthenone-7-aldehyde* [annexed formula], m. p. 163° [phenylhydrazone, m. p. 170° (decomp.), methyl ether, colourless needles, phenylhydrazone of the methyl ether, yellow needles, m. p. 172°].

Somewhat unexpectedly, β -ketohydrindene is found to condense with two molecular proportions of *p*-nitrobenzaldehyde to give the compound $C_{22}H_{14}O_5N_2$, and similarly with *p*-hydroxybenzaldehyde, giving the substance $C_{23}H_{16}O_3$, lustrous, yellow needles, m. p. about 265° (decomp.). It reacts, however, with a single proportion of α -isatin chloride to yield “2-indole-1'-indaneindigo” [2-indoxyl-1-indane-2-one] which is also produced from β -keto-hydrindene and α -isatinanilide in the presence of acetic anhydride. The dye is decomposed with great difficulty by solutions of alkali; it gives very intense, dark bordeaux shades on wool from a pale yellow hyposulphite vat. The composition of the dye is confirmed by the analysis of the similar product, $C_{17}H_9O_2NBr_2$, from β -keto-hydrindene and γ -dibromoisatin chloride. Thionaphthenquinone-2-anil and β -ketohydrindene give “2-thionaphthen-1'-indaneindigo”

[2-oxythionaphthenyl-1-indane-2-one], $C_6H_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{S} \diagup \end{array} C:C \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{C}_6\text{H}_4 \diagup \end{array} CH_2$,

reddish-violet crystals, which dye the textile fibres from a yellow vat in redder shades than the corresponding indole dye. Similarly, thionaphthenquinone-2-anil and $\alpha\gamma$ -indanedione yield “2-thionaphthen-2'-indoneindigo” [2-oxythionaphthenyl-2-indane-1:3-dione],

$C_6H_4 \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{S} \diagup \end{array} C:C \begin{array}{c} \diagup \text{CO} \diagdown \\ \diagdown \text{CO} \diagup \end{array} C_6H_4$, slender, reddish-violet needles. H. W.

1 : 1'-Diphenylindigotin. P. FRIEDLÄNDER and K. KUNZ (*Ber.*, 1922, **55**, [B], 1597—1607).—1 : 1'-Dimethylindigotin (A., 1912, i, 727) differs from the parent substance in its ready solubility in the customary indifferent media, its more basic character, its marked green shade, and its relative instability towards alkalis and acids. In 1 : 1'-diphenylindigotin, the presence of aromatic residues united to the nitrogen atoms so lessens the stability of the molecule that the substance has no value as a vat dye. The shade is also displaced markedly towards the green, but not so great an extent as with the methyl derivative.

N-Phenylanthranilic acid is converted by hot formaldehyde solution (30%) into the so-called *formalide*, $\text{C}_6\text{H}_4 \begin{array}{l} \text{CO-O} \\ \diagdown \\ \text{NPh-CH}_2 \end{array}$,

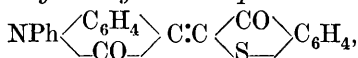
large, pale pink plates, m. p. 89° , which is transformed by a cold, concentrated solution of potassium cyanide into the *nitrile*, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CN}$, pale yellow, prismatic crystals, m. p. $133\text{--}134^\circ$; the latter is converted by concentrated sodium hydroxide solution into N-diphenylglycine-o-carboxylic acid, $\text{CO}_2\text{H}\cdot\text{C}_6\text{H}_4\cdot\text{NPh}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, pale yellow prisms, m. p. $160\text{--}163^\circ$ (evolution of carbon dioxide); the corresponding *methyl* and *ethyl* esters could not be caused to solidify. Similarly, N-p-chlorophenylanthranilic acid is transformed successively into the *formalide*, long, almost colourless crystals, m. p. $131\text{--}132^\circ$, the *nitrile*, prisms, m. p. $146\text{--}148^\circ$, and p-chloro-N-diphenylglycine-o-carboxylic acid, pale yellow crystals, m. p. $184\text{--}186^\circ$.

Diphenylglycine-o-carboxylic acid loses carbon dioxide when heated with sodium acetate and acetic anhydride, and the product, after being hydrolysed with sodium hydroxide, consists essentially of 1-phenylindoxyl, $\text{C}_6\text{H}_4 \begin{array}{l} \text{C(OH)} \\ \diagdown \\ \text{NPh} \end{array} \text{CH}$, which, however, could not

be caused to crystallise. A similar product is obtained from diphenylglycine-o-carboxylic acid and sodium hydroxide at $190\text{--}200^\circ$. The crystalline *sodium* salt of phenylindoxyl also gives a non-crystalline phenylindoxyl when treated with ammonium chloride. The action of sodium alkyl oxide on methyl diphenylglycine-o-carboxylate gives *methyl phenylindoxylate*, pale yellow crystals, m. p. $114\text{--}115^\circ$; the corresponding *ethyl* ester has m. p. $75\text{--}76^\circ$. Although, however, phenylindoxyl could not be isolated in the homogeneous condition, its presence in the crude products is established by the isolation of 4-chlorophenylindoxyl, long, yellow prisms, m. p. $110\text{--}111^\circ$, by the similar treatment of the p-chloro-acid. In general, the reactivity of phenylindoxyl (and chlorophenylindoxyl) is less than that of the parent substance; thus it could not be condensed with isatin or isatinanilide. With p-nitrosodimethylaniline, on the other hand, it gives 1-phenylisatin-2-p-dimethylaminoanil, $\text{C}_6\text{H}_4 \begin{array}{l} \text{CO} \\ \diagdown \\ \text{NPh} \end{array} \text{C:N}\cdot\text{C}_6\text{H}_4\cdot\text{NMe}_2$, prisms, m. p. 173° . The latter is converted by 3-hydroxythionaphthen in

the presence of acetic anhydride into 2'-1-phenylindoxyl-2-thionaphthen-3'-one, $C_6H_4 \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown NPh \diagup \end{smallmatrix} C:C \begin{smallmatrix} \diagup CO \diagdown \\ \diagdown S \diagup \end{smallmatrix} C_6H_4$, dark red needles.

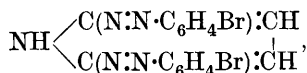
N-Phenylisatin, red needles, m. p. 135—136°, is prepared from phenylindoxyl through the anilide or by direct oxidation of its solution in alcohol and acetic acid with solid ferric chloride; it is also obtained smoothly by the gradual addition of dilute nitric acid to a solution of diphenylindigotin in glacial acetic acid. Boiling sodium hydroxide solution converts phenylisatin into acridine-5-carboxylic acid. Equivalent quantities of 1-phenylisatin and indoxyl react with the formation of N-phenylindirubin, needles, m. p. 238°; 3'-1-phenylindoxyl-2-thionaphthen-3-one,



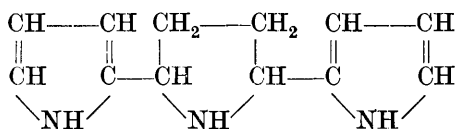
long, red needles, is prepared from phenylisatin and 3-hydroxythionaphthen. In a similar manner, 4-chlorophenylindoxyl is converted into 4-chlorophenylisatin, yellow needles, m. p. 197—198°; sodium 4-chlorophenylisatin is also described.

1:1'-Diphenylindigotin, almost black, lustrous plates, is most conveniently prepared by the oxidation of 1-phenylindoxyl by potassium ferricyanide in faintly alkaline solution. The corresponding 1:1'-di-p-chlorophenylindigotin is scarcely distinguishable in shade and properties from the chlorine-free dye. H. W.

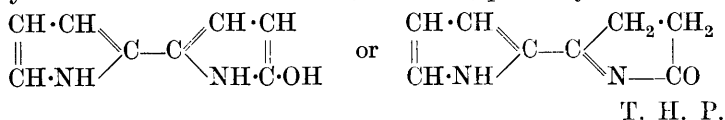
Constitution of certain Polypyrroles. ANTONIO PIERONI and ALDO MOGGI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 381—385).—Since *p*-bromobenzeneazoxycarboxylamide reacts readily with pyrrole and many of its derivatives to form the compound



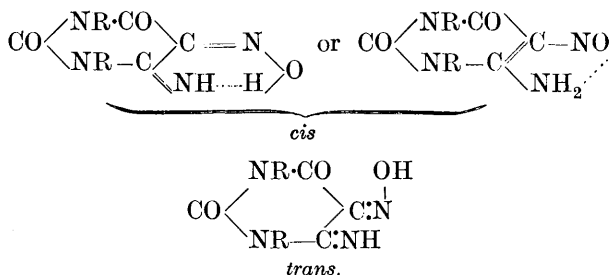
it serves as a reagent for the detection of the pyrrole nucleus. Quantitative investigation of the action of this reagent on tripyrrole (cf. Dennstedt, A., 1887, 598; 1888, 849; 1889, 400; 1894, i, 259) shows that the latter contains in its molecule at least two pyrrole nuclei connected at the 2- or 5-position with a third nucleus. Consequently, the formulæ ascribed to tripyrrole by Dennstedt and Voigtländer (A., 1894, i, 259) and by Tschelincev, Tronov, and Voskresenski (A., 1915, i, 1008) cannot be accepted. Further, the ready decomposition of tripyrrole into indole, pyrrole, and ammonia when heated indicates that the third nucleus is a pyrrolidine nucleus, and this indication is confirmed by the observation that oxidation of tripyrrole by means of potassium dichromate and sulphuric acid results in the formation of succinic acid. The conclusion is drawn that tripyrrole has the annexed formula.



As regards hydroxydipyrrole, $C_8H_8ON_2$, it is found that this compound yields pyrrole-2-carboxylic acid when treated with permanganate, forms succinic acid when oxidised with potassium dichromate and sulphuric acid, and gives 2 : 5-di-*p*-bromobenzene-azopyrrole in the proportion corresponding with one pyrrole nucleus in the molecule when treated with *p*-bromobenzenazoxy-carboxylamide. The constitution is, therefore, probably



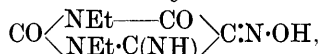
Colour Isomerism and Salt Formation with Iminovioluric Acids. II. I. LIFSCHITZ [and, in part, B. B. HEPNER] (*Ber.*, 1922, **55**, [B], 1619—1631).—A further series of iminoviolic acids has been prepared and their chromoisomerism investigated. These metal-free compounds show in every detail the peculiarities which have been observed with the polychromic salts of ordinary violuric acid and related oximino-ketones. Whilst the violuric acids are all colourless, the iminoviolic acids are not merely coloured, but also give an absorption spectrum completely analogous to that of the violurates, whereas the salts with acids absorb similarly to the free violuric acids. Like the violurates, the iminoviolic acids exist in differently coloured modifications which in certain cases can be transformed reversibly into one another. It appears, therefore, that the existence of variochromic phenomena in the case of the violurates and analogous oximino-ketone salts does not depend on the presence of a metallic atom or an external base. It is only necessary that salt formation should occur such as exists in the iminoviolic acids which may be regarded as internal ammonium salts. As is to be expected, the iminoviolic acids behave as typical amphoteric electrolytes. The colour and variochromism of the violurates cannot be explained by their electrolytic character, but only by the arrangement of the subsidiary valencies, thus :



The optical data show that the coloured forms of the acids all belong to the *cis*-series; the colour depends on the presence of the

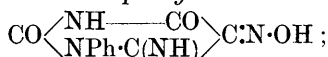
imino-group in the 4-position. They are all internal salts and only bimolar salts to a very slight degree. The trans-structure is characteristic of the unstable colourless forms which are permanent in the acid salts and are directly comparable with the colourless, free violuric acids.

4-Imino-2 : 6-diketo-1 : 3-diethylhexahydropyrimidine, colourless crystals, m. p. 127°, is conveniently prepared by heating diethylcarbamide with cyanoacetic acid and acetic anhydride and treatment of the product with sodium hydroxide. It is transformed by nitrous acid into *diethyliminovioluric acid*,



dark red needles which become blue when heated cautiously at 90°. It forms colourless salts with strong acids, of which the hygroscopic *hydrochloride* and *sulphate* and the *hydrobromide* have been examined. With bases it gives yellow, unstable salts which cannot be isolated in the pure condition (*lithium* and *sodium* salts) and very stable red salts (*sodium* and *potassium*).

Cyanoacetylphenylcarbamide, $\text{NHPh} \cdot \text{CO} \cdot \text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CN}$, m. p. 198°, is conveniently prepared by the condensation of phenylcarbamide with cyanoacetic acid in the presence of acetic anhydride. It is converted by potassium hydroxide solution (50%) into 4-*imino-3-phenylbarbituric acid*, leaflets, which does not melt below 230°, which yields 4-*imino-3-phenylvioluric acid*,



the latter exists in two forms, red needles and bluish-violet crystals, the former of which is the more stable at the atmospheric temperature. A pure blue *variety* was also obtained incidentally during an attempt to isolate the quinine salt. Iminophenylvioluric acid gives colourless salts with acids and coloured, somewhat unstable metallic salts which usually contain alcohol or water of crystallisation (the *sodium*, *potassium*, and *silver* salts are described).

The action of nitrous acid on 4-imino-6-keto-2-methoxytetrahydropyrimidine leads to the formation of *methyliminoisovioluric acid*, $\text{OMe} \cdot \text{C} \begin{array}{c} \text{NH} \text{---} \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{C}(\text{NH}) \end{array} \text{C:N} \cdot \text{OH}$, pale red to carmine-red crystals (? + H_2O), which are remarkably stable towards rise of temperature. The red *alkali* salts, pink *barium* salt, bluish-violet *silver* salt and tile-red *silver ammonium* salt are described. The *hydrochloride* was prepared. Methylation of the pyrimidine and subsequent treatment with sodium nitrite and acetic acid gives dimethyliminoisovioluric acid, $\text{OMe} \cdot \text{C} \begin{array}{c} \text{NMe} \cdot \text{CO} \\ \diagup \quad \diagdown \\ \text{N} \cdot \text{C}(\text{NH}) \end{array} \text{C:N} \cdot \text{OH}$, which has been obtained in violet, blue, bluish-green, green, and wine-red modifications. The behaviour of the acid toward bases and mineral acids is precisely similar to that of the iminovioluric acids described previously.

H. W.

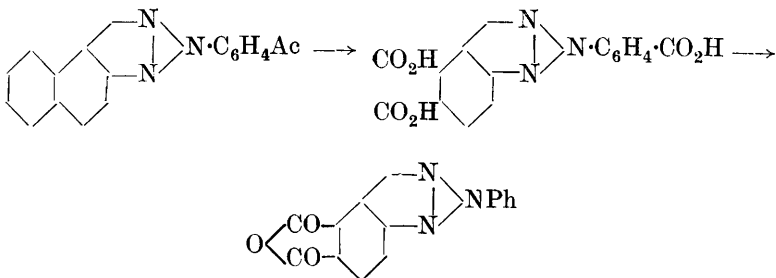
Aminoazo-, Hydroxyazo-, and Hydrazo-compounds.

G. CHARRIER (*Gazzetta*, 1922, **52**, i, 261—277).—The author has shown (A., 1910, i, 287) that *o*-amino-compounds of the benzene and naphthalene series are transformed when heated into *N*-arylbenz- or naphtha-triazoles, *o*-diamines, and primary amines in accordance with the general scheme: $3\text{NH}_2 \cdot \text{Ar}'' \cdot \text{N} : \text{N} \cdot \text{Ar}' \rightarrow 2\text{Ar}'' : \text{N}_3 \cdot \text{Ar}' + \text{Ar}''(\text{NH}_2)_2 + \text{Ar}' \cdot \text{NH}_2$. It is now shown that a similar reaction is shown by *o*-aminoazobenzene, which decomposes at above 300° into 2-phenylbenztriazole, *o*-phenylenediamine, and aniline. The structure of *o*-aminoazobenzene, established by Witt (A., 1912, i, 921) by means of its reduction, is confirmed by its conversion into *o*-hydroxyazobenzene.

The synthesis of 2-*p*-aminophenyl- $\alpha\beta$ -naphthatriazole has been effected in two ways: (1) *p*-nitrobenzeneazo- β -naphthylamine (Meldola and Hughes, T., 1891, **59**, 372) is either heated or oxidised by means of chromic acid in acetic acid solution, the corresponding nitrotriazole thus obtained being then reduced; (2) β -naphthylamine is treated with *p*-acetylaminophenyldiazonium chloride, the resulting *o*-aminoazo-compound being then oxidised and deacetylated. This aminoarylnaphthatriazole is the first such compound which has been prepared.

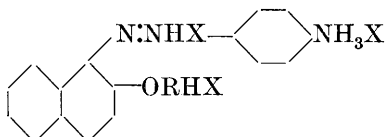
p-Acetylbenzeneazo- β -naphthylamine yields 2-*p*-acetylphenyl- $\alpha\beta$ -naphthatriazole when oxidised by means of chromic acid in acetic acid solution, but when heated it undergoes a more complex reaction, which appears to consist first of formation of the keto-triazole according to the scheme, $3\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4\text{Ac} =$

$2\text{C}_{10}\text{H}_6 \left\langle \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{smallmatrix} \right\rangle \text{N} \cdot \text{C}_6\text{H}_4\text{Ac} + \text{C}_{10}\text{H}_6(\text{NH}_2)_2 + \text{NH}_2 \cdot \text{C}_6\text{H}_4\text{Ac}$, followed by condensation of the ketotriazole with the naphthylenediamine to a compound, m. p. 288° , now being investigated. Oxidation of 2-*p*-acetylphenyl- $\alpha\beta$ -naphthatriazole by means of alkaline permanganate solution appears to yield the tricarboxylic acid, *vic.* 2-*p*-carboxyphenylbenztriazole-4 : 5-dicarboxylic acid, which loses water and carbon dioxide when fused, with formation of 2-phenyl-*p*-benztriazole-4 : 5-dicarboxylic anhydride :

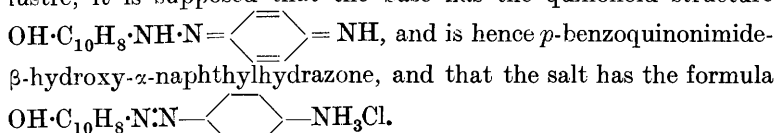


1-*p*-Aminobenzeazo- β -naphthol, prepared by treating β -naphthol

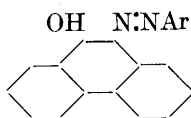
in alkaline solution with *p*-acetylaminobenzenediazonium chloride and hydrolysing the resulting acetyl derivative, is a stable compound and, when subjected to the action of alkyl sulphates in presence of excess of alkali, undergoes etherification at the naphtholic hydroxyl. The ethers thus formed are obtained as dense, impure oils, and react with acids giving crystalline salts which contain three univalent acid residues (X) and have probably the general formula,



By diazotisation *p*-aminobenzeneazo- β -naphthol may be converted into the corresponding *p*-hydroxyazo-compound. Since *p*-aminobenzeneazo- β -naphthol hydrochloride is pale red whereas the free base is deep brownish-red with a cantharides-green, metallic lustre, it is supposed that the base has the quinonoid structure



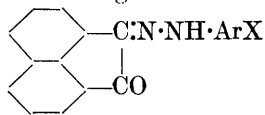
The following compounds have also been prepared: 9-*o*-, 9-*m*-, and 9-*p*-nitrobenzeneazo-10-phenanthrols, 9-*p*-bromobenzeneazo-10-phenanthrol, and 9-*p*-acetylbenzeneazo-10-phenanthrol. These



compounds may be obtained either by the action of diazonium salts on 10-phenanthrol or by the action of the arylhydrazine hydrochloride on phenanthraquinone, the latter reaction giving first the arylhydrazone, which rapidly undergoes transformation into the hydroxyazo-compound.

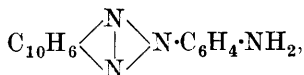
They crystallise well, are highly stable, dissolve in concentrated sulphuric acid giving reddish-violet solutions, and have the annexed general formula.

Acenaphthenequinone behaves like dibromoanthrone towards arylhydrazines, giving the arylhydrazones, whereas phenanthraquinone gives hydroxyazo-compounds under similar conditions. Acenaphthenequinone *o*-, *m*-, and *p*-nitrophenylhydrazones and *p*-acetylphenylhydrazone, prepared by treating the quinone in acetic acid solution with the hydrochlorides of the respective hydrazines, correspond with the general formula,



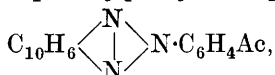
[With C. SALA].—The action of nitrous acid on *o*-aminoazobenzene yields *o*-hydroxyazobenzene.

[With S. VIOLA.]—2-*p*-Aminophenyl- $\alpha\beta$ -naphthatriazole,



forms slender, straw-yellow crystals, m. p. 198—199°, and is rapidly turned brown by the action of air and light. It dissolves sparingly in dilute mineral acids, forming the corresponding salts, which are readily hydrolysed by water; the sulphate crystallises in minute, lustrous scales. *p*-Acetylaminobenzeneazo- β -naphthylamine forms slender, red needles with brownish-green, metallic reflexion, m. p. 203°.

[With G. CRIPPA.]—2-*p*-Acetylphenyl- $\alpha\beta$ -naphthatriazole,



crystallises in slender, straw-white needles, m. p. 185°, is a highly stable compound, and dissolves in concentrated sulphuric acid, giving an intense yellow solution. Its *p*-bromophenylhydrazone, $\text{C}_{24}\text{H}_{18}\text{N}_5\text{Br}$, forms, thin, lustrous, yellow leaflets, m. p. 215°, and is phototropic; its phenylhydrazone, pale yellow leaflets, m. p. 181°, darkening in the light; its oxime, microscopic, yellowish-white crystals, m. p. 253°, and the *o*-nitrophenylhydrazone, reddish-yellow leaflets, m. p. 180°. These arylhydrazones dissolve in concentrated sulphuric acid, giving yellow colorations similar to that with the ketotriazole itself, but the oxime yields an almost colourless solution.

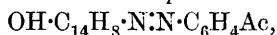
vic-2-*p*-Carboxyphenylbenztriazole-4 : 5-dicarboxylic acid, $\text{C}_{15}\text{H}_9\text{O}_6\text{N}_3$, forms minute, white crystals, m. p. 291—292° (decomp.), decomposes carbonates, and is strongly acid to litmus in aqueous or aqueous-alcoholic solutions; the anhydride has m. p. 225—230° (impure).

p-Acetylbenzeneazo- β -naphthylamine, obtained by the action of *p*-acetylbenzenediazonium chloride on β -naphthylamine in alcoholic solution, crystallises in long, flat, intensely red needles, with brilliant metallic green lustre, m. p. 170°, and dissolves in concentrated sulphuric acid with a deep wine-red coloration. It yields a *p*-bromophenylhydrazone, $\text{C}_{24}\text{H}_{20}\text{N}_5\text{Br}$, bright red leaflets, m. p. 217°; a phenylhydrazone, thin, garnet-red leaflets, m. p. 187°, giving a violet-blue solution in concentrated sulphuric acid, and an oxime, which crystallises in dense, garnet-red prisms, m. p. 206°, and dissolves in concentrated sulphuric acid, giving a solution red by transmitted and indigo-blue by reflected light.

[With C. CORTASSA.]—*p*-Acetylaminobenzeneazo- β -naphthol, $\text{OH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{N} : \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{NHAc}$, forms slender, bright red needles, m. p. 259—260°, and gives a red solution in concentrated sulphuric acid, *p*-Aminobenzeneazo- β -naphthol, $\text{C}_{16}\text{H}_{13}\text{ON}_3$, crystallises in reddish-brown needles with metallic or golden lustre, m. p. 159—160°, and forms a hydrochloride, $\text{C}_{16}\text{H}_{13}\text{ON}_3 \cdot \text{HCl}$, crystallising in slender, pale red needles with golden lustre and yielding a bright red powder.

The *methyl ether*, $C_{17}H_{15}ON_3$, obtained by the action of methyl sulphate in large excess on the base in presence of 30% sodium hydroxide solution, forms a dense, reddish-brown oil. The *ethyl ether* forms a dense oil, and gives a *nitrate*, $C_{18}H_{17}ON_3 \cdot 3HNO_3$, crystallising in slender, metallic green needles, m. p. 95—96° (decomp.), and a *hydrochloride*, $C_{18}H_{17}ON_3 \cdot 3HCl$, forming slender crystals with metallic green lustre, both salts being readily decomposed by water; the ethyl ether is easily hydrolysed to *p*-aminobenzeneazo- β -naphthol when boiled with a dilute acid.

[With L. DEMICHELIS.] — 9-*p*-Bromobenzeneazo-10-phenanthrol, $OH \cdot C_{14}H_8 \cdot N:N \cdot C_6H_4Br$, crystallises in small, bright red needles, m. p. 188°; 9-*p*-acetylbenzeneazo-10-phenanthrol,



in slender, brick-red needles, m. p. 219°; 9-*o*-nitrobenzeneazo-10-phenanthrol, $C_{20}H_{13}O_3N_3$, in slender, bright red, acicular crystals with golden lustre, m. p. 185°, giving a violet-red solution in concentrated sulphuric acid; the 9-*m*-isomeride in orange-red needles, m. p. 196—197° (decomp.), and the 9-*p*-isomeride in garnet-red, flat needles, m. p. 185°. The compound described by Hyde (A., 1899, i, 688) as phenanthraquinone *p*-nitrophenylhydrazone has m. p. 245°.

[With M. SPEIRANI.]—Acenaphthenequinone *o*-nitrophenylhydr-

azone, $\begin{array}{c} C_{10}H_6 \\ \diagup \quad \diagdown \\ CO \quad \quad C:N \cdot NH \cdot C_6H_4 \cdot NO_2 \end{array}$, crystallises in slender, lustrous,

orange-red needles, m. p. 249°; the *m*-nitrophenylhydrazone forms golden-yellow needles, m. p. 229—230°, the *p*-nitrophenylhydrazone, slender orange-red needles, m. p. 247°, and the *p*-acetylphenylhydrazone, $C_{20}H_{14}O_2N_2$, heavy, reddish-brown prisms, m. p. 244—245°. All these hydrazones dissolve in concentrated sulphuric acid, giving ruby-red colorations.

T. H. P.

The Occurrence of Free Radicles in Chemical Reactions. The Radicles of the Basic Triphenylmethane Dyes. HEINRICH WIELAND, EGON POPPER, and HERMANN SEEFRIED (*Ber.*, 1922, 55, [B], 1816—1834).—An experimental examination of the probability of the occurrence of free radicles during the course of simple chemical changes has been commenced. For example, in the case of phenylazotriphenylmethane it is possible that decomposition occurs with the formation of nitrogen, triphenylmethyl and phenyl (and that the two latter combine to a slight extent as shown by Gomberg with the formation of tetraphenylmethane). On the other hand, it is conceivable that the free valencies remain in mutual attraction and that combination between them occurs before the components separate as free radicles.

The decomposition of phenylazotriphenylmethane has been studied in light petroleum, b. p. 90—120°, xylene, and ethyl benzoate. In all cases it is found that nitrogen is evolved completely at a temperature considerably below the melting point of the compound

(80°). In all fissions, triphenylmethyl is produced ; it is identified by its spectrum, and its appearance in hot and cold solution, and is isolated after treatment with air or oxygen in the form of its peroxide. The varying yields attained their maximum in one experiment, in which 35% of the theoretically possible quantity was produced. The observations indicate beyond all doubt that the azo-compound decomposes with the formation of radicles. The fate of the phenyl radicle is less easily ascertained. Experimental confirmation of the obvious hypothesis that it becomes polymerised to diphenyl could not be obtained. It is shown, however, that phenyl is found as benzene (*p*-chlorophenyl as chlorobenzene and *p*-nitrophenyl as nitrobenzene) at the conclusion of the reaction. The partner in the change which is poorer in hydrogen has not yet been identified.

The observations have been extended to azo-compounds containing the phenyl group and a group similar to those contained in the basic triphenylmethane dyes, for example, phenylazobis-*p*-dimethylaminotriphenylmethane, $\text{NPh}:\text{NPh}(\text{C}_6\text{H}_4\cdot\text{NMe}_2)_2$. These substances with equal definiteness decomposed, with the formation of free radicles. It is very remarkable that bis-*p*-dimethylamino- and tri-*p*-dimethylamino-triphenylmethyl are scarcely more intensely coloured than triphenylmethyl itself. The radicles and their peroxides are very unstable. The observations are considered to bring important confirmation of the quinonoid structure of the triphenylmethane dyes.

The following compounds do not appear to have been described previously. *p*-Chlorophenylazotri-*p*-tolylmethane, from tri-*p*-tolyl chloromethane and *p*-chlorophenylhydrazine and subsequent oxidation of the product with bromine water, intensely yellow crystals, decomp. 116°. Phenylhydrazotri-*p*-anisylmethane, colourless prisms, m. p. 154° (decomp.). Phenylazotri-*p*-anisylmethane, from the preceding compound and silver oxide, large yellow prisms, m. p. 106° (decomp.). Phenylhydrazobis-*p*-dimethylaminotriphenylmethane, colourless crystals, m. p. 170° (decomp.). Phenylazobis-*p*-dimethylaminotriphenylmethane, a golden-yellow, crystalline powder, m. p. 120° (decomp.) Bis-*p*-dimethylaminotriphenylmethyl peroxide, a colourless, amorphous solid which rapidly darkens and resinifies. *p*-Chlorophenylhydrazobis-*p*'-dimethylaminotriphenylmethane, colourless crystals, m. p. 124.5°. *p*-Chlorophenylazobis-*p*'-dimethylaminotriphenylmethane, slender, golden-yellow needles, decomp. 116°. Phenylhydrazotri-*p*-dimethylaminophenylmethane, needles, m. p. 172° (decomp.). Phenylazotri-*p*-dimethylaminophenylmethane, m. p. 150° (decomp.). *p*-Chlorophenylhydrazotri-*p*'-dimethylaminophenylmethane, plates, m. p. 178° (decomp.). *p*-Chlorophenylazotri-*p*'-dimethylaminophenylmethane, golden-yellow prisms, decomp. 142°. Phenylhydrazotri-*p*-aminophenylmethane, colourless needles, m. p. 200° (decomp.) Phenylazotri-*p*-aminophenylmethane, small, golden-yellow needles, m. p. 195° (decomp.). *p*-Chlorophenylhydrazotri-*p*'-aminophenylmethane,

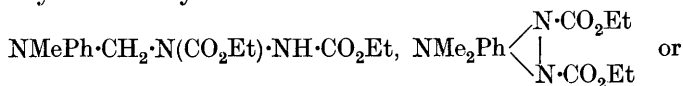
colourless leaflets, m. p. 204° (decomp.), which is dehydrogenated with difficulty.

H. W.

Diazo-compounds. ANGELO ANGELI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 283—293).—The author criticises a number of statements made by Hantzsch and Reddelien ("Die Diazoverbindungen," 1921), especially from the point of view of priority, and states that no mention is made of some of his own work.

T. H. P.

The Azo-ester Reaction of Amines and Enols. OTTO DIELS (*Ber.*, 1922, **55**, [B], 1524—1528; cf. Diels and Fritzsche, A., 1911, i, 957; Diels and Paquin, A., 1913, i, 839; Diels and Fischer, A., 1914, i, 989; Diels, A., 1921, i, 280).—Azodicarboxylic ester unites with amines to give additive compounds of three distinct types: (1) compounds in which the azo-ester is united to the aromatic nucleus [naphthylamine type], (2) compounds which are stable in themselves but are only attacked by reagents after fission into amine and azo-ester [aniline type], and (3) compounds which are decomposed by acids with production of formaldehyde, hydrazo-ester and secondary base [dimethylaniline type]. The initial product in every case appears to have the constitution $\text{NHR} \cdot \text{N}(\text{CO}_2\text{Et}) \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, and reaction stops at this point with the aniline type. With the naphthylamine type, on the other hand, a sufficiently activated double bond or hydrogen atom appears to be present to enable the azo-ester to unite with the nucleus, thus giving, for example, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_6 \cdot \text{N}(\text{CO}_2\text{Et}) \cdot \text{NH} \cdot \text{CO}_2\text{Et}$. The constitution of the additive products derived from tertiary amines cannot yet be decided definitely; thus the compound with dimethylaniline may be formulated



$\text{CH}_2 \cdot \text{NMePh} \cdot \text{N}(\text{CO}_2\text{Et}) \cdot \text{NH} \cdot \text{CO}_2\text{Et}$.

The hypothesis that the azo-ester action depends on the additive power of a sufficiently activated double bond or on the mobility of a hydrogen atom is greatly strengthened by the observation that enols, apparently without exception, combine with azo-esters. Thus methyl azodicarboxylate and ethyl acetoacetate yield the compound $\text{COMe} \cdot \text{CH}(\text{CO}_2\text{Et}) \cdot \text{N}(\text{CO}_2\text{Me}) \cdot \text{NH} \cdot \text{CO}_2\text{Me}$, m. p. 113°, and ethyl azodicarboxylate reacts readily with acetylacetone in the presence of potassium acetate, giving γ -NN'-dicarbethoxyhydrazinoacetylacetone, $\text{CH}(\text{COMe})_2 \cdot \text{N}(\text{CO}_2\text{Et}) \cdot \text{NH} \cdot \text{CO}_2\text{Et}$, colourless, lustrous prisms, m. p. 123°.

The previous hypothesis that azo-esters react only with aromatic amines is now abandoned owing to the observation that ethyl β -aminocrotonate combines with methyl azodicarboxylate to give the compound $\text{NH}_2 \cdot \text{CMe} \cdot \text{C}(\text{CO}_2\text{Et}) \cdot \text{N}(\text{CO}_2\text{Me}) \cdot \text{NH} \cdot \text{CO}_2\text{Me}$, m. p. 140°.

The communication is of a preliminary nature, the full experimental details being promised for a subsequent paper. H. W.

Decomposition of Benzyl Azide in Indifferent Media and in Malonic Ester. THEODOR CURTIUS and GUSTAV EHRRHART (*Ber.*, 1922, **55**, [B], 1559—1571).—Benzyl azide is decomposed when heated in xylene, but the stable residue, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$, unlike that derived from benzenesulphonazide, is unable to combine with the hydrocarbon, which itself takes no further part in the chemical changes. Addition, however, does occur with substances such as ethyl malonate and ethyl methylmalonate, with production of ethyl benzylaminomalonate, $\text{CH}(\text{CO}_2\text{Et})_2\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, and ethyl benzylmethylaminomalonate.

A modified process for the preparation of benzyl azide, b. p. $82.5^\circ/16.5$ mm., from benzyl chloride and sodium azide, is described in detail, the yield being 90% of that theoretically possible.

Benzyl azide decomposes very slowly in the presence of boiling xylene, and the action is therefore effected under pressure in a specially designed glass autoclave at 170 — 180° . *Dibenzylbenzoamidine*, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot\text{CPh}\cdot\text{NH}\cdot\text{CH}_2\text{Ph}$, a microcrystalline, feebly anisotropic substance, m. p. 106° , separates from the solvent [the corresponding *sulphate*, $\text{C}_{21}\text{H}_{20}\text{N}_2\cdot\text{H}_2\text{SO}_4$, coarse, colourless plates, m. p. 233° , *picrate*, prisms, m. p. 254° (decomp.), and *acetate*, coarse platelets, m. p. 299° (decomp.), are described]; the constitution of the substance is deduced from its hydrolysis by aqueous barium hydroxide solution at 120° to benzylamine and benzoic acid. The filtrate from the dibenzylbenzoamidine is distilled with steam, whereby tribenzylamine, m. p. 91° , is volatilised; the residue contains tetraphenylpyrazine, $\text{N}\langle\text{CPh}\cdot\text{CPh}\rangle\text{N}$, and *diphenylbenzylpyrrodiazole*,

$\text{CH}_2\text{Ph}\cdot\text{N}\langle\text{CPh}\cdot\text{N}\rangle\text{CPh}\cdot\text{N}$, m. p. 229° . In a second experiment, in which

the excess of xylene was immediately distilled and the total residue treated with steam and dissolved in ether, it was found possible to isolate benzylbenzylideneamine, $\text{CHPh}\cdot\text{N}\cdot\text{CH}_2\text{Ph}$, b. p. $230^\circ/20$ mm., whilst, on another occasion, the mother-liquors from the tetraphenylpyrazine and diphenylbenzylpyrrodiazole yielded a very small quantity of a substance, small needles, m. p. 186° , which gave benzaldehyde when gently warmed with acids and appeared to be a *polymeric benzylbenzylideneamine*, although the quantity of substance available was insufficient for an extended investigation. In the presence of boiling cymene, the decomposition of benzyl azide follows much the same course, but tetraphenylpyrazine is produced in rather larger quantity. In the presence of dimethylaniline at 170 — 180° , tetraphenylpyrazine is not produced, but more diphenylbenzylpyrrodiazole is obtained; the formation of dibenzylbenzoamidine is not observed. The hypothesis is advanced that the initial decomposition of benzyl azide results in the production of the radicles $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$ and (by loss of hydrazoic acid) $\text{Ph}\cdot\text{CH}\cdot$. Immediate union of these leads to the formation of benzylbenzylideneamine; addition of the residue, $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$, to the latter results in the production of dibenzylbenzoamidine.

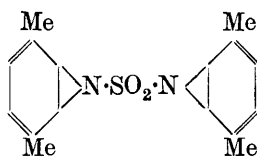
The occurrence of diphenylbenzylpyrroldiazole seems to be coupled with that of tribenzylamine and can be explained in the following manner. The radicle $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$ passes into its imino-form, CHPh:NH , which loses two atoms of hydrogen, these being utilised in the reduction of two $\text{PhCH}\cdot$ residues. A new radicle, $\text{C}\cdot\text{Ph:N}\cdot$, thus arises from which the unsaturated residue, $-\text{CPh:N:N}\cdot\text{CPh}-$ is formed; combination of the latter with the radicle $\text{CH}_2\text{Ph}\cdot\text{N}\cdot$ yields diphenylbenzylpyrroldiazole. Tribenzylamine is formed in accordance with the scheme: $2\cdot\text{CH}_2\text{Ph} + \text{CH}_2\text{Ph}\cdot\text{N}\cdot \longrightarrow \text{N}(\text{CH}_2\text{Ph})_3$.

The decomposition of benzyl azide in the presence of ethyl malonate at 170° differs from its reactions just described in that hydrazoic acid does not appear to be eliminated, and that complications caused by the occurrence of the radicle $\cdot\text{CHPh}$ are thus completely excluded. Reaction proceeds along simpler lines and results in the production of ethyl benzylaminomalonate, which, however, could not be isolated in the homogeneous condition. The hydrolysis of the crude ester by aqueous potassium hydroxide gives benzylaminomalonic acid, m. p. 115° (decomp.), whereas it yields benzylaminoacetic acid hydrochloride when treated with hydrochloric acid at 110° . Similarly, benzyl azide and ethyl methylmalonate react to form *ethyl benzylaminomethylmalonate*, from which impure *benzylaminomethylmalonic acid* is derived (it evolves carbon dioxide at the atmospheric temperature). The crude ester is transformed by concentrated hydrochloric acid at 120° into *α -benzylaminopropionic acid hydrochloride*, pale yellow, coarse, rectangular, anisotropic plates. H. W.

The Action of Sulphuryl Azide on *p*-Xylene. THEODOR CURTIUS and FRIEDRICH SCHMIDT (*Ber.*, 1922, 55, [B], 1571—1581).—Sulphuryl azide is prepared in a not quite homogeneous condition by the action of sulphuryl chloride on finely divided, slightly moist sodium azide. In contrast to the azides of organic sulphonic acids, it is violently explosive, frequently without apparent cause. Its decomposition in *p*-xylene solution (3%) begins at about 70° , and is completed by very gradually raising the temperature of the solution during about a week and continuing the process until further evolution of gas does not occur from the briskly boiling mixture. The unusual course of the change is indicated by the evolution of large quantities of sulphur dioxide. After removal of the *p*-xylene, the residue is made alkaline and distilled with superheated steam. The mixture of bases is separated and distilled, when a solid base (*C*, see below) separates from the distillate. This is removed, and two further bases (*A* and *B*) are isolated in the form of the picrates from the filtrate, which also yields a neutral substance, *D*. The work is rendered unusually difficult by the danger of the operations, the minimal yields of well-defined products and their close resemblance to one another. The actual substances isolated are the following. Base *A*, *ψ -xylylidine*, $\text{C}_8\text{H}_{11}\text{N}$, a liquid with an odour of pyridine, which gives a very hygroscopic *hydro*-

chloride, a *picrate*, m. p. 152° , moderately soluble in alcohol or water, two *platinichlorides*, pale yellow crystals, m. p. 148° , and dark yellow crystals, m. p. 181° , respectively; a liquid *base B*, C_8H_9N , with pyridine-like odour, yields a non-hygroscopic *hydrochloride*, m. p. $212-213^{\circ}$, a *picrate*, m. p. 239° , which is sparingly soluble in alcohol or water, and a *platinichloride*, plates, m. p. 260° ; a solid, odourless, crystalline *base, C*, C_8H_9N , m. p. 112° , which gives a non-hygroscopic hydrochloride, m. p. 218° , a *picrate*, m. p. 218° , and two *platinichlorides*, pale yellow crystals, m. p. 242° , and dark yellow crystals, m. p. 181° : a neutral *substance D*, C_8H_9N , m. p. 85° .

The constitution of the compounds *C* and *D* has not been elucidated. For the structure of *A* and *B*, the following hypothesis

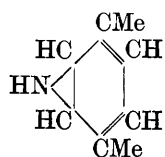


(I.)

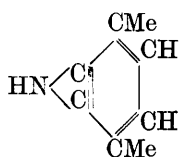


(II.)

is advanced. Sulphuryl azide decomposes initially into nitrogen and the residue $N \cdot SO_2 \cdot N$; the latter then combines with two molecules of *p*-xylene, giving the compound (annexed formula I). This is, however, unstable, and loses




(III.)



(IV.)

sulphur dioxide, with the production of the univalent radicle (annexed formula II). Two such radicles are unable to unite with one another to yield a ditertiary hydrazine, and re-arrangement of hydrogen atoms consequently occurs between them in accordance with Wieland's rule, thus leading to the production of the two compounds *A* and *B* (annexed formulæ III and IV). The constitution of the compound poorer in hydrogen cannot be regarded as established definitely, since it is possible that the methyl groups


play a part in the formation of the new ring; this possibility appears to be excluded in the case of ψ -xylylidine (III) by the observation (Schmidt, following abstract) that a completely analogous ψ -aniline is produced from benzene under comparable conditions. The addition of an imino-group to the benzene nucleus with the production of a three- and seven-membered ring has been observed previously in the case of nor-caradienecarboxylic acid. Additional evidence of the existence

of the  ring in ψ -xylylidine is adduced from the observation that the substance is gradually decomposed by repeated evaporation with hydrochloric acid, with formation of ammonium chloride.

H. W.

Action of Sulphuryl Azide on Benzene. FRIEDRICH SCHMIDT (*Ber.*, 1922, **55**, [B], 1581—1583; cf. Curtius and Schmidt, preceding abstract).—Sulphuryl azide decomposes extremely

slowly when dissolved in boiling benzene, so that continuous ebullition must be maintained for weeks to ensure the decomposition of any considerable proportion of material. This drawback has been overcome by the construction of an autoclave of glass without any metallic contact which permits the boiling point of the solution to be raised to the requisite extent. The product is worked up in the manner described by Curtius and Schmidt in their observations with *p*-xylene. Unexpectedly, the base obtained from the brown, humus-like product of the reaction is uniform: it has the composition C_6H_7N , and is termed ψ -aniline. It is quite distinct from the isomeric picolines. The yields are minimal, so that a complete examination of the new base is impossible. The observation that ammonium chloride is produced when it is repeatedly evaporated with hydrochloric acid indicates the presence

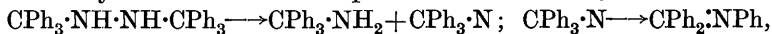
of the  ring. The mechanism of the change is less obvious

than in the case of *p*-xylene, since it has not been possible to isolate the "anti-substance" poorer in hydrogen.

ψ -Aniline picrate has m. p. 163° .

H. W.

The Molecular Rearrangement of *s*-Bistriphenylmethylhydrazine. JULIUS STIEGLITZ and RALPH L. BROWN (*J. Amer. Chem. Soc.*, 1922, **44**, 1270—1292).—The authors have repeated and extended the work of Stieglitz and Senior (A., 1917, i, 97). In addition to aniline, which was again isolated after hydrolysing the products of rearrangement of bistriphenylmethylhydrazine caused by heating the substance with anhydrous zinc chloride at 300° , benzophenone was isolated and identified. Triphenylmethylamine could not be found, but this substance itself undergoes decomposition when heated with zinc chloride, giving ammonia, phenyldiphenylenemethane, and triphenylmethane, and all these compounds were isolated from the material resulting from heating bistriphenylmethylhydrazine with zinc chloride. These results are taken as supporting the following scheme for the rearrangement of the hydrazine under the experimental conditions,



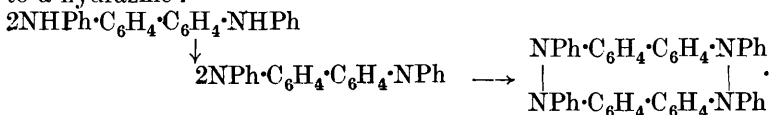
the phenyliminobenzophenone thus formed being hydrolysed to aniline and benzophenone. Quantitative estimations showed that the amount of ammonia or triphenylmethylamine formed is of the order demanded by the above scheme. This series of changes is discussed from the electronic point of view, in which it is considered that the rearrangement is the result of an intramolecular oxidation-reduction which involves a migration of electrons from the methyl carbon to the nitrogen. At the same time, a thermal decomposition proceeds, which is also an intramolecular oxidation-reduction, involving the migration of electrons from the nitrogen to the methyl carbon atom.

It was found that when the rearrangement reaction was carried

out in air, phenol was obtained in quantity, but none was found when the action was carried out in an atmosphere of carbon dioxide. Tentatively, it is suggested that the formation of phenol is due to the capture of oxygen by escaping migrating phenyl radicles, and in support of this view it was found that the sum of the aniline and the phenol obtained was roughly equal to the amount of ammonia formed. Further, it was observed that when bistriphenylmethylhydrazine is heated with zinc chloride in the absence of air there is no rearrangement to an aniline derivative, and there is thus a possibility that the rearrangement described above is the result of an oxidation reaction in which the oxygen of the air takes part.

W. G.

Hydrazines. XXV. A New Class of Ditertiary Aromatic Hydrazines. HEINRICH WIELAND and ALBERT WECKER (*Ber.*, 1922, 55, [B], 1804—1815).—*p*-Phenylenediamines of all types are converted by oxidation in acid solution to quinonedi-immonium salts; the corresponding free bases which have a hydrogen atom attached to the imino-group are reduced by silver oxide or lead dioxide to the di-imines. The reaction is observed, not only with *p*-phenylenediamines but, in principle, with benzidines also. It has, however, been observed by Albert (*Diss.*, Munich, 1916) that *NN'*-diphenylbenzidine behaves in a different manner, giving a product which resembles in composition but differs in molecular weight and properties from the di-imine. This reaction has now been studied more fully and extended to various substituted diphenylbenzidines. It is shown that, as in the case of diphenylamine, the primary product is a radicle with bivalent nitrogen which immediately polymerises to a hydrazine:



The products of the reaction represent a new class of ditertiary aromatic hydrazines; in bromoform solution, they have the simple molecular weight corresponding with the formula, but are polymerised in benzene solution. They are reduced by zinc dust and glacial acetic acid to the benzidines. The colourless bishydrazines dissociate in solution to the coloured radicles, and in this connexion the substituent in the para-position in the benzene nucleus exerts the same influence on the stability of the compound as was observed previously in the case of the tetra-arylhydrazines. Nitric oxide is absorbed readily by the coloured solutions. The radicles, when exposed to a high temperature for some time, exhibit the intermolecular dissociation characteristic of substances containing bivalent nitrogen; the diarylamine is re-formed, whereas the substance poorer in hydrogen has not been identified.

[With T. J. ALBERT.]—*NN'*-diphenylbenzidine is oxidised by solid potassium permanganate in the presence of acetone or by silver oxide in the presence of pyridine to *bisdiphenyldibiphenylene*

e e*

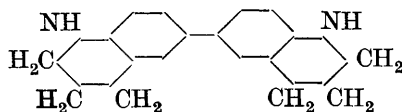
hydrazine, a colourless solid which could not be caused to crystallise. It dissociates in boiling xylene into intensely coloured, brownish-red radicles which re-unite when the solution is cooled. Protracted heating leads to the production of amorphous substances which have not been investigated closely and *NN'*-diphenylbenzidine. When dissolved in hot pyridine, it combines with nitric oxide, yielding diphenylbenzidinebisnitrosoamine, $\text{NO} \cdot \text{NPh} \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NPh} \cdot \text{NO}$, m. p. 158—160° (decomp.), which loses nitric oxide when heated in boiling xylene and regenerates the radicle, which suffers further change to diphenylbenzidine.

Phenyl-*p*-tolylamine is converted by sulphuric acid and sodium dichromate in glacial acetic acid solution and treatment of the product with bisulphite into *NN'*-*di-p*-tolylbenzidine, leaflets, m. p. 233°, which is transformed into the *bishydrazine*, an amorphous compound, m. p. 205° (indefinite). The latter exhibits strongly-marked dissociation in boiling toluene, in which it ultimately becomes converted into *di-p*-tolylbenzidine. The addition of triphenylmethyl could not be effected. On the other hand, the substance unites readily with nitric oxide in the presence of pyridine at 90°, giving the *dinitrosoamine* of *di-p*-tolylhydrazine, slender, yellow needles, m. p. 188—191° (decomp.). Elimination of nitric oxide and production of *di-p*-tolylbenzidine occurs in the same manner as with the derivative of diphenylbenzidine.

NN'-*Di-p*-anisylhydrazine, lustrous crystals, m. p. 226°, is most conveniently oxidised by silver oxide to the corresponding *bishydrazine*, an amorphous, pale-grey powder, m. p. 200° (indefinite). It dissociates more readily than the similar substances described above, thus giving an intensely green solution in warm benzene. At a moderate temperature, it adds nitric oxide with the formation of the *bisnitrosoamine*, $\text{C}_{26}\text{H}_{22}\text{O}_4\text{N}_4$, small, yellow needles, m. p. 160° (decomp.) which loses nitric oxide when heated in boiling toluene.

p-Chlorodiphenylamine, m. p. 74°, is prepared from *p*-chloroacetanilide, bromobenzene, potassium carbonate, and copper powder in boiling nitrobenzene solution, and is converted in the usual manner into *NN'*-*di-p*-chlorophenylbenzidine, lustrous leaflets, m. p. 205°. Dehydrogenation of the latter by potassium permanganate in the presence of acetone gives the corresponding *bishydrazine*, an amorphous substance, m. p. 230° (indefinite). Dissociation of this substance occurs in boiling toluene with the production of a brownish-red solution. The radicle is converted by nitric oxide into the *bisnitrosoamine*, pale yellow needles, m. p. 193° (decomp.).

[With FR. E. HAAS.]—Quinobenzidine (annexed formula) is converted by silver oxide in the presence of pyridine and anhydrous ether



into the corresponding *bishydrazine*, a colourless, amorphous powder, m. p. 172° (indefinite). The substance dissociates with difficulty; its solutions in boiling xylene are colourless, but coloured solutions are formed in

boiling ethyl benzoate. It is reduced by zinc dust and concentrated hydrochloric acid in the presence of glacial acetic acid to quinobenzidine.
H. W.

Physico-chemical Studies on Biological Reactions.
II. Spectro-chemical Investigations on Amino-acids and Polypeptides. PAUL HIRSCH and RUDOLF KUNZE (*Fermentforsch.*, 1922, 6, 30—55).—By means of the Pulfrich refractometer and the Löwe interferometer, the authors have investigated the refractions of a number of amino-acids and polypeptides with the view of obtaining data by means of which scission of polypeptides or proteins into their constituent amino-acids, as well as the reverse reactions, may be investigated.
T. H. P.

The Natural Proteins. I. Behaviour of Chlorine Dioxide towards Organic Substances. ERICH SCHMIDT and KARL BRAUNSDORF (*Ber.*, 1922, 55, [B], 1529—1534; cf. Schmidt and Graumann, A., 1921, i, 912; Schmidt and Duysen, this vol., i, 206).—The behaviour of substances closely allied to the natural proteins towards chlorine dioxide has been investigated by the method described previously (Schmidt and Graumann, *loc. cit.*) except that it has been found advisable to alter the order of addition of the reagents in the final titration, 3 c.c. of 2-*N*-sulphuric acid, followed by 1.5 c.c. of 2-*N*-aqueous potassium iodide solution and 2—3 c.c. of water being run into the liquid in the given sequence. The substances are considered to be stable towards the reagent when the chlorine dioxide content of the solution is not diminished by more than 2% after periods of twenty-four, forty-eight, or seventy-two hours. The following substances are stable: amino-acids and their derivatives (urethane, glycine, glycine hydrochloride, ethyl aminoacetate hydrochloride, aminoacetonitrile sulphate, glycineamide hydrochloride, phenylaminoacetic acid, hippuric acid, betaine, betaine hydrochloride, creatine, alanine, phenylalanine, valine, leucine and its hydrochloride, aspartic acid, asparagine, glutamic acid, serine, hydroxyproline, taurine, glycylglycine hydrochloride, leucylglycine, triglycine); amines and their derivatives (tetramethylenediamine hydrochloride, pentamethylenediamine hydrochloride, α -aminopropane- β -ol oxalate, guanidine hydrochloride, tetramethylammonium chloride, choline hydrochloride); amides and their derivatives (acetamide, chloroacetamide, propionamide, phenylacetamide, *s*-dimethyloxamide, carbamide, biuret, hydantoin); imides (glutarimide, phthalimide); polyhydroxy-alcohols (ethylene glycol, glycerol, mannitol, carbohydrates, inositol); mono- and poly-basic acids, esters (acetic acid, chloroacetic acid, stearic acid, benzoic acid, oxalic acid, adipic acid, trilaurin, tristearin, α -crotonic acid, maleic acid and its anhydride, fumaric acid); hydroxy-acids. esters (ethyl lactate, tartaric, citric, and quinic acids); nitriles (acetonitrile, benzonitrile, succinonitrile); cyclic compounds (benzene, naphthalene, cyclohexane, pyridine sulphate, quinoline hydrochloride, piperidine hydro-

chloride, β -nitroanethole). The following substances are attacked by chlorine dioxide: amino-acids and derivatives (tyrosine, *N*-benzoyltyrosine, 3:4-dihydroxyphenylalanine, tryptophan, histidine hydrochloride, cystine); mono- and poly-hydroxyphenols; unsaturated carbon compounds (*cyclohexene*, allyl alcohol, anethole, cinnamyl alcohol, cinnamaldehyde, oleic acid, triolein, uric acid, furfuraldehyde, indole, β -methylindole); carbon-sulphur compounds (mercaptans, dialkyl disulphides, compounds such as thiocarbamide).

Histologically, a solution of chlorine dioxide in acetic acid is found to be very useful for the removal of stains due to melanins from tissues without in the least affecting their anatomical features.

H. W.

Yeast-nucleic Acid. III. H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1922, **120**, 292—295).—Guanlyic acid can be obtained from yeast-nucleic acid when the sodium salt of the latter is treated with dilute sodium hydroxide solution. The guanlyic acid portion of the molecule can thus be completely removed if the reaction takes place at the ordinary temperature. No guanlyic acid is removed when the manipulation is carried out at 0°.

S. S. Z.

The Dissolution of Gelatin. FRED FAIRBROTHER and ENOCH SWAN (*T.*, 1922, **121**, 1237—1244).

The Sol-Gel Equilibrium in Protein Systems. ROBERT HERMAN BOGUE (*J. Amer. Chem. Soc.*, 1922, **44**, 1313—1322).—Viscosity-plasticity relations of solutions of gelatin of different concentrations and over a temperature range from 25° to 60° have been studied by measurements with a MacMichael torsional viscometer. The results indicate that gelatin in aqueous solution follows the laws of viscous flow at the higher temperatures and has the properties of plastic flow at lower temperatures. The transition between the sol and gel form does not take place at any definite temperature, but extends throughout a rather indefinite period of temperature. Further it was found that, at a given temperature, the increase or decrease in viscosity with time was dependent on the hydrogen-ion concentration, the nature of the inorganic ions present, and the amount of hydrolysed protein in the system. It is considered that the viscosity of pure gelatin at any given hydrogen-ion concentration is inversely proportional to some function of the temperature, and that, at equilibrium, there will be some viscosity which will correspond with every point of temperature.

W. G.

The Structure of Elastic Gels. ROBERT HERMAN BOGUE (*J. Amer. Chem. Soc.*, 1922, **44**, 1343—1356; cf. preceding abstract and *Chem. Met. Eng.*, 1920, **23**, 61).—The author restates his theory as to the catenary or fibrillar structure of gelatin-water systems and quotes further work and contemporary investigations

in support of this hypothesis and further postulates. According to this theory, the sol consists of slightly hydrated or swollen molecules united into short chains. When the temperature falls the threads increase in length and number, and their power of water absorption increases, resulting in an increase in viscosity. A solid jelly results when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity is dependent on the relative amount of free solvent in the interstices of the aggregates, and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is dependent on the length and number of the catenary threads. Solution is the reverse of gelation and the swelling is determined by osmotic forces and the Donnan equilibrium.

The results of a study of the influence of electrolytes, of varying hydrogen-ion concentration, and of the valency of the combining ion on several of the characteristic properties of gelatin, namely, swelling, viscosity, jelly consistency, foam, turbidity, and alcohol number, give additional support to the theory. Smith's data on mutarotation (cf. *J. Ind. Eng. Chem.*, 1920, **12**, 878) are in accord with the theory, as is Loeb's occlusion theory. W. G.

Action of Alum on Animal Glue. A. GUTBIER, E. SAUER, and F. SCHELLING (*Kolloid Z.*, 1922, **30**, 376—395).—Treatment of glue by alum brings about two actions, a strong increase in the viscosity without any visible change and at a higher temperature in faintly acid solutions the formation of a precipitate. The addition of alum to both bone and leather glue immediately reduces the colour. The sensitiveness of glue to alum varies with the different varieties, thus the viscosity of leather glue is increased by very small concentrations of alum, whilst very large concentrations are necessary to give a noteworthy increase of viscosity with bone glue. At higher temperatures, in the case of leather glue there is a continuous decrease in the viscosity, depending on the concentration of the alum and the time during which the two substances have been in contact. Bone glue is much more stable than leather glue to high temperatures and to alum. The basic aluminium compounds and aluminium hydroxide which are present in colloidal form in alum solution have a specific action on glue, and, further, the hydrogen ion, due to hydrolysis, also has a specific action. Glue jellies mixed with alum on dialysis allow all the other constituents of the alum to be removed, but hold the aluminium back quantitatively. The precipitates produced during the clarification of glue by alum and phosphoric acid contain both glue and aluminium in varying proportions, and belong to the group of adsorption compounds; they have a considerable surface energy and consequently possess a great clarifying power. The more rapidly the precipitate forms, the greater is its clarifying power.

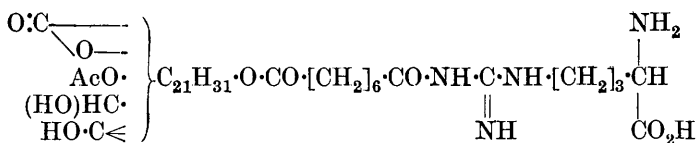
After a correctly carried out clarification, the glue contains only small quantities of aluminium, but it contains the whole of the acid added. The clarification of glue is accompanied always by a deterioration, as shown by the decrease in the viscosity. This is not due directly to the clarification process, but to secondary reactions. The acid added and the prolonged heating bring about hydrolysis which yields substances that are not glue-like. Leather glue is more sensitive than bone glue in this respect. J. F. S.

The Composition of Silk Fibroin and its Structure.

EMIL ABDERHALDEN (*Z. physiol. Chem.*, 1922, **120**, 207—213).—One hundred parts of ash-free silk fibroin yielded 25 of *d*-alanine, 2.5 of *l*-leucine, 1.5 of phenylalanine, 1.8 of *l*-serine, and 1 of *l*-proline. Altogether 86.4% of the amino-acids were accounted for. The examination of products in the intermediate stages of the process of hydrolysis showed the presence of considerable quantities of *d*-alanyl-glycine anhydride m. p. 240—247°, $[\alpha]_D -5.02^\circ$, small quantities of glycyl-*l*-tyrosine anhydride, and a compound containing serine, *d*-alanine, and glycine. S. S. Z.

The Protamines. R. EBERHARD GROSS (*Z. physiol. Chem.*, 1922, **120**, 167—184).—When clupeine is heated for eighty minutes with 4 vol. % sulphuric acid at 160°, it loses the property of giving the biuret reaction. The hydrolysed product contains arginine, and monoamino-acids as well as a dipeptide-like compound consisting of a combination of at least two arginine molecules. By precipitating with phosphotungstic acid in alcoholic solution, it is possible to separate free arginine from the arginine peptide. The author confirms Nelson-Gerhardt's deduction (A., 1919, i, 503) that in clupeine the monoamino-acids are linked together. S. S. Z.

The Poisonous Substance of Toads. HEINRICH WIELAND and RICHARD ALLES (*Ber.*, 1922, **55**, [B], 1789—1798; cf. Wieland and Weil, A., 1913, i, 1343).—Further attempts to isolate the poisonous material from the skin of the toad have led to an unexpected result, since a more careful repetition of methods that were previously successful did not lead to the isolation of bufotalin. It now appears that this is not present as such, but is a product of the decomposition of the actual poison, *bufotoxin*, $C_{40}H_{62}O_{11}N_4$, m. p. 204—205° (decomp.). The isolation of the latter from the extract of the skins and from the secretions of the glands is described in detail. Bufotoxin is readily reduced by hydrogen in alcoholic solution in the presence of palladium black to *hydrobufotoxin*, $C_{40}H_{64}O_{11}N_4$, slender needles, m. p. 187°. Bufotoxin is readily hydrolysed by mineral acids to bufotalein and suberylarginine; the latter could not be caused to crystallise, but its composition is established by hydrolysing it with more concentrated acid to suberic acid and arginine. The constitution of bufotoxin may be resolved as follows:



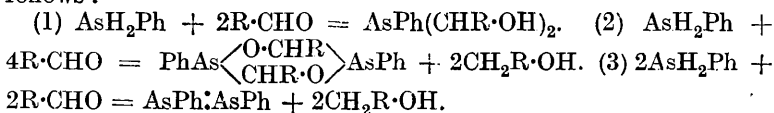
Its conversion into bufotalin is expressed by the scheme: $\text{C}_{26}\text{H}_{37}\text{O}_6 \cdot \text{O} \cdot \text{CO} \cdot \text{C}_{13}\text{H}_{25}\text{O}_3\text{N}_4 = \text{C}_{26}\text{H}_{36}\text{O}_6$ (bufotalin) + $\text{C}_{14}\text{H}_{26}\text{O}_5\text{N}_4$, whereas its hydrolysis by dilute hydrochloric acid takes place in accordance with the equation: $\text{C}_{40}\text{H}_{62}\text{O}_{11}\text{N}_4 \longrightarrow \text{C}_{24}\text{H}_{30}\text{O}_3$ (bufotalein) + $\text{C}_{14}\text{H}_{26}\text{O}_5\text{N}_4 + \text{CH}_3 \cdot \text{CO}_2\text{H} + \text{H}_2\text{O}$.

Acetylbufotalin is converted by concentrated hydrochloric acid into acetylbufotalein, $\text{C}_{26}\text{H}_{32}\text{O}_4$, which is identical with the product obtained by Wieland and Weil (*loc. cit.*) by the acetylation of bufotalein. Catalytic hydrogenation of acetylbufotalein in the presence of platinum black leads to the formation of acetylbufotalan, $\text{C}_{26}\text{H}_{40}\text{O}_4$, aggregates of needles, m. p. 165° . H. W.

Physico-chemical Studies on Biological Reactions. I. PAUL HIRSCH (*Fermentforsch.*, 1922, 6, 27—29).—The author is proposing to employ physico-chemical methods, particularly optical methods, for the investigation of the problems of enzymes and immuno-chemistry. T. H. P.

Dependence of the Action of Succinodehydrogenase on Hydrogen-ion Concentration. ERIK OHLSSON (*Skand. Arch. Physiol.*, 1921, 41, 77—100; from *Chem. Zentr.*, 1922, i, 58 (cf. this vol., i, 792, and Widmark, A., i, 600).—Succinodehydrogenase prepared from horse muscle has as optimum conditions P_{H} 8.7 and 45° . Higher temperatures depress activity. The enzyme is inactive at 55° . The velocity of reaction is independent of the concentration of the reacting substances, provided they are present in minimal amount. G. W. R.

The Reactions of the Arsines. II. Condensation of Aromatic Primary Arsines with Aldehydes. CHARLES SHATTUCK PALMER and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, 44, 1356—1382; cf. A., 1921, i, 70).—Primary arylarsines and aldehydes react in three ways, depending on the conditions of the reaction, as follows:—



Aromatic primary arsines and aliphatic aldehydes condense in the presence of concentrated hydrochloric acid at room temperature to give compounds of the type $\text{AsPh}(\text{CHR} \cdot \text{OH})_2$. With aromatic aldehydes, it is best to use dry hydrogen chloride, with or without a solvent.

Details are given for preparing phenylarsinic acid and phenylarsine on a large scale, and from the latter the following compounds

are prepared. Phenylarsine has d_{25}^{25} 1.349, n_D^{25} 1.6082. *Phenyldi- α -hydroxyethylarsine*, $\text{AsPh}(\text{CHMe}\cdot\text{OH})_2$, has b. p. 175—176°/22 mm., d_{25}^{25} 1.252, n_D^{25} 1.5619, giving a *platinichloride*, m. p. 169—170°. *Phenyldi- α -hydroxy-n-propylarsine*, b. p. 196—197°/24 mm., d_{25}^{25} 1.176, n_D^{25} 1.5425 giving a *platinichloride*, m. p. 148—149°. *Phenyldi- α -hydroxy-n-butylarsine*, b. p. 187°/10 mm., d_{25}^{25} 1.116, n_D^{25} 1.5271 giving a *platinichloride*, m. p. 119—121°. *Phenyldi- α -hydroxyisovalerylarsine*, b. p. 170°/6 mm., m. p. 62°, d_{25}^{25} 1.079, n_D^{25} 1.5202 giving a *platinichloride*, m. p. 84—85°. *Phenyldi- α -hydroxy-n-heptylarsine*, b. p. 263—264°/2 mm., d_{25}^{25} 1.069, n_D^{25} 1.4650. *Phenyldi- α -hydroxy-p-chlorobenzylarsine*, m. p. 164°. *Phenyldi- α -hydroxy-p-methoxybenzylarsine*, a yellow oil. *Phenyldi- α -hydroxy-o-carbomethoxybenzylarsine*, m. p. 145—147°.

[With W. A. CAROTHERS.]—*p-Chlorophenylarsine*, m. p. 30.5—30.7°; b. p. 116°/33 mm., 159°/200 mm.; d_{25}^{25} 1.507, n_D^{25} 1.6143 gives *p-chlorophenyldi- α -hydroxybenzylarsine*, m. p. 218—218.5°, and *p-chlorophenyldi- α -hydroxyethylarsine*, b. p. 183°/23 mm.; d_{25}^{25} 1.336; n_D^{25} 1.5728.

[With E. E. PARKS.]—*o-Chlorophenylarsine*, b. p. 206°, d_{25}^{25} 1.519, n_D^{25} 1.6250, obtained from *o-chlorophenylarsinic acid*, m. p. 186—187°, gives *o-chlorophenyldi- α -hydroxybenzylarsine*, m. p. 146—147°.

[With G. O. BURR.]—*p-Tolylarsine*, b. p. 113.5°/44 mm., m. p. 20°, d_{25}^{25} 1.295, n_D^{25} 1.5891, gives *p-tolyldi- α -hydroxybenzylarsine*, m. p., 208° and *p-tolyldi- α -hydroxyethylarsine*, b. p. 176—177°/22 mm., d_{25}^{18} 1.2331, n_D^{20} 1.5570.

[With J. S. PIERCE.]—*o-Tolylarsine*, b. p. 121°/93 mm., d_{25}^{25} 1.301; n_D^{25} 1.5925, gives *o-tolyldi- α -hydroxybenzylarsine*, m. p., 140° and *o-tolyldi- α -hydroxyethylarsine*, b. p. 165°/21 mm., d_{25}^{25} 1.244, n_D^{30} 1.5573.

Many of these compounds oxidise slowly in the air with the formation of an arsenic acid and aldehyde. The process is more rapid in the presence of a solvent such as carbon tetrachloride. With oxidising agents, halogens, phosphorus pentachloride and phenylarsenious chloride these compounds behave exactly as if they were a mixture of phenylarsine and aldehyde. The aliphatic derivatives may be titrated quantitatively in ethereal solution with iodine, the following reaction occurring: $\text{C}_6\text{H}_5\text{As}(\text{CHR}\cdot\text{OH})_2 + 2\text{I}_2 \longrightarrow \text{AsPhI}_2 + 2\text{HI} + 2\text{R}\cdot\text{CHO}$.

The compounds form unstable additive products with halogen acids and stable additive compounds with chloroplatinic acid. They are decidedly stable towards reducing agents and towards certain dehydrating agents. They do not react with Grignard reagents. With certain dehydrating agents such as acetyl chloride, acetic anhydride, or even anhydrous hydrogen chloride, they react to give tetrahydro-1:4:2:5-dioxadiarsines as shown in equation (2) above. These compounds are also obtained directly from primary aromatic arsines and aldehydes by leaving the mixture for two days in the presence of anhydrous hydrogen chloride; the following are described. 2:5-Diphenyltetrahydro-1:4:2:5-dioxadiarsine, b. p., 215

—216°/9 mm., d_{25}^{25} 1.547, n_D^{25} 1.6522. 2:5-Diphenyl-3:6-dimethyl-tetrahydro-1:4:2:5-dioxadiarsine, b. p. 257°/10 mm., d_{25}^{25} 1.369, n_D^{25} 1.6332, giving a *platinichloride*, m. p. 130—131°, and a *cuprichloride*, m. p. 150—152°. 2:5-Diphenyl-3:6-diethyltetrahydro-1:4:2:5-dioxadiarsine, b. p. 212°/2 mm., d_{25}^{25} 1.336, n_D^{25} 1.6217. 2:5-Diphenyl-3:6-di-n-propyltetrahydro-1:4:2:5-dioxadiarsine, b. p. 241—242°/2 mm., d_{25}^{25} 1.297, n_D^{25} 1.5856. 2:5-Diphenyl-3:6-di-isobutyltetrahydro-1:4:2:5-dioxadiarsine, b. p. 240°/16 mm., d_{25}^{25} 1.296, n_D^{25} 1.5869, giving a *platinichloride*, m. p. 76—77°, and a *cuprichloride*, m. p. 78—79°. 2:5-Diphenyl-3:6-difuryltetrahydro-1:4:2:5-dioxadiarsine. The tetrahydrodioxadiarsines oxidise in the air to give arylarsine oxides and aldehydes. With iodine and phosphorus pentachloride, products are obtained which might be expected from a mixture of arylarsine and aldehyde.

The reaction of type (3) given above occurs when a mixture of an aromatic primary arsine and an aromatic aldehyde is left at room temperature without a catalyst or if the mixture is heated with or without a catalyst.

W. G.

Physiological Chemistry.

Surface Reactions in Living Cells. O. WARBURG (*Z. Elektrochem.*, 1922, **28**, 70—75).—The processes of breathing and assimilation by living cells has been investigated in the case of red blood-corpuscles, and bacterial and plant cells in various circumstances. The rate of oxidation of cystine, and that of assimilation, in the presence of narcotics has been investigated, and the quantity of narcotic determined, in the case of alcohols, urethanes, ketones, nitriles, and substituted carbamides, which is necessary to reduce the assimilation by 50%. The quantity of narcotic decreases rapidly from member to member in an homologous series, thus a solution of methyl alcohol containing 5 mols. per litre cuts down the breathing and assimilation by 50%, whilst 0.045 mol. per litre of amyl alcohol has the same effect. The following hypothesis of the surface action of living cells is put forward. The surface of the solid cell constituents is to be regarded as a mosaic of regions poor in iron and rich in iron, of which those poor in iron are the most abundant. Both the metal-containing and metal-free areas adsorb dissolved substances from the cell fluids, and in general to the same extent. Hydrocyanic acid, on account of its affinity for the heavy metals, is mainly adsorbed on the metal-containing areas. Consequently the seat of the chemical processes, breathing and assimilation, is the iron-containing surface. When hydrocyanic acid is brought into a

living cell, its effect is to displace the reacting substances from the iron-containing regions and so stop assimilation and breathing. Very little hydrocyanic acid is sufficient to achieve this, since the metal-containing areas constitute only a small fraction of the whole surface. For the same reason, the displacement from the metal-containing areas leads to no noticeable reduction in the total amount of adsorbed substance. Consequently, the action of hydrocyanic acid depends on specific adsorption and displacement. Narcotics displace the reacting substances from both regions and to the same extent, and so stop breathing and assimilation, but in this case the whole surface must be covered with the displacing substance. The quantity of narcotic necessary to produce the same effect on assimilation and breathing is therefore extremely large in comparison with the amount of hydrocyanic acid. Hence it may be stated that the cause of the acceleration of reactions in living cells is the adsorption in iron-containing parts of the surface. J. F. S.

The Rôle of Vitamins in the Chemistry of the Cell. W. R. HESS (*Z. physiol. Chem.*, 1922, **120**, 277—280).—Polemical in reply to Abderhalden (this vol., i, 607).

The Action of Whole Blood on Acids. ERNEST LAURENCE KENNAWAY and JAMES MCINTOSH (*Biochem. J.*, 1922, **16**, 380—386).—If sulphuric acid (0.01*N*) containing 0.9% of sodium chloride be shaken with whole blood, and the mixture centrifuged, about 80% of the acid is removed, so that it is no longer titrable in the fluid. If acid be added to plasma, the amount neutralised is approximately constant for a given amount of plasma, and does not vary with the amount of acid used. On the other hand, the resulting P_H in the two cases is approximately the same for a given ratio of acid to blood, the plasma showing a rather greater acidity. Laked blood does not appear to neutralise so efficiently as whole blood, and so the action of the latter seems to be due to some form of adsorption, dependent on the structure of the corpuscles. W. O. K.

Carbonic Acid Compounds and Hydrogen-ion Activities in Blood and Salt Solutions. ERIK JOHAN WARBURG (*Biochem. J.*, 1922, **16**, 153—340).—This comprehensive paper deals with the equilibrium of dissolved substances in homogeneous and heterogeneous media, with particular reference to the theories of Bjerrum and of Donnan. The general theoretical results are applied to elucidate the carbon dioxide equilibrium and the hydrogen-ion concentration in blood and also the development of a modified Henderson-Hasselbach equation. For the mathematical and experimental investigations and results, the original must be consulted. The paper includes valuable reviews of previous work. W. O. K.

Calcium in the Blood of various Species of Animals. P. MAZZOCCO (*Anal. Asoc. Quím. Argentina*, 1921, **9**, 313—325).—The method of Halverson and Bergeim (*A.*, 1918, i, 50) is modified

by using trichloroacetic acid (cf. Lyman, A., 1917, ii, 271) instead of sodium picrate to precipitate albumins. An improved method of washing the precipitate of calcium oxalate by decantation is described. Data are given for the calcium content of entire blood, plasma, corpuscles, and serum for different species of animals. The calcium content of the blood constituents of the same animal species is **very constant**. Calcium occurs, although in small amounts, equally in nucleated and non-nucleated red corpuscles. The calcium content of plasma is practically identical with that of serum. G. W. R.

Does Cyanic Acid Exist in the Blood ? MAURICE NICLOUX and GEORGES WELTER (*Compt. rend.*, 1922, **174**, 1733—1735).—The authors find no indication of the presence of cyanic acid either in blood or lymph in the normal state. W. G.

Blood Sugar. II. Alimentary Hyperglycæmia under Normal and Pathological Conditions. MAX ROSENBERG (*Arch. expt. Path. Pharm.*, 1922, **93**, 208—240).—A comparative analysis of the type of curves obtained by estimating the sugar of the blood at intervals after the oral administration of 100 grams of dextrose in normal individuals, in diabetes and in hyperthyroidism.

C. R. H.

Creatine and Creatinine Metabolism. IV. The Question of the Occurrence of Creatinine and Creatine in Blood. JEANETTE ALLEN BEHRE and STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, **52**, 11—33).—In the estimation of creatinine in blood filtrates by Folin's method (A., 1914, ii, 505) the coloration produced with picric acid is due to a substance which differs from creatinine in two respects; it is not adsorbed by kaolin from acid solutions, neither is it destroyed by boiling with alkalis. The amount of chromogenic substance present in the blood increases when the kidney function is impaired, and, in this case, it is to some extent adsorbed by kaolin and destroyed by alkalis. Nevertheless, it was found impossible to isolate creatinine from such bloods, although small quantities of added creatinine were recovered almost quantitatively in the form of the zinc chloride compound. It is thus improbable that creatinine is present in blood in more than minute amounts.

The creatine content of blood is best estimated by a method similar to that used for urine (A., 1914, ii, 688). The preliminary conversion into creatinine must not be effected by heating with picric acid, since, under these conditions, picric acid reacts with blood to give a product yielding colour on addition of alkali. The blood of dogs with impaired kidney function showed a high creatine content; this suggests that blood creatine is a waste product which is eliminated by the kidney in the form of creatinine or of some other substance. E. S.

The Relation of Salivary to Gastric Secretion. TOMOICHI NAKAGAWA (*Biochem. J.*, 1922, **16**, 390—393).—Boiled potato

starch inhibits the action of the pepsin and accelerates the action of the rennin of the natural gastric juice, but not after being acted on by fresh human saliva. Saliva has a delaying action of its own on the clotting of milk. W. O. K.

Intestinal Intoxication. I. The Presence and Significance of Histamine in an Obstructed Bowel. R. W. GERARD (*J. Biol. Chem.*, 1922, **52**, 111—124).—The presence of histamine in the fluid contained in closed loops of the large and small intestine of dogs was indicated qualitatively by its depressant action when injected intravenously in dogs, and by its action on strips of the intestine of a guinea pig. Estimations by the method of Hanke and Koessler (A., 1920, ii, 784) gave average values corresponding with 2 to 3 mg. of the dihydrochloride per 100 c.c. of fluid. Evidence was also obtained of the presence of a histamine derivative of a peptide nature. No histamine was found in the sterile secretion of jejunum, although it was present in the sterile mucosa. Loop fluid and mucosa also contain histidine. E. S.

The Oxidising Enzymes in the Phenomena of Life in its Normal and Pathological States. G. MARINESCO (*Bul. Soc. Chim. Romania*, 1922, **4**, 3—12).—A more detailed account of work already published (A., 1920, i, 130). W. G.

Decomposition of Proteins of Organs. K. THOMAS (*Festschr. K. Wilhelm Ges. Förd. Wiss. Zehnjährigen Jubiläum.*, 1921, 205—207; from *Physiol. Abstr.*, 1922, **7**, 187).—Organ protein undergoes in the body changes which are different from those undergone by protein introduced in the food. For example, arginine is regularly formed from organ protein during minimum nitrogen excretion, whereas it is not formed from food protein. The amino-acids in the organ protein can apparently undergo chemical changes without cleavage of the peptide linking. W. O. K.

Origin and Destiny of Cholesterol in the Animal Organism. XIII. The Autolysis of Liver and Spleen. JOHN ADDYMAN GARDNER and WILLIAM FOX (*Proc. Roy. Soc.*, 1922, [B], **93**, 486—492).—The autolysis under aseptic conditions of liver and spleen is not accompanied by increase in the amount of cholesterol present. It is unlikely therefore that either of these organs is concerned with the synthesis of cholesterol in the body. C. R. H.

The Permeability of the Glomerulus Membrane for Stereoisomeric Sugars. H. J. HAMBURGER (*Berlin Klin. Woch.*, 1922, **1**, 418; from *Physiol. Abstr.*, 1922, **7**, 192).—The permeability of the membrane is not related to the size of molecule of the sugar, but to its configuration; thus lactose goes through although its molecule is twice the size of that of dextrose, which does not; *d*-galactose consists of α - and β -modifications, one of which passes; the other does not. The same is true for α - and β -xylose. W. O. K.

The Influence of Adrenaline on the Permeability of the Limiting Membrane of Muscle Fibres. HERMANN LANGE (*Z. physiol. Chem.*, 1922, **120**, 249—266).—It has been ascertained by chemical and physiological methods that adrenaline possesses the property of diminishing the permeability of the limiting membrane of the muscle fibres of the frog. S. S. Z.

Continuous Current and Permeability (in Muscle). II. Effect of Alkaloidal Salts and Other Organic Electrolytes. JOSEPH VORSCHÜTZ (*Pflüger's Archiv*, 1921, **190**, 54—65; from *Chem. Zentr.*, 1922, i, 3).—A continuation of work on the electrical effect of substances on muscle. Strychnine, pilocarpine, codeine, and brucine salts are electrically indifferent: atropine, cocaine, and morphine salts react electronegatively. Quinine, optochin, and caffeine salts, and to a lesser degree cinchonine salts, develop a strong continuous current. These alkaloids, which are muscle poisons, probably exert their effect on muscle by means of the free bases liberated by hydrolysis. Salts of quaternary ammonium bases, sodium salts of the lower fatty acids, sodium salicylate, and sodium benzoate are almost without effect or react slightly electronegatively. The effect is independent of the length of the carbon chain. G. W. R.

The Physiology of Creatine. OTTO RIESSER (*Z. physiol. Chem.*, 1922, **120**, 189—206).—Although the total creatine-content of the mixed skeletal muscles of the rabbit is always the same, those of the various muscles differ from one another by amounts depending on the rate of contraction. Parallelism exists between the creatine and the lactacidogen contents of the various muscles. This parallelism does not persist when the condition of the muscles is altered by various factors. The author cannot confirm R. Kahn's observations (*Pflüger's Archiv*, 1919, **177**, 294). S. S. Z.

The Effect of Cold Storage on the Carnosine Content of Muscle. WINIFRED MARY CLIFFORD (*Biochem. J.*, 1922, **16**, 341—343).—Using the colorimetric method previously described (Clifford, A., 1921, ii, 604), it has been found that the carnosine content of meat decreases during cold storage. W. O. K.

Influence of Minute Concentrations of Acid and Alkali on the Blood-vessels and other Smooth Muscle. PAUL HEYMANN (*Arch. expt. Path. Pharm.*, 1922, **90**, 27—76).—The existing literature dealing with the physiological action of acid and alkali on smooth muscle is reviewed at some length. A long series of experiments, performed for the most part by the perfusion of the blood-vessels of frogs or of surviving rabbits' ears, is described. The effect on the rate of flow of the perfusion fluid caused by the addition of small amounts of acid and alkali was investigated, and some experiments were also carried out on isolated strips of smooth muscle. It was found that concentrations

of acid or alkali of the order of $N/1000$ cause marked vaso-constriction; this is antagonised by sodium nitrite and by hypertonic salt and sugar solutions. The effect was obtained both with Ringer's solution and with serum as the original perfusion fluid. Simultaneously with the vaso-constriction, there appears marked oedema, the formation of which is, however, apparently dependent on the particular acid employed; those acids (sulphuric and phosphoric) which have the weakest vaso-constrictor effect produce the greatest oedema.

The constrictor effect of adrenaline is abolished or reversed during perfusion with acid fluids; it is unaffected by alkalis.

In physiological salt solution (free from calcium), lactic acid and carbon dioxide cause vaso-dilatation. Isolated smooth muscle is stimulated by small and inhibited by large concentrations of acid and alkali. Alkalis act directly on the muscle alone; acids also act on the nervous apparatus, which they first stimulate and then inhibit.

C. R. H.

Action of Muscle Tissue on Fumaric, Maleic, Glutaconic, and Malic Acids. H. D. DAKIN (*J. Biol. Chem.*, 1922, **52**, 183—189).—By the action of muscle enzymes, fumaric acid is converted into *l*-malic acid and not into *i*-malic acid, as stated by Einbeck (A., 1919, i, 467). Maleic acid, under the same conditions, gives no trace of malic acid; glutaconic acid, however, is to a small extent converted into β -hydroxyglutamic acid. When *i*-malic acid is submitted to the action of muscle tissue, the *lævo*-component is preferentially consumed and is converted, to some extent, into fumaric acid. The *bisphenylhydrazide* of *i*-malic acid, colourless prisms, m. p. 221—224° (uncorr.), has been prepared. E. S.

Spontaneous Reducing Effect of Muscle on Methylene-blue. Physiology of Dehydrogenases. GUNNAR AHLGREN (*Skand. Arch. Physiol.*, 1921, **41**, 1—30; from *Chem. Zentr.*, 1922, i, 58; cf. Widmark, A., i, 600).—By the agency of dehydrogenases occurring in muscle, hydrogen is abstracted from certain substances, called hydrogen "donators," and added to methylene-blue, which is changed thereby to the leuco-base. Methylene-blue, acting as hydrogen acceptor, thus plays the same physiological rôle as oxygen. Substances which can act as hydrogen donators have specific dehydrogenases. The reducing power of muscle is estimated by determining the time required for decolorisation of known amounts of methylene-blue. The red muscle of rabbits and doves has greater reducing power than white muscle. Heart muscle has greater reducing power than skeletal muscle. Seasonal variation in reducing power of frog muscle was observed with a summer maximum and a winter minimum. Reducing power is greatest in mammalian muscle. The lowest reducing power is shown by the muscle of worms.

G. W. R.

Alligator and Crocodile Oils. SHŪMEI KOBAYASHI (*J. Chem. Ind., Japan*, 1922, **25**, 691—703).—An alligator oil

obtained from *Alligator mississippiensis* from North America is a light yellow liquid of peculiar fishy odour (d_4^{15} 0.9285 and n^{20} 1.4795). Arachidonic, clupanodonic, oleic, and palmitic acids, and a new acid of the $C_nH_{2n-8}O_2$ series were detected in the saponification product of the oil. The new acid, $C_{22}H_{36}O_2$, has n^{20} 1.4888 and iodine value 308.0, and on hydrogenation gives an acid of m. p. 76—76.5°. A crocodile oil obtained from *Crocodilus niloticus* from Africa is a solid fat at room temperature (d_4^{10} 0.8989, n^{40} 1.4602, iodine value 60.3). It is mainly composed of almost equal amounts of oleic and stearic esters, a small amount of highly unsaturated acid esters being also present.

K. K.

The Dyes from *Purpura aperta* and *Purpura lapillus*. P. FRIEDLÄNDER (*Ber.*, 1922, **55**, [B], 1655—1658).—The dye obtained from *Purpura aperta* appears to be identical with 6 : 6'-dibromindigotin in so far as elementary analysis, solubility, dyeing capacity, and absorption spectrum allow a judgment to be formed. A more complete comparison of the natural and synthetic products was impossible by reason of the limited amount of dye available. The dye from *Purpura lapillus* appears to be identical with dibromindigotin, but the amount of material was too small to permit an elementary analysis.

H. W.

Comparative Spectroscopic Study of the Green Pigment of the *Chetoptera* and of the Chlorophyll of the *Ulva*. MARC ROMIEU and FERNAND OBATON (*Compt. rend.*, 1922, **175**, 51—54).—The spectra of chetopterins, the green pigment of *Chetoptera* and of the chlorophyll of *Ulva* coincide almost exactly, and thus indicate the relationship of the two pigments. Chetopterin is thus a pigment of extrinsic origin, which must be placed in the group of enterochlorophylls.

W. G.

The Origin of Creatine and Creatinine. H. STEUDEL and R. FREISE (*Z. physiol. Chem.*, 1922, **120**, 244—248).—The intravenous injection of the sodium salt of nucleic acid and of histidine in the dog did not alter the creatinine content of the urine. It was, however, observed in some of these experiments that the injection influenced the metabolic process.

S. S. Z.

Sulphohæmoglobinæmia. A. A. HIJMAN VAN DEN BERGH (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **23**, 1392—1398).—In the blood of a certain percentage of healthy rabbits and in that of human beings suffering from intestinal stasis, spectroscopic evidence is obtained of the presence of sulphohæmoglobin. Combined estimations of the available hæmoglobin by Barcroft's method and of the iron-content by the titanium method show that as much as 20% of the total hæmoglobin may be in the form of the sulphur compound. Sulphohæmoglobinæmia is not associated with the presence of demonstrable amounts of hydrogen sulphide in the blood serum.

C. R. H.

The Composition of the Scales in Psoriasis. EMIL APDERHAIDEN and BERNHARD ZORN (*Z. physiol. Chem.*, 1922, **120**, 214—219).—On extracting 9.2742 grams of the dry scales with carbon tetrachloride in a Soxhlet apparatus 0.6894 gram was obtained of a fraction containing 0.00075 of phosphorus. The extracted residue contained 0.0233 of phosphorus. The moisture varied from 7.45 to 9.5%. The average ash content of dry scales was found to be 1.185%. The following amino-acids were established in the substance:—Alanine 4.5%, serine 0.78%, cystine 1.85%, valine 3.25%, leucine 5.25%, glutamic acid 6.5%, phenylalanine 2.32%, tyrosine 3.25%, and proline 3.05%. S. S. Z.

The [Physiological] Action of Mercury. WILLIAM SALANT and NATHANIEL KLEITMAN (*J. Pharm. Expt. Ther.*, 1922, **19**, 315—330).—Mercury salts produce in animals a sudden fall of blood-pressure and depression and paralysis of respiration, and in some cases profound cardiac disturbances. W. O. K.

Pharmacological Studies on Acetone. WILLIAM SALANT and NATHANIEL KLEITMAN (*J. Pharm. Expt. Ther.*, 1922, **19**, 293—306).—The pharmacological action of acetone is considerable, especially in inhibiting the respiration and heart-beat, and in producing fall of blood-pressure. It is particularly potent when a number of just active doses are given. W. O. K.

Toxicity of Scatole. WILLIAM SALANT and NATHANIEL KLEITMAN (*J. Pharm. Expt. Ther.*, 1922, **19**, 307—313).—Scatole is a toxic substance, causing depression of the circulation and of the central nervous system. W. O. K.

Chemistry of Vegetable Physiology and Agriculture.

Effect of Sugar on the Production of Indole. R. APPELMANS (*Compt. rend. Soc. Biol.*, 1921, **85**, 725—727; from *Chem. Zentr.*, 1922, i, 52—53).—The production of indole was studied in media with and without sugars; the sugars used being dextrose, maltose, sucrose, lactose, and mannitol. With *Bacillus coli* there is a general parallelism between the inhibition of indole production and gas formation; two exceptions were observed in the presence of sucrose. Similar results were obtained with *Proteus vulgaris*, *Bacillus pseudodysentericus*, cholera vibrio, and *Vibrio septicus*. The production of indole can occur when the fermentable material is used up.

G. W. R.

Effect of Manganous Chloride on the Formation of Diphtheria Toxin. L. E. WALBUM (*Compt. rend. Soc. Biol.*, 1921, **85**, 619—620; from *Chem. Zentr.*, 1922, i, 51).—Diphtheria bacilli are cultivated in bouillon with 1.5% Witte peptone, 0.5% sodium chloride, and 0.2% invert-sugar. The formation of toxin is increased six-fold by the addition of 0.01 c.c. of *N*-manganous chloride to 1000 c.c. of the medium. Larger additions of manganous chloride decrease the formation of toxin. G. W. R.

Effect of Different Metallic Salts on the Formation of Staphylolysin. L. E. WALBUM (*Compt. rend. Soc. Biol.*, 1921, **85**, 376—377; from *Chem. Zentr.*, 1922, i, 51).—The addition of equivalent amounts of salts of magnesium, manganese, nickel, cadmium, gold, or platinum causes a decrease in the formation of staphylolysin; salts of other metals, particularly calcium, exert an inhibitory effect. G. W. R.

Nitrogen Nutrition of Yeast. FREDERICK K. SWOBODA (*J. Biol. Chem.*, 1922, **52**, 91—109).—The effect of various substances on the nitrogen nutrition of yeast was studied, the special feature of the experiments being the addition to the synthetic media employed of a constant quantity of growth-promoting vitamin ("bios"). In a medium containing asparagine, succinamide, succinimide, or aspartic acid, the growth is better in the presence than in the absence of ammonium sulphate. Of the nitrogen contained in asparagine, the α -amino-group appears to stimulate nitrogen assimilation; the amide-group, however, in the presence of ammonium sulphate, also stimulates cell reproduction. The nutrient value of edestin is increased by mild acid hydrolysis, but is decreased by continued acid hydrolysis and by alkaline hydrolysis. In the latter case, subsequent acid hydrolysis again improves its nutrient value. The effect of various amino-acids both in the presence and absence of hydrolysed edestin was also studied. E. S.

The Conditions Influencing the Formation of Fat by the Yeast-cell. IDA SMEDLEY MACLEAN (*Biochem. J.*, 1922, **16**, 370—379).—Ether extracts considerably more fat from yeast if the latter is first boiled with *N*-hydrochloric acid for two hours. This is because a large part of the fat is in some form of combination in the plasma of the cell. Yeast grown under unfavourable conditions shows a large increase in the fat content (up to 9%). Aeration, and a non-nitrogenous medium rich in carbohydrate result likewise in increased fat-content, the increase being in the combined fat. W. O. K.

The Capacity of Yeast to Degrade Acid Amides. WALTER DIETER (*Z. physiol. Chem.*, 1922, **120**, 281—291).—Sterile experiments with a top fermentation pure culture yeast show that it

does not remove the amide nitrogen from asparagine and other acid amides under conditions such that it ferments but does not grow.
S. S. Z.

The Destruction of Lactic Acid by Yeast-cells. FRITZ LIEBEN (*Oesterr. Chem. Zeit.*, 1922, 25, 87—90).—Lactic acid is one of the products of the degradation of carbohydrates in muscle, and experiments were made *in vitro* to determine the ultimate fate of this substance under the influence of the ferments of the yeast-cell, which appear to be similar, at least, to the muscle enzymes. It was found that the lactic acid disappeared to within 3—5% in seven to eight hours under suitable conditions, and that about two-thirds of its carbon content appeared in the products as carbon dioxide, either liberated, or remaining combined with sodium; the remainder of the carbon was represented by an increase in weight of the yeast substance, and if calculated as $C_6H_{10}O_5$, practically accounted, with the carbon dioxide, for the whole of the lactic acid which had disappeared. It appears therefore that both synthesis and degradation had occurred simultaneously. No degradation products other than carbon dioxide could be detected. Similar experiments were made with vegetable acids and with amino-acids; the former were not attacked, the latter were in part consumed by the yeast, but no degradation to carbon dioxide could be detected.
G. F. M.

Influence of Substances obtained from Yeast-cells and Organs on the Time Course of the Fission of Substrates by Polypeptidases, Carbohydases, and Esterases. EMIL ABDERHALDEN and ERNST WERTHEIMER (*Fermentforsch.*, 1922, 6, 1—26).—The substances obtained from yeast by extraction with alcohol or by autolysis accelerate the fission of dipeptides by pancreas extract; this action requires both the dialysed and non-dialysed portions of the yeast extract and is annulled by boiling the latter. Certain of the optones behave similarly. Neither animal charcoal, nor kaolin, nor kieselguhr, nor talc adsorbs the peptolytic enzyme from yeast maceration juice, but the charcoal greatly retards the hydrolysis of *dl*-leucylglycine probably by adsorbing the dipeptide. The action of sucrose is retarded by alcoholic yeast extract; the retarding agent is non-dialysable, the dialysate being without effect. Diastatic action is not appreciably influenced by yeast extract or by various optones, and yeast extracts made in different ways are without influence on the action of lipase.
T. H. P.

Influence of Hydrogen-ion Concentration on the Action of the Amylase of *Aspergillus niger*. G. L. FUNKE (*Proc. K. Akad. Wetensch., Amsterdam*, 1922, 25, 6—8).—*Aspergillus niger* produces large quantities of amylase which diffuses into the surrounding nutritive medium; at the same time, the fungus produces acids which give the medium a high hydrogen-ion concentration.

This appears to have no unfavourable action on the behaviour of the amylase, and in consequence it is concluded that the optimum action of amylase could not be at the same hydrogen-ion concentration as that of the ptyalin, which works best in a neutral or faintly acid solution. To test this point, the rate of hydrolysis of starch by amylase in the presence of buffer solutions has been investigated, and it is shown that there is no optimum concentration of hydrogen-ions, but a region where the action is at a maximum which lies between $P_H=3.5$ and $P_H=5.5$. The results confirm Michaëlis's view (A., 1911, i, 1052; ii, 577) that enzymes are ampholytes, and on this basis the dissociation constants of the acid and base are determined as $k_a=6.3 \times 10^{-7}$ and $k_b=2.884 \times 10^{-12}$. Similar determinations with the amylase of malt yield a similar optimum region; the values being $k_b=5.76 \times 10^{-11}$ and $k_a=6.3 \times 10^{-7}$.

J. F. S.

Biological Signification of Alkaloids in Plants. G. CIAMICIAN and C. RAVENNA (*Biochem. terap. speriment.*, 1922, 9, 3—29).—A summary of the work carried out by the authors on this subject since 1908.

T. H. P.

The Distribution of Anthocyanidins in the Coloured Organs of Plants. ST. JONESCO (*Compt. rend.*, 1922, 174, 1635—1637; cf. *ibid.*, 1921, 173, 168, 426).—The anthocyanidins, either as a coloured pigment or in the free state, do not exist in all coloured tissues which contain anthocyanin. They appear to be characteristic of pure red organs, whilst in the blue, violet, or reddish-purple organs there occurs, in their place, a very intense, yellow pigment, and the anthocyanidins are entirely absent. This is shown to be the case for the violet-red leaves of beetroot, the violet flowers of *Gladiolus* and *Cobaea scandens*, the reddish-purple flowers of *Canna* and of a cultured rose, and the blue flowers of *Centaurea cyanus*. This yellow pigment is not coloured red by warming with 20% hydrochloric acid.

W. G.

Saponin from *Agave lechuguilla*, Torrey. CARL O. JOHNS, LEWIS H. CHERNOFF, and ARNO VIEHOEVER (*J. Biol. Chem.*, 1922, 52, 335—347).—A saponin, $C_{27}H_{44}O_{12}$, occurs in the cell-sap of *Agave lechuguilla*. It has been isolated in the form of an almost white, amorphous substance by extracting the air-dried rootstocks with 95% alcohol. It possesses hæmolytic action and is toxic towards fishes. On partial hydrolysis it yields dextrose and an amorphous pro-sapogenin, the latter being further hydrolysed to galactose and a sapogenin, $C_{15}H_{24}O_2$, acicular crystals or prisms, m. p. 183.5° , which is identical with that obtained from the saponin of *Yucca filamentosa* (A., 1917, i, 191).

E. S.

Comparative Plant Chemistry. III. *Campanula rotundifolia*, L. FRIEDRICH SPRINGER (*Monatsh.*, 1922, 43, 13—20).—The stems and leaves of the plant were examined. The portion of the dried material soluble in light petroleum, including

fats, chlorophyll, phytosterol, lecithin, and resinic acids, amounted to 6.09%. The crude fats gave an acid number 78.1, saponification number 130.8, iodine number 88.0, unsaponifiable 48.3%. The free fatty acids had m. p. 60–70°, but were insufficient in quantity for further examination. The ether-soluble resins in the dried material amounted to 2.01% and the alcohol-soluble portion to 17.39%. From the alcohol extract was extracted with ether a substance which, after purification, including reduction with zinc and hydrochloric acid, had m. p. 214–215° and a composition and molecular weight corresponding with $C_{22}H_{40}O_2$. The substance is semi-crystalline, shows Liebermann's cholestol reaction, and is dextrorotatory, $[\alpha] +37.7$ (mean). By oxidation with aqueous permanganate it gives a product, m. p. 232°, showing Liebermann's phytosterol reaction. There is a marked resemblance between the substance and Zellner's resin alcohol, polyporol, obtained from fungi (A., 1913, i, 573). The alcoholic extract of the plant contained a considerable amount of tannin, and when this had been precipitated with lead acetate, the filtrate contained invert-sugar in which lævulose predominated, indicating the presence of inulin. The water-soluble portion of the dried plant, 24.87%, contained a small amount of inulin. The insoluble portion contained 12.89% of pentosans and 35.5% of fibre; total ash 4.43%. The milky sap is probably responsible for the rather high resin content of the plant.

E. H. R.

The Fatty Acids of Colza Oil. E. RAYMOND (*Bull. Soc. chim.*, 1922, [iv], **31**, 414–419).—In the mixture of fatty acids obtained from the saponification of a sample of Indian colza oil, the author has identified the following fatty acids: erucic, linoleic, or linolenic giving soluble bromides, palmitic, oleic, stearic, and small amounts of linoleic or linolenic giving insoluble bromides.

W. G.

Effect of Cocaine on the Growth of *Lupinus albus*. DAVID I. MACHT and MARGUERITE B. LIVINGSTON (*J. Gen. Physiol.*, 1922, **4**, 573–584).—Experiments were made on the inhibiting effect of cocaine and its products of hydrolysis (ecgonine, methyl alcohol, and benzoic acid) on the growth of the young roots of *Lupinus albus*. The results show that cocaine and ecgonine are relatively very much less toxic to the plant than to animals, whilst sodium benzoate, which is practically non-toxic to animals, is highly toxic to the plant.

C. R. H.

Effect of Nitrogenous Fertilisers on the Alkaloid Content of Lupines. VOGEL and E. WEBER (*Z. Pflanz. Düng.*, 1922, [A], **1**, 85–95).—The alkaloid content of blue and yellow lupines respectively varies according as the plants receive their nitrogen through the medium of nitrogen fixing bacteria in root nodules, or from nitrogenous fertilisers. Smaller contents of alkaloid were observed in the latter than in the former type of nitrogen nutrition. The effect of certain materials for artificial inoculation was examined.

"Azotogen" and "nitragin" gave satisfactory results. "Azonutrin" was less satisfactory, whilst "legumin" was quite ineffective. A method for the estimation of alkaloids in lupines is described (cf. Mach and Lederle, A., 1921, ii, 718). G. W. R.

Comparative Plant Chemistry. I. *Lythrum Salicaria*, L. JULIUS ZELLNER (*Monatsh.*, 1921, **42**, 453—458).—The stems and leaves without the flowers were examined, and their composition showed nothing of special interest. The dried plant contained 3.69% soluble in light petroleum, 1.73% in ether, and 16.36% in 95% alcohol; phlobaphen 1.86%, tannin 5.65%, dextrose 4.55%, total water-soluble 31.27%, water-soluble mineral matter 5.18%, mucus 8.08% (giving mucic acid when oxidised with nitric acid), free acid 3.55% (estimated by titration), total nitrogen 2.15%, ash 7.62%. No alkaloids or glucosides were found. As characteristic of the plant may be mentioned tannin, giving a blue colour with iron, a carbohydrate of the pectin type and a relatively large proportion of calcium sulphate. In the petals, besides anthocyanin was found an amorphous polysaccharide containing dextrose or invert-sugar. E. H. R.

The Presence of Melampyritol and Aucubin in the Foliated Stems of *Melampyrum arvense*, L. MARC BRIDEL and (Mlle) MARIE BRAECKE (*J. Pharm. Chim.*, 1922, **25**, 449—457; cf. A., 1921, i, 840; this vol., i, 209).—From the entire plant of *Melampyrum arvense* the authors have extracted the glucoside aucubin, and a hexahydric alcohol, melampyritol or dulcitol. In examining the amount of glucoside present at different stages of the plant's growth, more than 2% of the glucoside was found in the plant after it had completed its life-cycle, when the stems were devoid of leaves. W. G.

The Carbohydrate Content of Navy Beans. MARIETTA EICHELBERGER (*J. Amer. Chem. Soc.*, 1922, **44**, 1407—1408).—The author directs attention to results obtained by herself in 1919 which are in fairly close accord with those of Peterson and Churchill (A., 1921, i, 643), for the composition of navy beans. W. G.

The Constituents of the Pollen Grain of *Pinus sylvestris*. ALEXANDER KIESEL (*Z. physiol. Chem.*, 1922, **120**, 85—90).—The ripe pollen contains potassium >0.59%, calcium >0.12%, trace of guanine, adenine, 0.02%, little histidine, arginine 0.52%, choline 0.21%, little colamine, and sucrose. The unripe pollen yielded very little in the nuclein bases fraction, and traces of histidine, arginine, and choline. S. S. Z.

The Presence of a Glucoside in the Stems and Roots of *Sedum Telephium*, L. MARC BRIDEL (*Bull. Soc. Chim. Biol.*, 1922, **4**, 242—250).—The stems and roots of *Sedum Telephium*, L., contain a glucoside which has been isolated in an amorphous form. It reduces Fehling's solution slightly, has $[\alpha]_D - 28.57^\circ$, and is hydrolysed by sulphuric acid to dextrose and a substance possessing

an odour similar to that of terpineol. When hydrolysed by emulsin, a rose-like odour is produced. From these facts it is suggested that the first product of hydrolysis is an olefinic terpene which, under the influence of acids, isomerises to a cyclic terpene.

E. S.

The Proteins of the Seed of the Tomato, *Solanum esculentum*. CARL O. JOHNS and CHARLES E. F. GERSDORFF (*J. Biol. Chem.*, 1922, **51**, 439—452).—The meal which remains after extracting ground tomato seeds with ether contains 37·28% of protein (nitrogen $\times 6\cdot25$). By extraction with salt solution followed by fractional precipitation of the extract with ammonium sulphate, an α - and a β -globulin have been isolated. Analysis by Van Slyke's method gave the following values for the basic amino-acids: α -globulin—cystine 1·28, arginine 13·97, histidine 1·16, lysine 4·89%; β -globulin—cystine 1·14, arginine 10·65, histidine, 3·80, lysine 6·35%. Qualitative tests were obtained for tryptophan and tyrosine in each case. Albumin and glutelin are absent from the seed.

E. S.

Relationship between Precipitation, Adsorption, and Charge on the Particles with particular reference to the Hydroxyl Ions. SANTE EMIL MATTSO (Koll. Chem. Beihefte, 1922, **14**, 227—316).—Using suspensions of quartz, clay, and humified sphagnum peat with particles of various sizes, the author has investigated the precipitating power of calcium salts in the presence of various concentrations of hydroxyl ions. The adsorption and charge on the particles during the precipitation of soil constituents by calcium salts in the presence of hydroxyl ions has also been investigated. The results are considered in connexion with the fertilisation of arable land by calcium compounds. It is shown that the hydroxyl ions are strongly adsorbed by soil and effect a discharging of the particles; in the presence of kations which have a weak or only moderately strong discharging effect they increase the action, since they facilitate the adsorption of the discharging kations. Precipitation is not only occasioned by the fact that the charge is reduced, since relatively strongly charged particles can be made to precipitate if the number of adsorbed ions is very large. The adsorbed ions appear to act as connecting links between the particles, and this is visualised by assuming that the positive ion attaches itself to two negative particles and so brings them together. Hydroxyl ions are not, of themselves, injurious to soil, but their action depends on the nature of the predominant kation in the soil. The hydroxides and oxides of iron and aluminium are negatively charged in aqueous suspensions, and only become positively charged by the adsorption of positive ions during the preparation. The power of soil to adsorb hydroxyl ions influences the solubility of various compounds and explains the acidity of many kinds of soil.

J. F. S.

Organic Chemistry.

Composition of Paraffin Wax. II. FRANCIS FRANCIS, CYRIL MERCER WATKINS, and REGINALD WILFRED WALLINGTON (T., 1922, **121**, 1529—1535).

Formation of Hydrocarbons from Carbon Monoxide and from Formates. M. G. LEVI (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 302).—Tropsch and Schellenberg's criticisms (*Brennstoff-Chemie*, Feb., 1922) of Vignon's statements concerning the formation of methane in the water-gas process (A., 1921, i, 217) are in agreement with the results of Levi and Piva (A., 1914, i, 480; 1916, ii, 525).
T. H. P.

Preparation of Ethylene by Reduction of Acetylene. JOSEPH-MARIE-ALPHONSE CHEVALIER and PAUL BOURCET (F.P. 526129; from *Chem. Zentr.*, 1922, ii, 142).—Purified acetylene is passed through a solution of chromous sulphate (obtained by electrolytic reduction of chrome alum) in the presence or absence of electrolytically prepared hydrogen. The acetylene is rapidly absorbed with formation of ethylene which can be purified by repeated passage through chromous sulphate solution.
G. W. R.

The Action of Sodammonium on Hydrocarbons. P. LEBEAU and M. PICON (*Compt. rend.*, 1922, **175**, 223—225).—Sodammonium has no action on aliphatic hydrocarbons excepting on the true acetylenes, which are partly converted into sodium compounds and the remainder is reduced by the hydrogen thereby liberated. Benzene and its homologues are also unattacked except in so far as the side chain, if containing a :CH group, reacts like an open chain acetylene, or if containing a double bond adjacent to the nucleus it undergoes reduction, for example, styrene is converted into ethylbenzene. Terpinene, terpinolene, carvene, terebene, α -pinene, and menthene are not attacked. Polycyclic hydrocarbons react in various ways. Stilbene and anthracene give dihydro-derivatives, the two benzene nuclei in each case remaining intact. Hydrocarbons the nuclei of which have two atoms of carbon in common have one nucleus only reduced by sodammonium, naphthalene, phenanthrene, etc., giving tetrahydro-derivatives. Diphenyl and dimethylfluorene also give tetrahydro-derivatives. Certain hydrocarbons having an acidic methylene group, for example, fluorene and indene, give sodium derivatives. The mechanism of the reduction is apparently complex, although the result may be expressed by the equation (for example, with naphthalene) $\text{C}_{14}\text{H}_{10} + 2\text{NH}_3\text{Na} = \text{C}_{14}\text{H}_{12} + 2\text{NH}_2\text{Na}$. Sodamide does not separate at low temperatures, however, but a red solution is formed, miscible with ether, which probably contains a sodammonium derivative of the hydrocarbon; this decomposes above -10° into sodamide and the reduction product.
G. F. M.

The Mobility and Valency Demand of the Ethyl Group in the Pinacolin Transformation. BERTIL NYBERGH (*Ber.*, 1922, 55, [B], 1960—1966).—Previous investigations have led Meerwein (A., 1919, i, 162) to the conclusion that the various alkyl groups exhibit little regularity in their mobility in the pinacolin transformation. An examination of the behaviour of *s*- and *as*-dimethyldiethylethylene glycols [$\gamma\delta$ -dimethylhexane- $\gamma\delta$ -diol and β -methyl- γ -ethylpentane- $\beta\gamma$ -diol] shows that both alkyl groups are mobile; the former substance, however, yields mainly γ -methyl- γ -ethylpentane- β -one, whereas the latter gives chiefly ethyl *tert*-amyl ketone. It follows therefore that the ethyl group is actually much more mobile than the methyl radicle; but, on the other hand, the valency demand of the ethyl group does not appear to be so much less than that of the methyl group as Meerwein has supposed. The position of the ethyl group in comparison with that of other aliphatic residues is no longer unique; Meerwein's view of the periodicity of the valency demand of aliphatic residues remains unaffected. *as*- and *s*-Dimethyldiethylethylene glycol are converted by concentrated sulphuric acid at -10° into a mixture of ethyl *tert*-amyl ketone, b. p. $150.5-152^\circ$, d_{20}^{20} 0.8298, and γ -methyl- γ -ethylpentane- β -one, b. p. $153.5-154^\circ$, d_4^{20} 0.8389, which are separated in the form of their *semicarbazones*, m. p. 98° and 168° , respectively. The constitution of γ -methyl- γ -ethylpentane- β -one is deduced from the observation that it is oxidised by bromine and sodium hydroxide solution to bromoform, acetic acid, α -methyl- α -ethyl-*n*-butyric acid, and a crystalline acid, m. p. 82° , which in all probability is α -hydroxy- β -methyl- β -ethylpentoic acid.

H. W.

$\alpha\beta'$ -Dichlorodiethyl Ether. V. GRIGNARD and A. C. PURDY (*Compt. rend.*, 1922, 175, 200—203).— $\alpha\beta'$ -Dichlorodiethyl ether was prepared by the condensation, at $0-10^\circ$, of ethylene chlorohydrin (1 mol.) and paracetaldehyde ($\frac{1}{3}$ mol.) by means of dry hydrogen chloride. After separating the aqueous layer which is formed, the dried product is rectified, and the ether, which is a colourless, fuming liquid, distils at $55-57^\circ/17$ mm. It is rapidly decomposed by water and also on distillation under ordinary pressures, and decomposes slowly on keeping. It has d_{19}^{19} 1.1823, and $n_D^{16.2}$ 1.4497. A small amount of the corresponding acetal, $\beta'\beta''$ -dichlorodiethylacetal, $\text{CH}_3\cdot\text{CH}(\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\text{Cl})_2$, is also produced in the above reaction, and it may be obtained in 36% yield by condensing acetaldehyde (1 mol.) with ethylene chlorohydrin (2 mols.). It is a colourless liquid, distilling with partial decomposition at $196-198^\circ$ under ordinary pressures, and at $106-108^\circ/17$ mm. It has d_{19}^{19} 1.1712, and $n_D^{16.2}$ 1.4532. On treatment with phosphorus pentachloride, it is converted into a mixture of $\alpha\beta'$ -dichlorodiethyl ether and ethylene dichloride.

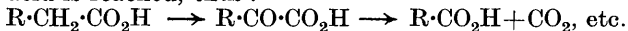
G. F. M.

Catalytic Decomposition of Formic Acid on Surfaces of Platinum and Silver. HAROLD CALVERT TINGEY and CYRIL NORMAN HINSHELWOOD (*T.*, 1922, 121, 1668—1676).

The Catalytic Decomposition of the Lower Acids.
 ALPHONSE MAILHE (*Bull. Soc. chim.*, 1922, [iv], **33**, 681—687; cf. A., 1909, i, 452).—The gaseous products obtained by heating acetic acid in the presence of copper-aluminium at about 600° are carbon monoxide, carbon dioxide, methane, and hydrogen. The same substances with the addition of other paraffins and of olefins are obtained from *isobutyric*, *butyric*, *isovaleric*, and *n-nonoic* acids. There appears to be little relation between the acids and their decomposition products, except in the case of *isobutyric* and *isovaleric* acids. Equations are given showing the mechanism of formation of the products from the original material and the conclusion is drawn that ketones are formed as intermediate products. This is found to occur under the conditions of experiment and acetone, *isobutyronc*, *butyrone*, *isovalerone*, and *nonylone* have themselves been treated in a similar manner to the acids in order to verify the author's inferences. With increasing molecular weight of the acid, decomposition products of higher molecular weight are obtained; this is marked in the case of *n-nonoic* acid which yields liquid unsaturated hydrocarbons. The latter, after hydrogenation, possess the properties of light petroleum. H. J. E.

The Oxidation of Potassium Acetate to Potassium Oxalate.
 WILLIAM LLOYD EVANS and PAUL R. HINES (*J. Amer. Chem. Soc.*, 1922, **44**, 1543—1546).—Potassium acetate may be oxidised to potassium oxalate with alkaline permanganate under certain definite conditions. The yield of oxalic acid is a function of the concentration of the reacting materials, the temperature, and the duration of the experiment. H. W.

The Chromic Oxidation of the Homologues of Acetic Acid.
 L. J. SIMON (*Compt. rend.*, 1922, **175**, 167—169).—Whilst within certain limits of temperature acetic acid is not attacked by a sulphuric acid-chromic acid mixture, it is completely converted into carbon dioxide by silver chromate under the same conditions. The homologues of acetic acid are likewise completely oxidised by silver chromate, but the chromic acid mixture leaves a non-combusted residue which for the homologues up to C₉ corresponds approximately with 1 atom of carbon, and increases slightly with the higher members, but never reaches 2. This result is interpreted by supposing that the acids are burnt atom by atom commencing with the carboxyl group, and the oxidation ceases when acetic acid is reached, thus:



Confirmation of this hypothesis is found in the oxidation of acetyl compounds and open-chain acids by lead chromate and sulphuric acid, where the evolution of gas accompanying the oxidation occurs in two well-defined stages, at a lower temperature corresponding with the more readily combustible part of the molecule, and at about 100°, the temperature at which acetic acid is oxidised by lead chromate. Methanesulphonic acid is not an intermediate product of chromic oxidation, as it is not oxidised even by silver chromate.

G. F. M.

ff2

Synthesis of Fats (Glycerides). C. AMBERGER and K. BROMIG (*Biochem. Z.*, 1922, **130**, 252—266).—The use of a high temperature is inadmissible for the preparation of mixed glycerides of known constitution. Fischer and Pfähler's process (A., 1920, i, 807) has therefore been employed. α -*Stearo- β -dipalmitin*, m. p. 63·5°, occurs in goose fat, and was prepared from α -monostearin and palmityl chloride. β -*Stearo- α -dipalmitin*, m. p. 59·1°, was prepared from α -*dipalmitin*, m. p. 69·5°. The latter is prepared from β -*dipalmitin- α -iodohydrin*, m. p. 46·2°, by the action of silver nitrite. α -*Palmito- β -distearin*, m. p. 63·2°, was prepared from α -monopalmitin and stearyl chloride. The isomeric β -*palmito- α -distearin*, m. p. 67·9°, was prepared from α -*distearin*. α -*Palmito- β -diolein*, prepared from α -palmitin, was an oil. α -*Olein*, a pale yellow oil, yields α -*oleo- β -distearin*, m. p. 42°. H. K.

Acids of Montan Wax. H. TROPSCH and A. KREUTZER (*Brennstoff-Chemie*, 1922, **3**, 177—180, 193—198, 212—215).—The small quantity of humic acids contained in montan wax can be extracted by treatment of the lignite with benzene or a mixture of benzene and alcohol. In 1852, Brückner isolated, from the lignite of Gerstewitz, an acid (geocerinic acid), $C_{28}H_{56}O_2$, m. p. 82°. Hell obtained this acid, m. p. 83—84°, by saponification of the refined wax with potassium hydroxide, etc., and assigned to it the formula $C_{29}H_{58}O_2$. Montanic acid was first so named by von Boyen, in 1901. The raw wax on which the authors carried out their investigations had a melting point of 80°, an acid value of 34·1, and a saponification value of 82·8. It was saponified, and the dried soap extracted with benzene. The residue consisted of the potassium salts of the acids in the wax. After purification, the acid had m. p. 84° and an equivalent weight of 420·2. On treatment with permanganate, however, the greater part of the product separated out and gave an equivalent weight of 416·5 and m. p. 80°. The acid was esterified, and the product fractionated under reduced pressure. From the fraction, b. p. 265—267·5°, an acid, $C_{27}H_{54}O_2$, crystallising in bunches of needles, m. p. 82°, was obtained, and proved to be identical with an acid prepared from Chinese wax by Gascard (A., 1920, i, 470). This investigator showed that the acid which he had isolated was not identical with cerotic acid from beeswax. The authors give the name *carboceric acid* to the new compound. From the fraction of esters boiling between 260° and 275° small quantities of an acid, $C_{25}H_{50}O_2$, m. p. 78°, were obtained, which is seemingly identical with the hyænic acid isolated by Carius from the fat of certain glands of the hyæna. True montanic acid was isolated, and the formula $C_{29}H_{58}O_2$ confirmed. It crystallises in needles very similar to fir-tree branches, and has m. p. 86·5°.

A. G.

Synthesis of Δ^6 -Decenoic Acid. AD. GRÜN and TH. WIRTH (*Ber.*, 1922, **55**, [B], 2206—2218).—The synthesis of Δ^6 -decenoic acid from undecylenic acid and from suberic acid is recorded. The

substance is identical with the acid isolated by Grün and Wirth (following abstract) from butter fat.

Ethyl undecenoate is reduced by sodium and ethyl alcohol to *undecenol*, $\text{CH}_2\text{:CH}[\text{CH}_2]_8\text{CH}_2\text{OH}$, b. p. $250^\circ/\text{atmospheric pressure}$, $122^\circ/3 \text{ mm.}$, m. p. -7° , which is converted by chlorosulphonic acid in dry ethereal solution into *undecenyl hydrogen sulphate* (the barium salt, colourless leaflets, is described). Oxidation of the ester (or of the corresponding acetate) with chromic acid or preferably with permanganate leads to the isolation of *1-hydroxydecoic acid*, $\text{OH}\cdot\text{CH}_2\cdot[\text{CH}_2]_8\cdot\text{CO}_2\text{H}$, indistinct, transparent crystals, m. p. 75° (*methyl ester*, m. p. 34.5° , b. p. $154^\circ/7 \text{ mm.}$, *amyl ester*, b. p. $179\text{--}180^\circ/8 \text{ mm.}$). *1-Acetoxydecoic acid* has b. p. $213^\circ/15 \text{ mm.}$; at $320^\circ/\text{atmospheric pressure}$ it loses acetic acid, but the formation of the olefinic acid proceeds only slowly. *Methyl 1-acetoxydecoate* is a moderately mobile liquid, b. p. $175^\circ/17 \text{ mm.}$, $295\text{--}300^\circ/\text{atmospheric pressure}$. *Amyl 1-acetoxydecoate*, b. p. $210^\circ/15 \text{ mm.}$, $310\text{--}312^\circ/\text{atmospheric pressure}$ (when rapidly distilled), decomposes more readily than the methyl ester into the unsaturated compound when it is heated. The derivatives just described are too stable to permit a ready transition from hydroxydecoic to decenoic acid, but better results are obtained after the introduction of a heavier radicle. Thus, *methyl 1-stearoxydecoate*, colourless, wax-like aggregates, m. p. 43° , decomposes readily when distilled under atmospheric pressure into stearic acid and methyl decenoate; the latter on hydrolysis gives decenoic acid, b. p. $143^\circ/6 \text{ mm.}$, whereas the product from butter fat has b. p. $142^\circ/4 \text{ mm.}$

Methyl 1-chlorodecoate, b. p. $153^\circ/15 \text{ mm.}$, could not be converted satisfactorily into methyl decenoate by loss of hydrogen chloride.

The preparation of alkyl hydrogen sebacates by partial esterification of sebacic acid cannot be satisfactorily accomplished, and the acid esters are obtained by partial hydrolysis of the normal compounds. Methyl sebacate crystallises in long, transparent prisms, m. p. $27\text{--}28^\circ$ (literature, m. p. 36° and 38°), whereas the *ethyl ester* is a liquid, b. p. $172^\circ/7 \text{ mm.}$ *Ethyl hydrogen sebacate* forms colourless, indistinct crystals, m. p. 36° , b. p. $210^\circ/18 \text{ mm.}$; when distilled under atmospheric pressure it is decomposed into sebacic acid and ethyl sebacate. Potassium ethyl sebacate is reduced by sodium and boiling ethyl alcohol to *1-hydroxydecoic acid*.

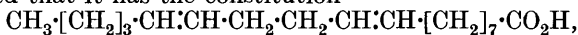
The iodine and acid numbers of Δ^9 -decenoic acid gradually diminish when the substance is preserved, thus indicating the formation of a lactone. Decenoic acid is converted by sulphuric acid (80%) at 90° into *decalactone*, $\text{C}_{10}\text{H}_{18}\text{O}_2$, a liquid, b. p. $153^\circ/15 \text{ mm.}$, which is saturated and neutral in character. It is hydrolysed by alcoholic potassium hydroxide solution with the production of a hydroxy-acid, leaflets, m. p. 44° , which gradually passes when preserved into water and the lactone. In all probability the substances are γ -decalactone and γ -hydroxydecoic acid, but this is not regarded as established definitely. H. W.

Δ^8 -Decenoic Acid, a Previously Unknown Acid from Butter.

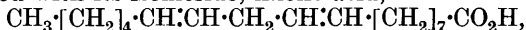
AD. GRÜN and TH. WIRTH (*Ber.*, 1922, **55**, [B], 2197—2205).—Butter fat is treated with methyl-alcoholic hydrogen chloride (1.5%) and the methyl esters are submitted to fractional distillation whereby a portion, b. p. 100—140°/15 mm., iodine number 9.8, is obtained. The fraction is hydrolysed and a partial separation of the saturated and unsaturated acids is effected by systematic treatment of the corresponding lead salts in the usual manner. A mixture of approximately equal amounts of decenoic and decoic acids is thus produced which cannot be more completely separated by any of the ordinary methods. It is therefore esterified and the methyl esters are brominated in dry chloroform solution. The products are readily separated from one another by distillation under diminished pressure, whereby *methyl dibromodecoate*, b. p. 185—186°/7 mm., is obtained. Treatment of the latter with 5*N*-methyl alcoholic hydrogen chloride and zinc yields *methyl Δ^8 -decanoate*, a colourless, mobile liquid, b. p. 115—116°/12 mm., which is hydrolysed to *Δ^8 -decanoic acid*, $\text{CH}_3\cdot\text{CH}[\text{CH}_2]_7\cdot\text{CO}_2\text{H}$, a colourless, fairly mobile liquid, b. p. 142°/4 mm., m. p. below 0°. The constitution of the acid is deduced from its conversion by ozone into azelaic and formic acids. This is the first instance on record of the isolation of an unsaturated acid of such low molecular weight or of one containing a terminal unsaturated bond, from a natural fat.

H. W.

China Wood Oil. K. H. BAUER and K. HERBERTS (*Chem. Umschau*, 1922, **29**, 229—232).—China wood oil occupies a special position among the drying oils in containing practically no saturated acid and very little oleic acid, elæostearic acid, $\text{C}_{18}\text{H}_{32}\text{O}_2$, having two unsaturated double bonds, being the characteristic acid. This acid, which forms large, colourless crystals, m. p. 48°, is designated α -elæostearic acid, whilst the β -form, to which it easily changes spontaneously, has m. p. 71°. Such transformation also takes place with the glyceride by exposure to light, or the catalytic influence of iodine, sulphur, etc. Since α -elæostearic acid on hydrogenation yields stearic acid, it is considered to be a straight chain fatty acid of the C_{18} series. From examination of the decomposition products of the ozonide of α -elæostearic acid, and from the results of oxidation by potassium permanganate, it is concluded that it has the constitution



as compared with its isomeride, linolic acid,



the melting points of the tetrabromides from these two acids being 114° and 114.5°, respectively. Nicolet has proved their separate identity by the considerable lowering of melting point which occurs when the two are mixed. This has been confirmed by the authors, who debrominated the bromo-derivative of α -elæostearic acid by means of zinc dust in alcohol and obtained a product free from bromine having m. p. 68—70°, β -elæostearic acid having m. p. 71°, thus showing a transformation of the α -form into the β -form and

a distinction of the bromo-derivatives of both forms from that of linolic acid. By esterification of α -elæostearic acid with methyl alcohol in the presence of sulphuric acid, separation of the ester by distillation (b. p. $220^{\circ}/35$ mm.) and subsequent saponification and separation of the acid, β -elæostearic acid alone, m. p. $69-70.5^{\circ}$, was found, the change from the α - to the β -form being attributed, not to the action of the alkali used for saponification, but to the sulphuric acid used in esterification, a result somewhat comparable with the observed obtainment of the β -glyceride by mere extraction of the seed with carbon disulphide. By saponifying the anhydride obtained by heating α -elæostearic acid with acetic anhydride and liberating the free acid, the original α -elæostearic acid was obtained with m. p. 46° . The authors conclude that the transformation of α -elæostearic acid into its β -isomeride is most probably not accounted for by the mere action of light, since exposure to light was as far as possible avoided and conditions maintained as equal as possible in the two experiments of esterification of α -elæostearic acid and saponification of its anhydride respectively.

A. DE W.

The Colouring Constituents of Montan Wax. J. MARCUSSEN and H. SMELKUS (*Chem. Ztg.*, 1922, **46**, 701—702).—On extracting montan wax with ether in a Soxhlet apparatus, 23% of the wax dissolves and the solution, on being mixed with an equal volume of 96% alcohol and cooled to -20° , yields 18% of low-melting wax which contains about 6% of hydroxy-acids. The ether-alcohol solution contains 9% of a resin having a dark brown colour and dissolving readily in benzene, chloroform, and pyridine. On heating with sulphuric acid the resin yields a green, insoluble compound containing 4% of sulphur; with fuming sulphuric acid a black mass containing 7.8% of sulphur and slowly soluble in water is formed, whilst nitric acid gives a characteristic cyclic nitro-compound.

The residue of the original wax insoluble in ether contains about 10% of a brownish-black, unsaponifiable substance soluble in benzene, whilst the remainder consists of esters of a mixture of hydroxy-acids. These acids form a dark brown, friable mass, which contains 3.1% of sulphur, is soluble in benzene, chloroform, and amyl alcohol, has a saponification value of 94, acid value 58, iodine value 13, and on reduction with sodium in amyl alcohol solution yields a mixture of fatty acids. No humic acids could be detected in the mixture. The potassium salts are soluble in 50% alcohol, benzene, and hot water.

A. R. P.

Some Derivatives of Ethyl Hydrogen Diethylmalonate. PHILIPPE DUMESNIL (*Bull. Soc. chim.*, 1922, [iv], **33**, 687—689; cf. A., 1921, i, 391).—The following substances have been prepared from ethyl hydrogen diethylmalonate. *Ethyl diethylmalonyl chloride*, $\text{COCl}\cdot\text{CEt}_2\cdot\text{CO}_2\text{Et}$, a colourless mobile liquid, b. p. $102^{\circ}/20$ mm., which gives the usual reactions of acid chlorides. *Ethyl diethylmalonic anhydride*, $\text{O}(\text{CO}\cdot\text{CEt}_2\cdot\text{CO}_2\text{Et})_2$, a colourless liquid, b. p. $210^{\circ}/24$ mm., which reacts with ammonia, yielding the corre-

sponding amide; attempts at esterification were unsuccessful. Ethyl diethylmalonamide (cf. Conrad and Zart, A., 1905, i, 754), formed by the action of ammonia on both the acid chloride and the anhydride; the *diethylamide*, $\text{NEt}_2\cdot\text{CO}\cdot\text{CEt}_2\cdot\text{CO}_2\text{Et}$, a colourless liquid, b. p. $170^\circ/28$ mm., by the action of diethylamine on the acid chloride; *benzyl ethyl diethylmalonate*, from the acid chloride and benzyl alcohol, a colourless liquid, b. p. $187^\circ/22$ mm.

H. J. E.

Some Derivatives of *n*-Butylmalonic Acid. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1922, **44**, 1578—1581).—A number of new derivatives have been prepared from ethyl *n*-butylmalonate. Of chief interest among these is 5-ethyl-5-*n*-butylbarbituric acid, which is a powerful hypnotic. The substitution of a phenoxy-group for either of the alkyl radicles in this substance destroys its physiological activity.

Ethyl *n*-butylmalonate is converted by concentrated aqueous ammonia into *n*-butylmalonamide, slender, hair-like needles, m. p. 200° , and by aqueous methylamine (33%) into *n*-butyl-*NN'*-dimethylmalonamide, colourless, glistening needles, m. p. 184° . *n*-Butylmalonanilide, colourless needles, m. p. 193° , is prepared by heating a mixture of aniline and ethyl *n*-butylmalonate at its boiling point; the similarly prepared *n*-butylmalono-*o*-toluidide crystallises in colourless needles, m. p. 202° . 5-*n*-Butylbarbituric acid, m. p. 214° , is converted by bromine in methylalcoholic solution into 5-bromo-5-*n*-butylbarbituric acid, colourless needles, m. p. 114° . Ethyl bromo-*n*-butylmalonate, a colourless liquid, b. p. $152\text{--}153^\circ/20$ mm., $252\text{--}253^\circ$ (decomp.)/737 mm., d_{25}^{25} 1.238, is obtained by the addition of bromine, containing a trace of iodine as catalyst, to ethyl *n*-butylmalonate; it is transformed by an alcoholic solution of sodium phenoxy into ethyl phenoxy-*n*-butylmalonate, a viscous liquid, b. p. $170\text{--}173^\circ/8$ mm., d_{24}^{24} 1.063. The latter ester is converted by carbamide and ethyl alcoholic sodium ethoxide solution at 105° into 5-phenoxy-5-*n*-butylbarbituric acid, small, colourless needles, m. p. 167° . Ethyl ethylbutylmalonate, b. p. $243\text{--}245^\circ/755$ mm., is converted in a similar manner into 5-ethyl-5-*n*-butylbarbituric acid, m. p. 125° .

H. W.

Action of α -Bromoisobutaldehyde on Sodiomalonic Ester. ADOLF FRANKE and GERALD GROEGER (*Monatsh.*, 1922, **43**, 56—60).—The reaction between ethyl sodiomalonate and α -bromoisobutaldehyde takes an unexpected course, yielding the ethyl ester of γ -isobutylidenemalonolactone, transparent crystals, m. p. 68° , b. p. $177\text{--}178^\circ/25$ mm., which, on oxidation by cold alkaline permanganate, gives $\alpha\beta$ -dihydroxy- γ -isohexolactone, m. p. 97° . Condensation of the same aldehyde with ethyl sodioacetoacetate gives a substance, $\text{C}_{10}\text{H}_{16}\text{O}_4$, b. p. $135\text{--}140^\circ$.

C. K. I.

A New Class of Active Racemic Substances. PH. LANDRIEU (*Bull. Soc. chim.*, 1922, **33**, 667—672; cf. Délépine, A., 1921, ii, 567).—A compound of *d*-tartaric acid with inactive tartaric

acid was prepared, containing one molecule of each acid with two molecules of water of crystallisation, the rotatory power of which is equal to half that of the active acid. In order to prove that the substance was a compound and not a mixture, its equilibrium with the mother-liquor from which it was crystallised was studied at a temperature of 13.5° , and the conditions under which either of the acids or the compound of the two could be deposited were ascertained. The equilibrium diagram is given and a similar curve was obtained from *l*-tartaric acid and the inactive form. The conclusion is drawn that it should be possible to obtain a triple compound of these acids which should be regarded as a compound of racemic acid with the inactive form. The author considers that, in order to obtain molecular compounds of optically active substances, it is not necessary that the activity of those substances should be of opposite sign.

H. J. E.

Preparation of Methylenecitric Acid. C. GASTALDI (*Boll. Chim. Farm.*, 1922, **61**, 353—357).—When 40 grams of crystallised citric acid and 6 grams of paraformaldehyde are heated together at 145° in a sealed tube of 90 c.c. capacity, methylenecitric acid is formed in 74% yield.

T. H. P.

Synthesis of the Polyacetic Acids of Methane. VII. *iso*Butylene- $\alpha\gamma\gamma'$ -tricarboxylic Acid and Methanetetra-acetic Acid. CHRISTOPHER KELK INGOLD and LEWIS CHARLES NICKOLLS (*T.*, 1922, **121**, 1638—1648).

Methylated Saccharic Acid and Methylated Mucic Acid. P. KARRER and J. PEYER (*Helv. Chim. Acta*, 1922, **5**, 577—581).—Potassium saccharate was methylated first with methyl sulphate in alkaline solution, and when the partly methylated product had been freed from inorganic salts, methylation was completed by boiling with methyl iodide in presence of silver oxide. Purified *methyl tetramethylsaccharate*, $\text{CO}_2\text{Me} \cdot [\text{CH} \cdot \text{OMe}]_4 \cdot \text{CO}_2\text{Me}$, crystallises from ether in stout needles or plates, m. p. 68° , $[\alpha]_D^{25} +8.88^{\circ}$ to 10.26° . *Tetramethylsaccharodiamide*, prepared by the action of ammonia on a cold concentrated aqueous solution on the above compound, forms colourless, apparently rhombic plates, m. p. 237° ; $[\alpha]_D^{25} +12.22^{\circ}$ in water. Mucic acid, when methylated in a similar manner to saccharic acid, gives *methyl tetramethylmucate*, crystallising in monoclinic or rhombic tablets, m. p. 103° . A second product, isolated in small quantity, is probably *methyl trimethylmucate*, m. p. 165 — 166° . *Tetramethylmucodiamide* forms small, tabular crystals, m. p. 276° . *Barium tetramethylsaccharate* crystallises in long needles, very soluble in water; the silver salt forms a very soluble, white powder.

E. H. R.

The Alcoholic Fermentation of Formaldehyde. HANS MÜLLER (*Helv. Chim. Acta*, 1922, **5**, 627—628).—To account for the alcoholic fermentation of formaldehyde by osmium, E. Müller supposed the intermediate formation of a compound, H_2CO_2 , containing sexavalent carbon (this vol., i, 110). On account of the widespread nature of Cannizzaro's reaction in physiological

ff*

change, it is interesting that in this case also it will explain the observed facts. Assuming that 2 mols. of formaldehyde give 1 mol. of methyl alcohol and 1 mol. of formic acid, the last can also behave as an aldehyde and by the same reaction give 0.5 mol. of formaldehyde and 0.5 mol. of carbon dioxide. The formaldehyde thus regenerated starts the cycle again. The products of fermentation, methyl alcohol and carbon dioxide, are thus produced in the molecular ratio 2 : 1, in agreement with the experimental results.

E. H. R.

Asymmetric Synthesis. J. PIRAK (*Biochem. Z.*, 1922, **130**, 76—79).—The combination of sodium hydrogen sulphite and acetaldehyde and subsequent addition of potassium cyanide was carried out slowly in the circularly polarised light from a metal filament lamp of 250 candle power or from a mercury lamp. The cyanohydrin was converted into lactic acid. The latter was invariably inactive, even in presence of molybdic acid.

H. K.

The Preparation of Aldehydes from Tertiary Alcohols. R. LOCQUIN and SUNG WOUSENG (*Compt. rend.*, 1922, **175**, 100—102).—It has previously been shown (this vol., i, 710) that tertiary alcohols of the type $\text{HO}\cdot\text{CRR}'\cdot\text{CH}\cdot\text{CH}_2$ are readily converted by acids into primary alcohols of the type $\text{CRR}'\cdot\text{CH}\cdot\text{CH}_2\cdot\text{OH}$, and it is now shown that, if these tertiary alcohols are acted on by chromic acid mixture, they give aldehydes of the type



Thus this oxidation process is not necessarily a means of differentiating a primary from a tertiary alcohol.

W. G.

Preparation of Ketones from Secondary Alcohols. SETH BLISS HUNT (F.P. 523108; from *Chem. Zentr.*, 1922, ii, 142).—Secondary alcohols in the state of vapour are mixed with oxygen and an indifferent gas in the presence of metallic catalysts, preferably copper or copper alloys, at 475—800°. Acetone is thus prepared from an alcoholic mixture containing principally isopropyl alcohol (from petroleum hydrocarbons). The alcohol, heated at 65°, is mixed with sufficient air for its oxidation and the mixture is passed over a copper catalyst at 500°. The yield of acetone amounts to 75% of the theoretical yield.

G. W. R.

Catalysis. XVI. The Inversion of Sucrose by Hydrogen Ion. THOMAS MORAN and WILLIAM CUDMORE McCULLAGH LEWIS (T., 1922, **121**, 1613—1623).

Methyl Ethers of Xylan. EMIL HEUSER and WILHELM RUPPEL (*Ber.*, 1922, **55**, [B], 2084—2088; cf. Heuser, Braden, and Kürschner [this vol., i, 113]).—The presence of two hydroxyl groups in xylan has been shown by the formation of a diacetate and dibenzoate, and is now further confirmed by the production of a dimethyl ether.

Although xylan is very readily soluble in solutions of alkali hydroxides, it cannot be converted by methyl sulphate in these media into methylated products containing more than 1—1.5

methoxyl groups for each $C_5H_8O_4$ complex. The products thus obtained are freely soluble in cold water, but the solutions become turbid when they are warmed owing to separation of methyloxylan. Better results are obtained with silver oxide and methyl iodide. Xylan, pre-methylated with sodium hydroxide and methyl sulphate, is almost completely methylated by these reagents boiling under slightly increased pressure, and is completely converted into *dimethylxylan*, a brittle mass which softens at 65–70°, when similarly treated under pressure at 100°. H. W.

Constitution of Polysaccharides. I. Xylan and its Acetyl Derivatives. I. SHIGERU KOMATSU and KOZO KASHIMA (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1922, 5, 307–314).—The isolation of xylan from wheat straw and corn cobs is described in detail. It is noteworthy that xylan prepared from the latter source yields scarcely any acetyl derivative by the action of acetic anhydride and acetyl chloride with or without catalytic agents, whereas that derived from wheat straw easily yields acetyl compounds.

Monoacetyl xylan, $[\alpha]_D^{20} -202^\circ 6'$ when dissolved in chloroform (cf. Bader, T., 1896, 70, 1335), is prepared from xylan and acetyl chloride, or in better yield from xylan, and glacial acetic acid and acetic anhydride containing chlorine and sulphur dioxide. Its molecular weight in boiling chloroform solution corresponds with the formula $(C_7H_{10}O_5)_2$. Diacetyl xylan (cf. Bader, *loc. cit.*) is prepared by treating xylan with acetyl chloride and pyridine, acetic anhydride, chlorine, and sulphur dioxide, or acetic anhydride and zinc chloride; it has $[\alpha]_D^{20} -135^\circ 9'$ in chloroform solution.

The hydrolysis of xylan and its acetates by *N*/5-benzenesulphonic acid has been investigated. H. W.

Galactosan. AMÉ PICTET and HENRY VERNET (*Helv. Chim. Acta*, 1922, 5, 444–448).—Galactosan is difficult to separate from its polymerisation products. When galactose is dehydrated at 180°/15 mm., the molecular weight of the product corresponds with $(C_6H_{10}O_5)_3$; at 145°/15 mm. the product corresponds with $(C_6H_{10}O_5)_2$, whilst at 135°/2 mm. the product, which is very hygroscopic, appears to be a mixture of galactosan and digalactosan. The galactosan was partly purified by extraction with boiling alcohol, in which it is more soluble than its polymerides. In its chemical behaviour it is similar to glucosan, and is undoubtedly an anhydride of the α -series. It polymerises slowly at the ordinary temperature; in the hot, polymerisation is accelerated by zinc chloride, which brings about, at 170°, the formation of a mixture of tetra- and penta-galactosan.

With cold hydrochloric acid, galactosan forms galactosyl chloride, but the product is contaminated with polygalactosides, through the polymerising action of the acid. The impure α -galactosyl chloride forms a transparent, brown, amorphous residue from alcohol. Condensed with dextrose and sodium in alcoholic solution, it forms a disaccharide, probably *glucose- α -galactoside*, giving an *osazone*, yellow needles, m. p. 158°. This osazone is not identical

with that of glucose- β -galactoside prepared by Fischer and Armstrong (A., 1902, i, 746). E. H. R.

Sublimation Experiments with Carbohydrates. P. KARRER and J. O. ROSENBERG (*Helv. Chim. Acta*, 1922, 5, 575—576).—It was shown by Pictet and Sarasin (A., 1918, i, 59) that when starch was distilled under reduced pressure, lævoglucozan could be identified in the distillate. The same compound has now been obtained as a sublimate by heating potato starch at about 220° in a very thin layer, having a cold condensing surface within 2 mm. of the heated starch, at atmospheric pressure. Lævoglucozan was obtained in a similar manner from α -tetra-amylose at 220°, and with rhamnose at 120°/12 mm. the sugar itself was sublimed. E. H. R.

Viscosity of Cellulose in Cuprammonium Hydroxide Solution. I. Determination of the Viscosity. REGINALD ARTHUR JOYNER (T., 1922, 121, 1511—1525).

Constitution of Polysaccharides. V. The Yield of Glucose from Cotton Cellulose. JAMES COLQUHOUN IRVINE and EDMUND LANGLEY HIRST (T., 1922, 121, 1585—1591).

Oxidation of Lignin and Lignosulphonic Methyl Ethers. EMIL HEUSER and SIGURD SAMUELSEN (*Cellulosechem.*, 1922, 3, 78—83).—Hitherto it has not been possible, by the oxidation of lignin or lignosulphonic acid, to obtain products intermediate between the original complex and oxalic acid. It was thought, by analogy, that the complete methoxylation of the lignin might stabilise the molecule and lead to oxidation products having a direct constitutional relationship to the original lignin. Both lignosulphonic acid and lignin isolated by Willstätter and Zechmeister's method were completely methoxylated by six successive treatments with methyl sulphate and sodium hydroxide at 70°. The methoxyl value of the sulphonic acid was thus increased from 13.07 to 25.43% and that of the lignin from 14.15 to 26.05%. These products were then oxidised by alkaline permanganate at 90° and by alkaline peroxide, but no product other than oxalic acid could be isolated. The volatile acids, calculated as acetic, amounted only to 0.9% of the methyl-lignin oxidised. A statistical account of the oxidation of methyl-lignin by alkaline permanganate showed 44.76% of the original carbon in the form of carbon dioxide and 10.69% in the form of oxalic acid; thus only 55.65% of the total carbon oxidised has been accounted for. J. F. B.

The Effect of Dakin's Hypochlorite Solution on certain Organic Substances. N. O. ENGFELDT (*Z. physiol. Chem.*, 1922, 121, 18—61).—The action of Dakin's hypochlorite solution, containing 0.5% of sodium hypochlorite, 0.5% of sodium carbonate, and 0.45% of sodium hydrogen carbonate, on carbohydrates, fats, soaps, and glycerol, proteins, amino-acids, ammonia, and aldehydes, has been investigated. The general method is to treat a given amount of the substance with the hypochlorite solution for a given time at a given temperature, and to estimate the amount of hypo-

chlorite left by treatment with an iodide and estimation of the iodine set free. Fats, soaps, and glycerol react only to a small extent; most of the other substances investigated react much more completely and rapidly. In particular, hippuric acid is found to be attacked, yielding benzoic acid, formaldehyde, and ammonia, in opposition to the results of Langheld (A., 1909, i, 138, 557) and Dakin. W. O. K.

Optically Active Amine Oxides. III. JAKOB MEISENHEIMER (*Annalen*, 1922, 428, 252—253).—A general introduction to the accompanying papers (cf. following abstracts, and this vol., i, 822). C. K. I.

Optically Active Amine Oxides. III (i). Methylethylpropylamine Oxide. J. MEISENHEIMER and HERMANN BERNHARD (*Annalen*, 1922, 428, 254—268).—The optical resolution of this oxide was not accomplished although the *d*-bromocamphorsulphonate, *d*-tartrate, and *d*-camphornitronate were fractionally crystallised.

Methylethylpropylamine, prepared from propyl bromide and methylethylamine, has b. p. 91—92°, yields a *hydrochloride*, m. p. 177—179°, a *picrate*, m. p. 94—95°, and a *platinichloride*, m. p. 176—177°. The oxide is extremely hygroscopic, and yields a *hydrochloride*, m. p. 53—56°, a *picrate*, m. p. 106—107°, a *platinichloride*, m. p. 204—216°, a *d*-bromocamphorsulphonate, m. p. 89—91°, a *d*-tartrate, m. p. 99—100°, and a *d*-camphornitronate, m. p. 82—83°. C. K. I.

Optically Active Amine Oxides. III (ii). Methylethylallylamine Oxide. J. MEISENHEIMER and ARTUR LOHSNER (*Annalen*, 1922, 428, 269—278).—Methylethylallylamine oxide has been resolved into its optical antipodes by fractional crystallisation of its *d*-bromocamphorsulphonate.

Methylethylallylamine, prepared from methylethylamine and allyl bromide, has b. p. 88—89°, forms a *picrate*, m. p. 90°, and an *oxide*, which gave a *dl*-*picrate*, m. p. 134—135°. The *d*-bromocamphorsulphonate of the *l*-amine oxide, which was crystallised from ethyl acetate, crystallises with 1H₂O, has m. p. 66—68°, and yields the *l*-*picrate*, having m. p. 133—134° and $[\alpha]_D - 2.6^\circ$. The *d*-bromocamphorsulphonate of the *d*-amine oxide, which was purified with the aid of ethyl nitrate, crystallises with 2H₂O, has m. p. 57—58°, and gives the *d*-*picrate*, m. p. 133—134°, $[\alpha]_D + 2.9^\circ$. C. K. I.

Proteinogenous Amino-alcohols and Cholines. II. P. KARRER, M. GISLER, E. HORLACHER, F. LOCHER, W. MÄDER, and H. THOMANN (*Helv. Chim. Acta*, 1922, 5, 469—489).—In a previous paper (A., 1921, i, 228) the preparation was described of a number of amino-alcohols and cholines from naturally occurring amino-acids. On account of their close crystallographic, chemical, and physiological relation to one another and their possible occurrence in the plant and animal organism, the study of these compounds has been extended. In most cases the racemic forms only were prepared.

Alanine-choline was prepared in the following stages. α -Bromopropionic acid was condensed with dimethylamine, and the crude product esterified with ethyl alcohol, giving *ethyl α -dimethylamino-propionate* (*N-dimethylalanine ethyl ester*), a pale yellow oil, b. p. $150^{\circ}/740$ mm. This was reduced with sodium and alcohol, giving *N-dimethylalaninol*, a pale yellow oil, b. p. $140-141^{\circ}/738$ mm. With methyl iodide, this readily gives *alanine-choline iodide*, $\text{OH}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{NMe}_3\text{I}$, m. p. 296° . Free *alanine-choline* is similar to the base of ordinary choline and very hygroscopic. Its *aurichloride*, $\text{C}_6\text{H}_{16}\text{ON}\cdot\text{AuCl}_4$, has m. p. 247° . The *platinichloride*, $(\text{C}_6\text{H}_{16}\text{ON})_2\text{PtCl}_6$, m. p. 228° , crystallises in stout, rhombic prisms, $a:b:c=0.7072:1:0.5689$; $d^{20} 1.863$. The *picrate* of alanine-choline forms golden-yellow crystals, m. p. 265° .

Valinol, $\text{CHMe}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{OH}$, was prepared by the reduction of valine ethyl ester (ethyl α -aminoisovalerate); it forms a colourless oil with a strong odour, b. p. $181-186^{\circ}/720$ mm.; the *hydrochloride*, m. p. 114° , is very hygroscopic. Valine-choline was synthesised as follows: α -Bromoisovaleric acid was condensed with dimethylamine, and the product ethylated, giving *ethyl α -dimethylaminoisovalerate*, b. p. about 160° . This was reduced with sodium and alcohol to *dimethylvalinol*, which with methyl iodide gave *valine-choline* in the form of its *iodide*, m. p. 195° . The *aurichloride*, $\text{C}_8\text{H}_{20}\text{ON}\cdot\text{AuCl}_4$, forms yellow leaflets, m. p. 225° ; the *platinichloride*, brownish-red prisms, m. p. $210-211^{\circ}$. Attention is directed to the hindering effect of the *isopropyl* group on the condensation of α -bromoisovaleric acid with dimethylamine.

Attempts to reduce the esters of *N*-acetyl-*l*-tyrosine and *N*-acetyl-*O*-methyl-*l*-tyrosine to amino-alcohols were unsuccessful. *N*-Acetyl-*l*-tyrosine forms white crystals, m. p. 165° ; by methylation with methyl sulphate it gives *N*-acetyl-*O*-methyl-*l*-tyrosine, white needles, m. p. $147-148^{\circ}$. When hydrolysed in acid solution this gives *O*-methyl-*l*-tyrosine, white, glistening leaflets, m. p. 243° ; its *ethyl ester* forms a *hydrochloride*, fine, white needles. *dl*-Tyrosine-choline and its *O*-methyl ether were prepared as follows: α -Bromo- β -*p*-anisylpropionic acid was condensed with dimethylamine and the product esterified, giving *O*-methyl-*N*-dimethyltyrosine *ethyl ester*, an oil of unpleasant odour, b. p. $165^{\circ}/4$ mm. By reduction this gave *O*-methyl-*N*-dimethyltyrosinol, a nearly colourless oil, b. p. $133^{\circ}/4$ mm. The corresponding choline, *O*-methyltyrosine-choline, forms a crystalline *iodide*, m. p. $137-139^{\circ}$; the *aurichloride* forms large, flat leaves or rosettes of yellow needles, m. p. $112-115^{\circ}$; the *platinichloride*, orange-yellow leaflets, m. p. 204° . By demethylation of the above, *tyrosine-choline* was obtained; its *iodide* forms small, white needles, m. p. 176° ; the *chloride*, small leaflets.

The acetyl derivatives of the synthetic cholines show similar pharmacological behaviour, for instance, in their action on an isolated frog's heart, to ordinary acetylcholine, but greater concentrations are required. When injected intravenously they are much less active than ordinary acetylcholine.

l- $\alpha\alpha$ -Dimethyl-leucinol was obtained by the action of magnesium methyl iodide on *l*-leucine ethyl ester. It is an oil of unpleasant

odour, b. p. 187—190°/720 mm.; its *hydrochloride* forms white needles, m. p. 166°, and its *sulphate*, m. p. 237°.

The stearic and palmitic esters of the synthetic cholines show a similar hæmolytic behaviour to those of ordinary choline (cf. Fourneau and Le Page, A., 1914, i, 938). These esters generally show the phenomenon of a double melting point, first melting to oily drops which adhere to the walls of the tube and then becoming fluid at a higher temperature with decomposition. The esters were prepared by the action of the acid chlorides on the choline iodides and chlorides. *l-Leucinecholine iodide stearate*, fine needles, m. p. 108—110° and 138—140°; the corresponding *chloride* forms white needles, m. p. 100° and 120°. *l-Leucinecholine iodide palmitate*, m. p. 105° and 113—115°; corresponding *chloride*, m. p. 100° and 110°. *dl-Phenylalaninecholine iodide stearate*, groups of needles, m. p. 124—125°; corresponding *chloride*, crystal aggregates, m. p. 147° and 172°. *dl-Phenylalaninecholine iodide palmitate*, m. p. 125°; corresponding *chloride*, m. p. 147° and 172°.

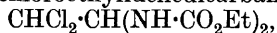
E. H. R.

Direct Synthesis of Carbamide starting from Carbon Dioxide and Ammonia. KENNETH C. BAILEY (*Compt. rend.*, 1922, **175**, 279—281).—A yield of 14% of carbamide calculated on carbon dioxide was obtained by passing this gas with an excess of ammonia through a quartz tube, heated to redness, and traversed by a concentric glass tube through which cold water was circulated. The carbamide was deposited on the cool walls of the latter, and by using alumina or thoria as catalysts the yield was increased to 19%. By recirculation of the unused carbon dioxide, the yield was further raised to 50% or more. Above 500°, no carbamide was formed, and at 450° only small quantities. As the experiments were conducted at atmospheric pressures and the product was always accompanied by a small amount of ammonium cyanate, ammonium carbamate cannot be considered as an intermediate product of the reaction, which probably takes the course represented by the equations following: (1) $\text{CO}_2 + \text{NH}_3 = \text{H}_2\text{O} + \text{HO}\cdot\text{C}\text{:}\text{N}$; (2) $\text{HO}\cdot\text{C}\text{:}\text{N} \rightleftharpoons \text{HN}\cdot\text{CO}$; (3) $\text{HN}\cdot\text{CO} + \text{NH}_3 = (\text{NH}_2)_2\text{CO}$; (4) $\text{HO}\cdot\text{CN} + \text{NH}_3 = \text{NH}_4\text{OCN}$.

G. F. M.

Halogenation. XXI. Some Derivatives of Carbamic Esters. Chlorine as a Simultaneous Oxidising and Condensing Agent. RASIK LAL DATTA and BIBHU CHARAN CHATTERJEE (*J. Amer. Chem. Soc.*, 1922, **44**, 1538—1543).—When chlorine is passed into a solution of a carbamic ester in methyl alcohol, the latter is oxidised to formaldehyde, which then condenses with two molecular proportions of the ester, giving a methylenedicarbamic ester. A similar reaction occurs in benzyl-alcoholic solution. With ethyl alcohol, simultaneous chlorination and oxidation of the alcohol occurs, with ultimate production of a dichloroethylidene carbamic ester. With substituted urethanes containing an aromatic nucleus, the latter also undergoes chlorination. Condensations of this type do not occur with secondary alcohols.

The following compounds have been prepared. Ethyl methylenedicarbamate, colourless, silky needles, m. p. 131°; the methyl ester, $\text{CH}_2(\text{NH}\cdot\text{CO}_2\text{Me})_2$, slender needles, m. p. 124° (cf. Conrad and Hock, A., 1903, i, 607); the *propyl* ester, colourless, silky needles, m. p. 113°; the *isobutyl* ester, slender needles, m. p. 115°; the *isoamyl* ester, a colourless, microcrystalline powder, m. p. 80°. Ethyl benzylidenedicarbamate, $\text{CHPh}(\text{NH}\cdot\text{CO}_2\text{Et})_2$, silky needles, m. p. 175°; ethyl dichloroethylidenedicarbamate,



slender needles, m. p. 122°; methylenedi-*p*-chlorodiphenyldiurethane, $\text{CH}_2[\text{N}(\text{C}_6\text{H}_4\text{Cl})\cdot\text{CO}_2\text{Et}]_2$, colourless needles, m. p. 87°; methylenedi-tetrachloro- α -naphthyldiurethane, $\text{CH}_2[\text{N}(\text{C}_{10}\text{H}_5\text{Cl}_2)\cdot\text{CO}_2\text{Et}]_2$, colourless needles, m. p. 160—161°.

Urethane in aqueous solution is converted by chlorine into monochlorourethane, which is hydrolysed slowly by cold water to ethyl 4-chloromethylcyclohexylmethylenehydrazineimide-1:3-dicarboxylate, $\text{CH}_2\text{Cl}\cdot\text{CH}<\frac{\text{N}(\text{CO}_2\text{Et})}{\text{N}(\text{CO}_2\text{Et})}>\text{NH}$, colourless needles, m. p. 143—144° (cf. Datta and Gupta, A., 1915, i, 122). The constitution of the substance is established by the isolation of the corresponding *acetyl* derivative, colourless, granular crystals, m. p. 117—118° and *imide chloride*, $\text{CH}_2\text{Cl}\cdot\text{CH}(\text{N}\cdot\text{CO}_2\text{Et})_2\text{NCl}$, unstable, granular crystals, m. p. 75—76°.

Methyl dichlorocarbamate is obtained as a yellow liquid by the action of chlorine on an aqueous solution of methyl carbamate.

H. W.

Amide Formation from Esters of Secondary Alkylmalonic Acids. ARTHUR W. DOX and LESTER YODER (*J. Amer. Chem. Soc.*, 1922, 44, 1564—1567).—Fischer and Diltthey's observations (A., 1902, i, 169) on the difference in the rate of amide formation from ethyl esters of mono- and di-alkylmalonic acids and Meyer's observation (A., 1906, i, 358) on the difference in rate of amide formation from methyl and ethyl esters of dialkylmalonic acids have been extended to include the methyl and ethyl esters of *sec.*-alkylmalonic acids. With respect to amide formation, the secondary alkylmalonic esters are found to resemble the dialkylmalonic esters.

isoPropylmalonamide, rhombohedra, m. p. 260°, is prepared by agitating methyl isopropylmalonate with aqueous ammonia (28%) at the atmospheric temperature. Methyl *sec.*-butylmalonate, b. p. 217—218°/748 mm. (prepared by the action of methyl alcohol and a little sodium methoxide on the corresponding ethyl ester, b. p. 234—236°/755 mm.), is transformed similarly into *sec.*-butylmalonamide, m. p. 242°. On the other hand, the ethyl esters of isopropyl- and *sec.*-butylmalonic acids only give small quantities of the corresponding amides after protracted treatment with a large excess of concentrated aqueous ammonia, the greater part of the esters remaining unchanged. Methyl cyclohexylmalonate, b. p. 121—122°/6 mm., d_{20}^{25} 1.0737, is prepared in poor yield by the action of ethyl-alcoholic sodium ethoxide solution on methyl

malonate and *cyclohexyl* bromide; it is converted by concentrated ammonia into *cyclohexylmalonamide*, scaly crystals, m. p. 305°, and a *product*, needles, m. p. 169°, which is probably the imide. Methyl phenylmalonate gives *phenylmalonamide*, m. p. 233°.

The ethyl *sec.*-alkylmalonates have been transformed into the corresponding *sec.*-alkylbarbituric acids by treatment with carbamide and an excess of sodium ethoxide at about 105°; 5-*sec.*-butylbarbituric acid, pearly scales, m. p. 199°, 5-*cyclohexylbarbituric acid*, m. p. 254—256°, and 5-*cyclohexyl-2-thiobarbituric acid*, small, flat, pale yellow needles, m. p. 188—189°, are described. H. W.

Tautomerism of Dyads. I. Detection of Tautomeric Equilibria in Hydrocyanic Acid. EDITH HILDA USHERWOOD (T., 1922, 121, 1604—1612).

The Action of Organomagnesium Compounds on Nitriles. FRANZ BAERTS (*Bull. Soc. chim. Belg.*, 1922, 31, 184—192).—A study of the action of Grignard's reagent on propionitrile in order to determine whether the latter yields condensation products similar to those obtained from acetonitrile (cf. Bruylants, *Bull. Acad. Belg.*) and also ketones according to Blaise's reaction (A., 1901, i, 133). With magnesium ethyl bromide, after treatment with water, two substances are obtained from the nitrile, termolecular cyanoethane, $(\text{EtCN})_3$, and diethyl ketone, the latter in much larger proportion. In addition, a considerable quantity of triethylcarbinol and bimolecular cyanoethane, $(\text{EtCN})_2$, is formed in the reaction. The bimolecular polymeride, which is the major product in the case of acetonitrile, is in this case about 25% of the total. The formation of the polymerides is explained on the hypothesis that the nitrile acts as a pseudo-acid and schemes are suggested to account for the formation of these and other products.

H. J. E.

Butenonitriles. P. BRUYLANTS (*Bull. Soc. chim. Belg.*, 1922, 31, 175—184).—The preparation of β -butenitrile (vinylacetonitrile) from allyl iodide and cuprous cyanide (Henry, A., 1916, i, 549) need not be carried out under pressure; the reaction takes place with equal ease in the case of allyl bromide, and, in addition, the yield is quantitative. The following physical constants for the substance are given: b. p. 118.4—118.6°/760.5 mm.; m. p. (after solidification in liquid air) 84°; n_{D}^{20} 1.40297; n_{D}^{20} 1.40602; n_{D}^{20} 1.41170; d_4^{20} 0.83409. An isomeride may be obtained by gently heating γ -chlorobutyronitrile and also from the corresponding bromo-compound. Decomposition into the unsaturated nitrile and the halogen acid takes place, but in the latter case β -bromobutyronitrile is formed simultaneously. This isomeride, crotononitrile, may also be obtained from vinylacetonitrile by addition of gaseous hydrochloric or hydrobromic acid and subsequent treatment with potassium hydroxide or pyridine. It consists of a mixture of the two possible stereoisomerides, which can only be separated after repeated fractionation. Physical constants have been determined as follows:—

Fraction b. p. 107·6—107·8°, n_{D}^{20} 1·41503; n_D^{20} 1·41821; $n_{H\beta}^{20}$ 1·42650; d_4^{20} 0·8244; fraction b. p. 120·3—120·5°, $n_{H\alpha}^{20}$ 1·41835; n_D^{20} 1·42161; $n_{H\beta}^{20}$ 1·42985; d_4^{20} 0·8239; and it is on the evidence afforded by these that the author bases his views as to the space configuration of the substances, as chemical methods of investigation have not, as yet, given any trustworthy indication.

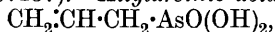
H. J. E.

Possible Asymmetry of Aliphatic Diazo-compounds. II.

P. A. LEVENE and L. A. MIKESKA (*J. Biol. Chem.*, 1922, 52, 485—494).—The diazosuccinic ester previously obtained (A., 1921, i, 233) was converted into malic, chlorosuccinic, and bromosuccinic esters. In each case the products had small rotations, thus indicating the existence of optically active diazosuccinic esters. Further work, however, is necessary completely to solve the problem (cf. also Marvel and Noyes, A., 1921, i, 15).

E. S.

Preparation of Allylarsinic Acid. F. HOFFMANN-LA ROCHE & Co., AKT.-GES. (Swiss Pat. 89055; from *Chem. Zentr.*, 1922, ii, 201. Additional to E.P. 167157).—*Allylarsinic acid*,



forms colourless needles or stout prisms, m. p. 129—130°. The white *silver* salt is soluble in dilute nitric acid. The acid decolorises bromine water, and permanganate solution made alkaline with sodium carbonate. The primary *sodium* salt, which forms lustrous leaflets, is not hygroscopic and melts partly at 87—88° in its water of crystallisation. The aqueous solution is weakly acid to litmus and can be heated to 120° without decomposition. The hygroscopic *secondary sodium* salt has an alkaline reaction. The acid is decomposed by mineral acids with the separation of arsenious oxide. The zinc, lead, copper, cobalt, and iron salts are insoluble.

G. W. R.

Preparation of Hydrocarbons. HERMAN PLAUSON and GEORG V. TISCHENKO (D.R.-P. 346065; from *Chem. Zentr.*, 1922, ii, 442).—Carbides which on treatment with water give acetylene, ethylene, or methane are treated, either singly or mixed with steam, at 500—700°. The carbides of calcium, aluminium, manganese, cerium, lanthanum, and uranium are used. With calcium carbide, a mixture of hydrocarbons containing more than 60% of benzene is obtained. A mixture of calcium and aluminium carbides at 600° in a vacuum gives pentinene, whilst at higher pressures polymerised hydrocarbons, for example, terpenes, are obtained.

G. W. R.

The Rôle of Mercuric Nitrate in the "Catalysed" Nitration of Aromatic Substances. II. Nitration of Naphthalene. TENNEY L. DAVIS (*J. Amer. Chem. Soc.*, 1922, 44, 1588—1591; cf. A., 1921, i, 338).—Since naphthalene is very easily nitrated, concentrated nitric acid, even in the presence of mercuric nitrate, converts it promptly into nitronaphthalenes

and the amount of nitronaphthols which is formed is exceedingly small. The best conditions for the production of the latter directly from naphthalene are moderately dilute acid and moderately low temperature. In addition to nitronaphthalenes, 2:4-dinitro- α -naphthol and probably 2-nitro- α -naphthol are produced. The unexpected formation of derivatives of α -naphthol renders the interpretation of the course of the action a matter of considerable difficulty.

H. W.

Preparation of α -Chloronaphthalene Derivatives. KALLE & Co., AKT.-GES. (D.R.-P. 343147; from *Chem. Zentr.*, 1922, ii, 143—144).—Nitronaphthalene- α -sulphonic acids or naphthasultone- α -sulphonic acids are treated with chlorine or chlorinating agents. The sulphonic acid group is thereby replaced by chlorine and chloronitronaphthalenes or chloronaphthasultones are formed. 1-Nitronaphthalene-8-sulphonic acid gives, by the action of chlorine, hydrochloric acid and sodium chlorate, or a hypochlorite, 8-chloro-1-nitronaphthalene. Similarly, from 2-nitronaphthalene-4:8-disulphonic acid, 4:8-dichloro-2-nitronaphthalene is obtained; it forms yellow needles, m. p. 132°. By reduction, 4:8-dichloro-2-aminonaphthalene is obtained; it has m. p. 133°. Chlorination of 1-chloro-5-nitronaphthalene-4-sulphonic acid gives 1:4-dichloro-5-nitronaphthalene. 1:5-Dichloro-4-nitronaphthalene is similarly obtained. Sodium naphthasultone-4-sulphonic acid gives in the same way 4-chloronaphthasultone, m. p. 181—183°. It yields 4-chloro-1-hydroxynaphthalene-8-sulphonic acid by warming with dilute sodium hydroxide solution. This compound gives by hydrolysis 4-chloro-1-hydroxynaphthalene. The products are used in the preparation of colouring matters.

G. W. R.

Preparation of Naphthasultonesulphonyl Chlorides. KALLE & Co., AKT.-GES. (D.R.-P. 343056; from *Chem. Zentr.*, 1922, ii, 144—145).—Naphthasultone or its sulphonic acids are treated with chlorosulphonic acid. In the case of naphthasultone, a sulphonyl chloride group enters the 5-position, whilst in that of the sulphonic acids the sulpho-group is chlorinated. The products are very reactive, and may be used in the preparation of colouring matters. With ammonia or amines, the sultone ring is broken with formation of sulphonamides or amide-substituted sulphonamide derivatives of the corresponding α -naphthalenesulphonic acids. By heating sodium naphthasultone-3-sulphonate with chlorosulphonic acid at 40—100°, naphthasultone-3-sulphonyl chloride is obtained; it forms crystals, m. p. 185°. The corresponding anilide has m. p. 212—213°. Naphthasultone-5-sulphonyl chloride, similarly prepared, forms crystals, m. p. 194°. The anilide has m. p. 146—147°. Naphthasultone-3:6-disulphonyl chloride forms needles, m. p. 163°.

G. W. R.

Hydrogenation of 1:6-Dimethylnaphthalene. FRITZ MAYER and THERESE SCHULTE (*Ber.*, 1922, 55, [B], 2164—2167).—1:6-Dimethylnaphthalene is reduced by sodium and boiling

amyl alcohol to 1:6-dimethyl- $\Delta^{6,7}$ -5:8-dihydronaphthalene, b. p. 118°/10 mm., d^{16}_4 0.9700; the $\beta\beta'$ -position of the double bond in the hydrogenated nucleus is established by the observation that the substance yields a liquid dibromide which regenerates 1:6-dimethylnaphthalene when it is distilled in a vacuum. If the dihydro-compound is reduced by hydrogen in aqueous alcoholic solution in the presence of palladium, 1:6-dimethyl-5:6:7:8-tetrahydronaphthalene, a colourless liquid, b. p. 110—111°/10 mm., d^{16}_4 0.9487, is obtained which is stable towards bromine and is oxidised by nitric acid to benzene-1:2:3-tricarboxylic acid. On the other hand, if 1:6-dimethylnaphthalene is reduced at 240° and 20—25 atmospheres pressure in the presence of a nickel catalyst, it gives a mixture (b. p. 108—110°/10 mm., d^{16}_4 0.9504) of 1:6-dimethyl-1:2:3:4-tetrahydronaphthalene and 1:6-dimethyl-5:6:7:8-tetrahydronaphthalene which is oxidised by nitric acid to a mixture of benzene-1:2:3- and -1:2:4-tricarboxylic acids.

H. W.

Constitution of Carbonium Dyes. Halochromism. HUGO KAUFFMANN (*Ber.*, 1922, 55, [B], 1967—1968).—In reply to Hantzsch (this vol., i, 24), the author maintains his priority in the formulation of the triphenylmethane dyes and other halochromic compounds as complex salts. His formulation of carboxylic acids antedates that of Hantzsch by six years.

H. W.

The Nature of Carbonium Salts. A. HANTZSCH (*Ber.*, 1922, 55, [B], 2043—2048).—A reply to the criticisms of Fierz (this vol., i, 445), Kehrman (this vol., i, 331) and Dilthey (this vol., i, 668) (cf. Hantzsch, this vol., i, 24).

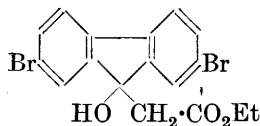
H. W.

The Fluorene Series. VII. Dibenzofulvene. A. SIEGLITZ and H. JASSOY (*Ber.*, 1922, 55, [B], 2032—2040).—Attempts to transform fluorenyl-9-methylurethane, $\text{CH}(\text{C}_6\text{H}_4)_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, into fluorenyl-9-methylamine have met with considerable difficulty (cf. A., 1921, i, 791), and the further conversion of the latter by Hofmann's degradation into dibenzofulvene, $\text{C}(\text{C}_6\text{H}_4)_2\cdot\text{CH}_2$, appeared not to be realisable. Unexpectedly, it is now found that the urethane can be converted directly into the desired hydrocarbon in small yield.

Dibenzofulvene is prepared by the distillation of fluorenyl-9-methylurethane with calcium oxide in a current of hydrogen under 20—30 mm. pressure. It crystallises in long, colourless needles, m. p. 46—48° (51° was observed on one occasion). In substance and in solution it becomes rapidly converted into amorphous products of high melting point. It is oxidised to fluorenone. The corresponding *picrate*, stable, orange-red crystals, and a colourless, resinous, *polymeric dibenzofulvene*, m. p. 290° after softening at 255°, are described.

Attempts to prepare 2:7-dibromodibenzofulvene by an analogous method were unsuccessful; the following series of substances was incidentally prepared. *Ethyl 2:7-dibromo-9-hydroxyfluorene-9-*

acetate (annexed formula), from 2:7-dibromofluorenone, ethyl bromoacetate, and zinc, colourless leaflets, m. p. 106—107°, which is reduced by zinc and hydrochloric acid to 2:7-dibromofluorene-9-acetic acid. 2:7-Dibromo-9-hydroxyfluorene-9-acetic acid, small, colourless needles, m. p. 205—206°. Ethyl 2:7-dibromodibenzofulvene- ω -carboxylate, from the hydroxy-ester at 100°/18 mm., m. p. 172—173°. 2:7-Dibromofluorene-9-acetylhydrazide, colourless needles, m. p. 247—248°, and the corresponding acetonehydrazone, colourless needles, m. p. 234—235°, and benzaldehydehydrazone, colourless needles, m. p. 256—257°. 2:7-Dibromofluorenyl-9-methylurethane, colourless needles, m. p. 191—192°. The latter when distilled with calcium oxide did not appear to yield the corresponding amine or unsaturated hydrocarbon.



In a further series of experiments, 2:7-dibromofluorenone was converted by magnesium and methyl iodide in the presence of ether into 2:7-dibromo-9-hydroxy-9-methylfluorene, colourless prisms, m. p. 162—163°, which was transformed by concentrated hydrochloric acid in the presence of glacial acetic acid into 9-chloro-2:7-dibromo-9-methylfluorene, slender, colourless needles, m. p. 182—183°. The latter gave 2:7-dibromo-9-methylfluorene when distilled under diminished pressure, but was rapidly converted in boiling glacial acetic acid into 2:7-dibromodibenzofulvene, slender, colourless needles, m. p. 205—206°, which may be preserved unchanged for some days in a vacuum. It did not appear to yield a picrate. In a similar manner, 2:7-dibromo-9-hydroxy-9-ethylfluorene, colourless rodlets or coarse prisms, m. p. 133—134°, was transformed successively into 9-chloro-2:7-dibromo-9-ethylfluorene, colourless, lustrous needles, m. p. 171°, and 2:7-dibromo- ω -methylidibenzofulvene, $C(C_6H_5Br)_2 \cdot CHMe$, colourless, woolly needles, m. p. 130—131°, which can be preserved indefinitely. 2:7-Dibromo-9-hydroxy-9-n-propylfluorene crystallises in small, colourless plates, m. p. 150—151°.

2:7-Dibromo-9-hydroxyfluorene, colourless needles, m. p. 168°, is prepared by the reduction of 2:7-dibromofluorenone by aluminium amalgam in the presence of moist ether. 2:7-Dibromofluorene, which has been shown previously (Sieglitz, A., 1920, i, 605) to be an excellent reagent for a series of aromatic acids, can also condense readily with aldehyde acids. Thus, with *o*-phthalaldehydic acid it yields 2:7-dibromo-9-benzylidenefluorene-2'-carboxylic acid, small, yellow needles, m. p. 224° after softening at 218° (ethyl ester, matted, yellow needles, m. p. 140°), and with opianic acid it gives 2:7-dibromo-9:3':4'-dimethoxybenzylidenefluorene-2'-carboxylic acid, dull yellow, microscopic rodlets, m. p. 249—250° after previous softening (ethyl ester, large, dark yellow crystals, m. p. 135°; corresponding dihydro-ester, colourless needles, m. p. 90°).

H. W.

Chlorination of *p*-Iododimethylaniline. GEORG SACHS and LUDWIG LEOPOLD (*Monatsh.*, 43, 1922, 49—53).—Direct chlorination

of *p*-iododimethylaniline in chloroform solution at -12° yields *o*-chlorodimethylaniline-*p*-iododichloride hydrochloride, a yellow, amorphous powder, decomp. $78-85^{\circ}$, which, on reduction by hydrogen sulphide, gives *o*-chloro-*p*-iododimethylaniline, b. p. $159-161^{\circ}/18$ mm., $276-278^{\circ}/760$ mm. (partial decomposition). More vigorous reduction of the iododichloride with zinc dust and hydrochloric acid gives *o*-chlorodimethylaniline. C. K. I.

Preparation of *N*-Nitroso-derivatives of Secondary Amines.

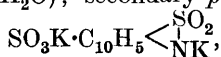
ERICH SCHMIDT and HEINRICH FISCHER (D.R.-P. 343249; from *Chem. Zentr.*, 1922, ii, 202; cf. A., 1920, i, 727-728).—Tetranitromethane is allowed to react with a boiling alcoholic solution of pyridine and a tertiary amine. *o*-Tolylmethylnitrosoamine is prepared from *o*-tolylldimethylamine, diethylnitrosoamine from triethylamine, and diphenylnitrosoamine from diphenylmethylamine. Diphenylnitrosoamine forms light yellow crystals, m. p. 66.5° . Nitroform, obtained as a by-product, may be reconverted into tetranitromethane. G. W. R.

Optically Active Amine Oxides. III (iii). Benzylmethylethylamine Oxide. J. MEISENHEIMER and ARTUR LOHSNER (*Annalen*, 1922, 428, 278-285).—Benzylmethylethylamine oxide has been resolved by means of its *d*-bromocamphorsulphonates.

Benzylmethylethylamine, prepared from methylethylamine and benzyl chloride, has b. p. $85-87^{\circ}/10$ mm., forms a *picrate*, m. p. 113° , and an *oxide*, which gives a *dl-picrate*, m. p. $106-107^{\circ}$. *l*-Benzylmethylethylhydroxylammonium *d*-bromocamphorsulphonate has m. p. $149-151^{\circ}$, and yields a *l-picrate*, m. p. $100-101^{\circ}$, $[\alpha]_D -0.25^{\circ}$. *d*-Benzylmethylethylhydroxylammonium *d*-bromocamphorsulphonate has m. p. $141-143^{\circ}$, and gives a *d-picrate*, m. p. $101-103^{\circ}$, $[\alpha]_D +0.25^{\circ}$ (cf. this vol., i, 813). C. K. I.

1 : 8-Naphthasultam-4-sulphonic Acid and certain of its Derivatives. W. KÖNIG and J. KEIL (*Ber.*, 1922, 55, [B], 2149-2155).—The preparation of 1 : 8-naphthasultam-4-sulphonic acid and several of its derivatives is described. The sulphonic acid and its anilide are much less reactive towards diazo-compounds than the unsubstituted naphthasultam or α -naphthol-4-sulphonic acid. The tendency towards the formation of *o*-sulphaminydyes is considerably less than towards the formation of the analogous *p*-derivatives and very much less than towards the production of *o*-hydroxyazo-dyes.

1 : 8-Naphthasultam-4-sulphonic acid, pale pink needles which are very freely soluble in water, is obtained by the action of phosphoryl chloride on potassium α -naphthylamine-4 : 8-disulphonate at 145° or by the action of sulphuric acid monohydrate on 1 : 8-naphthasultam alone or in the presence of glacial acetic acid. The primary potassium salt, $\text{SO}_3\text{K}\cdot\text{C}_{10}\text{H}_5\text{SO}_2\text{NH}$, almost colourless prisms ($+1.5\text{H}_2\text{O}$); secondary potassium salt,



intensely yellow crystals with green fluorescence ($+H_2O$); secondary *barium* salt, $C_{10}H_5O_5NS_2Ba \cdot 4H_2O$, and secondary *calcium* salt, $C_{10}H_5O_5NS_2Ca \cdot H_2O$, are described. 1 : 8-Naphthasultam-4-sulphonyl chloride crystallises in small, almost colourless leaflets, decomp. above 185° . The corresponding *anilide* forms colourless plates, decomp. above 230° , whilst the α -naphthalide crystallises in pale brown leaflets, m. p. about 240° (decomp.). Secondary potassium naphthasultam-4-sulphonate couples very slowly with *p*-nitrobenzenediazo hydroxide solution with the formation of 2-*p*'-nitrobenzeneazo-1 : 8-naphthasultam-4-sulphonic acid, long needles, decomp. 280° (the *potassium* salt is described). 2-*o*'-Methoxybenzeneazo-1 : 8-naphthasultam-4-sulphonic acid crystallises in dark violet leaflets which have no distinct melting point (the *potassium* salt is described).

H. W.

α -1-Naphthylethylamine. E. SAMUELSSON (*Svensk Kem. Tidskr.*, 1922, **34**, 7—9).—Naphthyl methyl ketones were prepared in 75% yield by the Friedel-Crafts' reaction; from 50 to 70% of the substance consisted of the α -isomeride, regardless of the temperature of preparation (0 — 50°). In no case was the product the pure α -compound, but when the reaction took place in nitrobenzene, the pure β -form was obtained. α -Naphthyl methyl ketoxime has m. p. 135° , and appears to exist in isomeric forms (cf. Betti and Poccianti, A., 1914, i, 550). α -Naphthylethylamine is a colourless liquid, b. p. 153° , d^{19}_4 1.063; the β -isomeride is a colourless liquid, b. p. 157° . Resolution of the α -isomeride was effected by means of camphoric acid. The *d*-form was not obtained pure; the *l*-form had $[\alpha]^{25}_D$ -80.8° ; and in ethyl alcohol $[\alpha]^{25}_D$ -62.5° . The hydrochloride and oxalate were prepared.

CHEMICAL ABSTRACTS.

The 2-Hydroxy-1-arylnaphthylamines. A. WAHL and R. LANTZ (*Compt. rend.*, 1922, **175**, 171—174).—The halogen atoms in α -chloro- and α -bromo- β -naphthol react readily with aromatic amines with the formation of hydroxyarylnaphthylamines. These are crystalline substances, insoluble in water, soluble in alkali hydroxides, and forming crystalline hydrochlorides, which are dissociated by water. β -Hydroxyphenyl- α -naphthylamine was obtained by boiling α -chloro- or α -bromo- β -naphthol with aniline. It forms white needles, m. p. 155 — 156° . β -Hydroxy- α -*o*-tolyl-naphthylamine, m. p. 114 — 115° , β -hydroxy- α -*p*-tolyl-naphthylamine, white prisms, m. p. 138 — 139° , β -hydroxy- α -*o*-anisyl-naphthylamine, white needles, m. p. 110° , and β -hydroxy- α -(*o*-methoxy-*m*-tolyl)-naphthylamine, white needles, m. p. 118° , were also prepared in a similar way. The methyl ethers of hydroxyphenylnaphthylamine and hydroxy-*p*-tolyl-naphthylamine are also described. The former forms white prisms, m. p. 82 — 83° , and the latter, needles, m. p. 94° .

G. F. M.

Preparation of 1-Arylamino-4-hydroxynaphthalenes. KALLE & Co., AKT.-GES. (D.R.-P. 343057; from *Chem. Zentr.*, 1922, ii, 145).—1 : 4-Dihydroxy- or 1-amino-4-hydroxynaphthalene

is heated with aromatic amino-compounds. 1-Amino-4-hydroxynaphthalene or its hydrochloride, heated at 180° with aniline, gives 1-anilino-4-hydroxynaphthalene; this forms colourless crystals, m. p. 92° . When dissolved in dilute sodium hydroxide solution and exposed to air naphthaquinoneanil (Euler, A., 1906, i, 369) separates. The hydrochloride forms colourless prisms. The methyl ether, $C_{10}H_{16}(OMe) \cdot NHPH$, crystallises in platelets, m. p. 139° . 1-op-Dichloroanilino-4-hydroxynaphthalene, prepared from 1:4-dihydroxynaphthalene and 2:4-dichloro-1-aminobenzene, forms colourless needles, m. p. 73° . 1-p-Chloroanilino-4-hydroxynaphthalene (from *p*-chloroaniline) has m. p. 96° . 1-p-Toluidino-4-hydroxynaphthalene, m. p. 109° , is prepared from *p*-toluidine. 1-Anilino-4-hydroxynaphthalene-2-carboxylic acid (from anthranilic acid) has m. p. $247-249^{\circ}$. When benzidine is heated with 1:4-dihydroxynaphthalene, it gives 4-amino-1:4'-hydroxynaphthylaminodiphenyl. The products are used in the preparation of colouring matters. By the oxidation of their alkaline solutions coloured compounds of the quinoneanil type are formed. G. W. R.

Preparation of a Derivative of 2-Amino-5-hydroxynaphthalene-7-sulphonic Acid. KALLE & Co., AKT.-GES. (D.R.-P. 342733; from *Chem. Zentr.*, 1922, ii, 202—203).—2-Amino-5-hydroxynaphthalene-7-sulphonic acid (2 mols.) is heated with *p*-phenylenediamine (1 mol.) in the presence of sodium hydrogen sulphite. For example, by heating at 105° in the presence of sodium hydrogen sulphite and sodium hydroxide for twelve hours and cooling, crystalline condensation products separate which are freed from sodium hydrogen sulphite by heating with hydrochloric acid. 1:4-Di(5'-hydroxy-7'-sulpho-2'-naphthylamino)benzene is formed with elimination of ammonia. This compound differs from 2:4'-aminophenylamino-5-hydroxynaphthalene-7-sulphonic acid in that it does not form a crystalline sodium salt or give a coloration with a nitrite and alkaline resorcinol solution. G. W. R.

Auto-oxidation. Anti-oxygens, and Various Phenomena Related Thereto. II. CHARLES MOUREU and CHARLES DUFRAISSE (*Compt. rend.*, 1922, 175, 127—132).—As previously recorded (this vol., i, 250), the auto-oxidation of many substances is checked by the presence of traces of certain compounds, notably phenols, to which the name anti-oxygens was given. Quantitative experiments have now been made to compare the inhibitive effect of proportions of phenols varying from 1 in 10 to 1 in 1,000,000 on the rate of the absorption of oxygen by acetaldehyde. The measurements were made by observing the rate of the ascension of the mercury column in barometer tubes charged with the reagents, and comparing with a control containing only acetaldehyde and oxygen. Quinol was the most effective phenol in suppressing auto-oxidation, as little as 1 in 100,000 having a very marked effect. Slightly less active were pyrogallol and catechol, followed by resorcinol and 1:3:4-trihydroxybenzene. At a concentration of 1 in 400, phloroglucinol has a maximum retarding effect, but at certain concentrations it actually accelerates

oxidation. Attention is directed to various well-known phenomena which may be attributed to anti-oxygens, for example, to the action of sulphurous gases in preventing the luminescence of phosphorus in dilute oxygen, the action of benzyl alcohol, glycerol, phenol, etc., in retarding the oxidation of sulphite solutions, the prevention of the oxidation of synthetic caoutchouc by phenols, the improved keeping property of essential oils as such, compared with that of the auto-oxidisable substances they contain, when isolated in a pure condition, etc. G. F. M.

Chemistry of Terpenes, Phytosterols, and Resins. I. Extraction of Amyrin. K. ALB. VESTERBERG (*Annalen*, 1922, 428, 243—246).—Historical and bibliographical. C. K. I.

Chemistry of Terpenes, Phytosterols, and Resins. II. Separation of α - and β -Amyrin. Preparation of α -Amyrilene. K. ALB. VESTERBERG and S. WESTERLIND (*Annalen*, 1922, 428, 247—251).—Details are given for the preparation of crude amyrim, $C_{30}H_{49}OH$, for its separation into α - and β -amyrim by fractional crystallisation of the benzoates, and for the preparation of α -amyrilene, $C_{30}H_{48}$, by the action of phosphorus pentachloride on α -amyrim. C. K. I.

The Reduction of some Aromatic Compounds by means of Sodium and Absolute Alcohol. HERVÉ DE POMMEREAU (*Bull. Soc. chim.*, 1922, 33, 689—697; cf. A., 1921, i, 567; Bouveault and Blanc, A., 1903, i, 673).—As a result of the reduction of ethyl benzoate, benzyl alcohol, benzaldehyde, nitrobenzene, ethyl α -naphthoate and α -naphthylcarbinol in order to study the effect of substituents in the ring on the reaction, the author shows that the benzene ring is easily reduced to hexahydrogenated derivatives when it is directly united to a carboxyl group, and that when that group is esterified the reduction is incomplete, some tetrahydrogenated compounds being produced. On the other hand, reduction of naphthalene derivatives takes place readily, as does that of a primary alcohol group directly attached to the aromatic nucleus. The following have been prepared: *tetrahydrobenzyl alcohol* is a colourless liquid, b. p. $188^{\circ}/760$ mm.; α -naphthyl acetate has b. p. $175^{\circ}/18$ mm.; di- α -naphthyl ether forms small, white crystals, m. p. 118° . H. J. E.

The Decomposition of Proteinogenous Cholines into Alcohols of the Cinnamyl Alcohol Type. P. KARRER and E. HORLACHER (*Helv. Chim. Acta*, 1922, 5, 571—575).—The decomposition of the proteinogenous cholines containing an aromatic nucleus in the β -position to the ammonium group (cf. A., 1921, i, 228, and this vol., i, 813) proceeds with formation of an alcohol of the cinnamyl type and trimethylamine. The course of the reaction is different, therefore, from the decomposition of ordinary choline (Meyer and Hopff, A., 1921, i, 851). Thus phenylalanine-choline gives, by simply shaking in aqueous solution with silver oxide, cinnamyl alcohol, whilst *p*-methoxyphenylalaninecholine gives *p*-methoxycinnamyl alcohol, a pleasant-smelling substance,

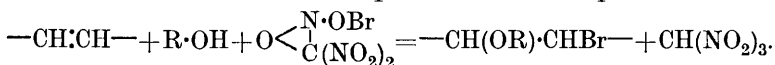
m. p. 73°. The reaction takes place by merely warming the aqueous solution of the choline, the instability of which is probably due to the aromatic nucleus in the β -position to the ammonium group. It is significant that the naturally occurring alcohols of the type, such as cinnamyl alcohol itself, coniferyl alcohol, and syringenin, are all closely related to the naturally occurring amino-acids, from which they may be formed through the cholines. Fresh support is thus given to the hypothesis of choline formation in the plant organism.

E. H. R.

Identity of Xanthosterol with Lupeol. A. J. ULTÉE (*Bull. Jardin Bot. Buitenzorg*, 1922, [iii], 4, 315; cf. Dieterle, this vol., i, 652).—The phytosterol isolated by Dieterle (A., 1920, i, 42) from *Xanthoxylon Budrunga* has been re-obtained, and proves to be identical with lupeol as already suggested by Goodson (A., 1921, i, 488).

Oestling's phytosterol (*Ber. Deut. Pharm. Ges.*, 1914, 24, 308) from *Fagara xanthoxyloides*, Lam. (*X. senegalense*, DC.) is also lupeol.

Bromotrinitromethane. I. ERICH SCHMIDT, WALTER BARTHOLOMÉ, and ALFRED LÜBKE (*Ber.*, 1922, 55, [B], 2099—2107).—The bromine atom can be introduced into the aromatic nucleus of certain compounds, for example, dimethyl-*o*(or *m*)-toluidine by the action of an alcoholic solution of bromotrinitromethane. Addition of alkyl hypobromite at the olefinic bond is effected by the action of bromotrinitromethane on a series of unsaturated substances in the presence of the requisite alcohol:



In general, the solution of one molecular proportion of bromotrinitromethane is added gradually to a molecular proportion of the unsaturated compound dissolved in the same solvent; the mixture is preserved in ice water or if necessary heated under a reflux condenser until the smell of bromotrinitromethane disappears, after which it is poured into water and extracted with ether after addition of saturated sodium chloride solution. The ethereal solution is subjected to protracted mechanical agitation with sodium hydroxide solution (15%) and twice subsequently with potassium hydroxide solution (15%), to which ultimately a yellow colour must not be imparted; it is then washed with water, and dried over sodium sulphate, after which the desired product is isolated by distillation under diminished pressure. (A second method of operating in the presence of pyridine will be described subsequently.)

The following compounds have been prepared. In so far as they have been described previously their constitution is known, but otherwise more attention has been directed to the applicability of the reaction than to the precise constitution of the products: β -Bromo- α -methoxypropylbenzene (from propenylbenzene), a colourless liquid, b. p. 110—111°/12 mm. β -Bromo- α -ethoxypropylbenzene,

a colourless liquid, b. p. 119—120°/13 mm. *o*-Methoxy- β -bromo- α -methoxypropylbenzene, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CHBrMe}$, an almost colourless liquid, b. p. 100°/0.2 mm. *o*-Methoxy- β -bromo- α -allyloxypropylbenzene, $\text{OMe}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{O}\cdot\text{C}_3\text{H}_5)\cdot\text{CHBrMe}$, a pale yellow liquid, b. p. 113°/0.33 mm. *p*-Methoxy- β -bromo- α -methoxypropylbenzene, an almost colourless liquid, b. p. 105°/0.21 mm.; 108°/0.31 mm. *p*-Methoxy- β -bromo- α -ethoxypropylbenzene, b. p. 110—112°/0.21 mm. *p*-Methoxy- β -bromo- α -allyloxypropylbenzene, a pale yellow liquid, b. p. 126—127°/0.3 mm. 3:4-Methylenedioxy- β -bromo- α -methoxypropylbenzene, a pale yellow liquid, b. p. 108—110°/0.14 mm. 3:4-Methylenedioxy- β -bromo- α -ethoxypropylbenzene, b. p. 119—120°/0.2 mm. (if light petroleum or glacial acetic acid is used as solvent, an unstable additive *product*, $\text{C}_{11}\text{H}_{10}\text{O}_8\text{N}_3\text{Br}$, of isosafrole and bromotrinitromethane is obtained; it has decomp. 100—101°). *Bromocyclohexyl methyl ether* (from cyclohexene), a colourless liquid, b. p. 78—79°/12 mm.; n_D^{18} 1.4910, d_4^{18} 1.3400. *Bromocyclohexyl ethyl ether*, a colourless liquid, b. p. 84—85°/10 mm., n_D^{18} 1.4818, d_4^{18} 1.2751. *Bromocyclohexyl allyl ether*, a colourless liquid, b. p. 100—101°/11 mm. *Bromomethoxy-p-menthan-8-ol* (from terpineol), an almost colourless liquid, b. p. 110—111°/0.42 mm. *Dibromodimethoxy-p-menthane* (from *l*-limonene), an almost colourless liquid, b. p. 136°/0.3 mm. *Methyl bromomethoxystearate*, b. p. 192°/0.37 mm. *Bromomethoxytetrahydronaphthalene* (from Δ^1 -dihydronaphthalene), a colourless liquid, b. p. 101°/0.31 mm. *Bromomethoxytetrahydronaphthalene* (from Δ^2 -dihydronaphthalene), a colourless liquid, b. p. 115°/0.8 mm. H. W.

Reaction of Carbonyl Chloride with Benzene and *m*-Xylene in the Presence of Aluminium Chloride. ROBERT E. WILSON and EVERETT W. FULLER (*J. Ind. Eng. Chem.*, 1922, **14**, 406—409).—Carbonyl chloride reacts with benzene in the presence of anhydrous aluminium chloride, yielding benzoyl chloride and benzophenone, but no trace of anthraquinone is produced. The reaction takes place in two stages with the intermediate formation of the compound $\text{C}_6\text{H}_5\cdot\text{COCl}\cdot\text{AlCl}_3$, which can be hydrolysed to give benzoic acid; this compound then reacts rapidly with a further quantity of benzene, and the final product is almost entirely benzophenone, irrespective of change of temperature, method of mixing, ratio of reactive substances, etc. When carbon disulphide is used as a diluent a large proportion of the product can be obtained as benzoic acid; this seems to be due to the slight solubility of the intermediate compound in the carbon disulphide, so that it is removed before it can react with more benzene. Reaction between carbonyl chloride and *m*-xylene yields a dixylyl ketone having at least two of the methyl groups in the ortho-position to the carbonyl group; attempts to convert this ketone by oxidation into a derivative of anthraquinone have, so far, not been successful.

W. P. S.

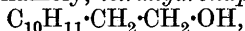
Preparation of *n*-Butyl *p*-Aminobenzoate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (Swiss Pat. 90590; from *Chem. Zentr.*, 1922, ii, 202).—*p*-Aminobenzoic acid is esterified with

n-butyl alcohol, for example in the presence of hydrogen chloride, and heated. On cooling, the *hydrochloride* of the ester crystallises. By addition of alkali hydroxide to an aqueous solution, the free *n*-butyl *p*-aminobenzoate is precipitated. It has m. p. 59°, b. p. 173—174°/8 mm. (cf. A., 1921, i, 26). G. W. R.

γ -Dibutylaminopropyl *p*-Aminobenzoate. O. KAMM and R. ADAMS (Can. Pat. 217486).—*p*-Nitrobenzoyl chloride dissolved in benzene and γ -dibutylaminopropyl alcohol are heated and the reaction mixture is shaken with excess of tin and hydrochloric acid at a temperature maintained at 50°. The mixture is diluted and the tin removed with hydrogen sulphide. When the aqueous layer is made alkaline, γ -dibutylaminopropyl *p*-aminobenzoate (a local anæsthetic) is precipitated. CHEMICAL ABSTRACTS.

Preparation of Benzyl *p*-Aminobenzoate. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 90587; from *Chem. Zentr.*, 1922, ii, 202).—Compounds containing a *p*-nitrobenzoyl group are benzylated and the resulting benzyl *p*-nitrobenzoate is reduced. For example, dry hydrogen chloride is passed into a benzyl alcoholic solution of *p*-nitrobenzoic acid, or *p*-nitrobenzoates are warmed with benzyl chloride in aqueous solution, or *p*-nitrobenzoyl chloride is heated with benzyl alcohol under a reflux condenser. Benzyl *p*-nitrobenzoate is crystalline. It gives, by reduction with iron and dilute hydrochloric acid, benzyl *p*-aminobenzoate (cf. Shonle and Row, A., 1921, i, 341), which forms white needles, m. p. 90°, and acts as a local anæsthetic. G. W. R.

The Reduction of Ethyl α -Naphthylacetate and the α -Naphthylethanols by Sodium and Absolute Alcohol. HERVÉ DE POMMEREAU (*Compt. rend.*, 1922, 175, 105—106).—Ethyl α -naphthylacetate on reduction with sodium in absolute alcohol yielded two products, namely, *tetrahydronaphthylethanol*,



b. p. 187°/25 mm., giving a *phenylurethane*, m. p. 91°, and *ethyl tetrahydronaphthylacetate*, from which the free acid, m. p. 131°, was prepared. Primary α -naphthylethanol, when similarly reduced, gave a *dihydronaphthylethanol*, $\text{C}_{10}\text{H}_9\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$, b. p. 190°/22 mm., giving a *phenylurethane*, m. p. 106°, and secondary α -naphthylethanol gave *ethyl dihydronaphthalene*, b. p. 240°/760 mm. W. G.

Fission of $\alpha\alpha$ -Diphenylethyl- β -urethane. A. SIEGLITZ (*Ber.*, 1922, 55, [B], 2040—2042).—The unexpected, direct conversion of fluorenyl-9-methylurethane into dibenzofulvene (Sieglitz and Jassoy, this vol., i, 820) has led the author to investigate the behaviour of the closely similar $\alpha\alpha$ -diphenylethyl- β -urethane under analogous conditions. This substance gives the corresponding amine in the usual manner, the unsaturated hydrocarbon not appearing to be produced.

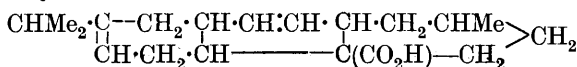
[With HANS SPITZER.]—Ethyl $\beta\beta$ -diphenylpropionate is converted by hydrazine hydrate into the corresponding *hydrazide*, colourless, lustrous leaflets, m. p. 127—128° (*anisylidene* compound,

colourless needles, m. p. 196°) which is transformed further into the *azide*. The latter is converted by boiling absolute ethyl alcohol into $\alpha\alpha$ -diphenylethyl- β -urethane, $\text{CHPh}_2\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$, colourless needles, m. p. 69° (if aqueous alcohol is used *diphenylethylcarbamide*, slender, colourless needles, m. p. 198°, is also obtained). The urethane is decomposed by distillation with calcium oxide under 12 mm. pressure in an atmosphere of hydrogen into $\beta\beta$ -diphenylethylamine (hydrochloride, m. p. 253°; *picrate*, m. p. 212–213°); the presence of the hydrocarbon, $\text{CPh}_2\cdot\text{CH}_2$, in the non-basic portion of the distillate could not be established. H. W.

Effect of Attached Groups on the Ease of Formation of the *cyclopentane* Ring. JUAN PEDIGE CHARLES CHANDRASENA and CHRISTOPHER KELK INGOLD (T., 1922, 121, 1552–1555).

A New Example of Hemihedral Forms not Conforming to the Sign of the Optical Activity. A. DUFFOUR (*Compt. rend.*, 1922, 175, 109–112).—The author records the case of a sample of abietic acid recently isolated by Dupont from the Aleppo pine (cf. A., 1921, i, 510) the goniometric measurements of which conform with those of an abietic acid obtained by Mach from rosin. The specimen was, however, an enantiomorphic form, but did not show opposite optical activity. W. G.

Abietic Acid. A. MADINAVEITIA (*Anal. Fís. Quím.*, 1922, 20, 183–189; cf. Sureda Blanes, A., 1915, i, 493).—The author's analyses lend support to the formula $\text{C}_{19}\text{H}_{28}\text{O}_2$ for abietic acid. The nucleus of the molecule must be retene, since it is obtained by the catalytic dehydrogenation of abietene. The result of hydrogenation of the ethylene linkings by the Willstätter method renders it probable that the carboxyl group in abietic acid is linked to a tertiary carbon atom, and the formula



is suggested.

G. W. R.

Higher Terpene Compounds. V. Conversion of Abietic Acid into Methylretene. L. RUZICKA and JULES MEYER (*Helv. Chim. Acta*, 1922, 5, 581–593).—When abietic acid, $\text{C}_{20}\text{H}_{30}\text{O}_2$, is heated with sulphur it is converted into retene (1-methyl-7-isopropylphenanthrene), $\text{C}_{18}\text{H}_{18}$, dehydrogenation being accompanied by loss of a carboxyl group and another carbon atom. Abietic acid is probably therefore a methyldecahydroretenecarboxylic acid, and experiments have been made with the object of determining the orientation of the two groups removable by sulphur. The position of the double linking in abietic acid is unknown, but it is found that dihydroabietic acid also gives retene when heated with sulphur. This practically excludes the possibility of the grouping $\text{C} > \text{CH}=\text{CH}_2$ in abietic acid, the alternative

combination for a mobile carbon atom being $\begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array} \text{C}-\text{CH}_3$. The

methyl ester of abietic acid and the corresponding alcohol, abietinol, likewise give retene when heated with sulphur. When abietinol is treated with phosphorus pentachloride, a new hydrocarbon, $\text{C}_{20}\text{H}_{30}$, which may be called methylabietin, is obtained which, when dehydrogenated with sulphur, gives a methylretene. Since the methyl group which has replaced the carboxyl group in abietic acid is no longer removable, it is argued that the carboxyl group is not attached to a tertiary carbon atom of the phenanthrene nucleus. Methylretene is oxidised by chromic acid to methylretenequinone. Assuming that the abietic acid skeleton consists, like all known mono- and sesqui-terpene compounds, of isoprene residues (cf. this vol., i, 560, 562), and taking into account the above facts, the only possible positions for the carboxyl and methyl groups under discussion in the phenanthrene nucleus of abietic acid are 2 : 12, 3 : 11, and 4 : 11.

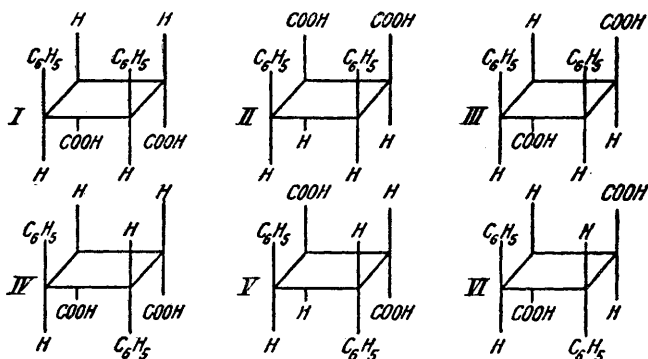
Abietinol, $\text{C}_{20}\text{H}_{32}\text{O}$, prepared by reduction of methyl abietate with sodium and alcohol, has b. p. $169-172^\circ/0.2$ mm., d_4^{25} 1.0305, n_D^{25} 1.5487. *Dihydroabietinol*, by reduction of abietinol with hydrogen in presence of platinum black, forms a colourless, viscous mass, b. p. $169-171^\circ/0.5$ mm. *Methylabietin*, $\text{C}_{20}\text{H}_{30}$, is a viscous, colourless oil, b. p. $147-152^\circ/0.8$ mm., d_4^{25} 0.9750, n_D^{25} 1.54435, $\alpha_D + 56.2^\circ$. It does not form a picrate. Methylretene, $\text{C}_{19}\text{H}_{20}$, forms colourless leaflets, m. p. 79° , and gives an unstable picrate. *Methylretenequinone*, $\text{C}_{19}\text{H}_{18}\text{O}_2$, crystallises in red leaflets, m. p. 147° , and with *o*-phenylenediamine it gives a *quinoxaline*, m. p. 165° . *Retene styphnate* has m. p. 142° . E. H. R.

Preparation of *o*-, *m*-, and *p*-Nitrophenoxyacetic Acids and Various Nitrotoloxycetic Acids and their Derivatives. THOMAS HOSKER MINTON and HENRY STEPHEN (T., 1922, **121**, 1591—1598).

The Nitro- and Amino-derivatives of *o*- and *p*-Methoxybenzoic Acids and of α - and β -Methoxynaphthoic Acids. VICTOR FROELICHER and JULIUS BEREND COHEN (T., 1922, **121**, 1652—1660).

Configuration of the Truxinic and Truxillic Acids. VI. R. STOERMER and F. BACHÉR (*Ber.*, 1922, **55**, [B], 1860—1882).—Of the six theoretically possible truxinic acids, four (β -, δ -, ζ -, and neo-) have actually been isolated. The constitution IV has definitely been assigned to ζ -truxinic acid, since this is the only *cis*-acid of the series which is resolvable into its optical antipodes. The β -acid must have the configuration I or II, of which I is the more probable. Both formulæ represent meso-forms and, up to the present, it has not been found possible to resolve the β -acid by alkaloids. The configurations III, V, and VI are available for neo- and δ -truxinic acids, all of which represent resolvable racemic forms. Both acids have now been resolved into their

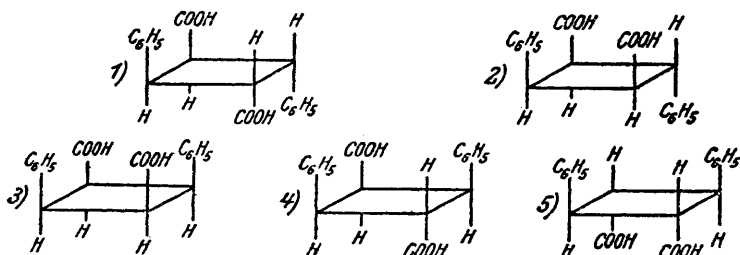
optical antipodes. The δ -acid is closely related to the ζ -acid (conversion of δ -acid into the anhydride or imide of ζ -acid; trans-



formation of ζ - into δ -acid in the presence of pyridine), so that the phenyl groups must be in the trans-position to one another in it, thus limiting the choice of the configuration to V or VI. Similarly, neotruxinic acid is related closely to the β -acid, and for it, as a *trans*-acid, only the configuration III is available. The same configurations have been assigned to β -, δ -, and ζ -truxinic acids from considerations based on their formation by the polymerisation of the cinnamic acids on exposure to light. In the authors' opinion, the coincidence is accidental, and de Jong's arguments are not founded on a sufficiently firm theoretical basis.

It is remarkable that δ - and neo-truxinic acids occur in the optically inactive forms in the crude mixture of acids in which they are united to the optically active ecgonine. The technical treatment of the products is not such as would be likely to cause racemisation of the (actually very stable) optically active acids.

In a modified form, the possibility of fission into optically active components can be utilised in elucidating the configuration of the truxillic acids, for which the following formulæ are possible:



All these are forms which cannot be resolved into optical antipodes. If dissimilarity is introduced into the carboxyl groups (by conversion of one of them into the ester, amide, anilide, etc.), the forms 1 and 2 become racemic and resolvable, whereas 3, 4, and 5 remain non-resolvable. α - and γ -Truxillic acid anilides

have actually been resolved into their active forms, and therefore must have the configurations 1 and 2. To the γ -acid, which alone yields its proper, stable anhydride, the constitution 2 must be assigned, thus leaving constitution 1 for the α -acid.

Since ϵ -truxillic acid is converted by magnesium phenyl bromide into a ditertiary alcohol, $\text{OH}\cdot\text{CPh}_2\cdot\text{C}_4\text{H}_4\text{Ph}_2\cdot\text{CPh}_2\cdot\text{OH}$, which is readily converted into an oxide and by hydrogen bromide into a dibromide which can also be formed from the oxide, it is probable that it is a *cis*-form and not, as previously assumed, a *trans*-acid.

The theoretical portion concludes with a lengthy reply to de Jong (this vol., i, 339) with regard to the nomenclature of the truxillic and truxinic acids.

A more convenient process for the conversion of β - into neotruxinic acid than that used previously consists in heating the β -acid with concentrated ammonia solution at 170 – 190° , with water at 215° , or alone at 215° . 2.1835 Grams of the acid are soluble in 100 grams of glacial acetic acid at 20° . It is converted quantitatively by molten potassium hydroxide into the δ -acid and by acetic anhydride at 160° into the β -acid. The latter is conveniently identified as the amidic acid, m. p. 194° . The *chloride*, m. p. 83 – 84° , and *dianilide*, m. p. 226 – 227° , of the neo-acid are described. Neotruxinic acid can be resolved by cinchonine in alcoholic solution; the alkaloidal salt of the *d*-acid [m. p. 216 – 217° (decomp.)] being the more sparingly soluble. *d*-Neotruxinic acid has m. p. 236 – 237° , $[\alpha]_D^{20} + 52.63^\circ$ in acetone. *l*-Neotruxinic acid, m. p. 236 – 237° , $[\alpha]_D^{20} - 53.95^\circ$ in acetone is obtained by treating the acid residues from the resolution of the *r*-acid by cinchonine with quinine in alcoholic solution; *quinine l*-neotruxinate has m. p. 138° . The following derivatives of *d*-neotruxinic acid are described: *chloride*, m. p. 103 – 104° , $[\alpha]_D^{15} - 15.98^\circ$ in acetone solution; *dianilide*, m. p. 226 – 227° , $[\alpha]_D^{15} - 53.23^\circ$ in acetone; *amide*, m. p. 260 – 261° ; *ethyl ester*, slender needles, m. p. 53° , $[\alpha]_D^{20} + 18.33^\circ$ in acetone; *methyl ester*, m. p. 100° , $[\alpha]_D^{20} + 48.11^\circ$ in acetone. *l*-Neotruxinic acid yields the following derivatives: *methyl ester*, m. p. 100 – 101° , $[\alpha]_D^{20} - 51.99^\circ$ in acetone; *ethylamide*, m. p. 175° , $[\alpha]_D^{15} + 30.30^\circ$ in acetone; *methylamide*, slender, matted needles, m. p. 126 – 127° .

Ammonium δ -truxinate, long, transparent prisms, m. p. 206 – 208° (decomp.) is converted at 215° into ζ -truxinimide, m. p. 168° , which is further identified by its transformation into the ζ -amidic acid, m. p. 222° ; the latter is re-converted by alcoholic potassium hydroxide into the δ -acid. δ -Truxinic acid can be resolved by means of cinchonine in alcoholic solution; *cinchonine l*- δ -truxinate has m. p. 192° . *l*- δ -Truxinic acid, slender needles, m. p. 158 – 159° , $[\alpha]_D^{20} - 8.3^\circ$ in acetone, dissolves in glacial acetic acid to the extent of 17.89 parts in 100 at 20° , whereas only 10.38 parts of the *r*-acid dissolve under the same conditions. *d*- δ -Truxinic acid is obtained from the residues of the above resolution by means of quinine. *Quinine d*- δ -truxinate, m. p. 135° (decomp.), is described. *d*- δ -Truxinic acid, m. p. 157 – 158° , has $[\alpha]_D^{20} + 8.06^\circ$ in acetone. The following derivatives of *dl*- δ -truxinic acid are described: *chloride*,

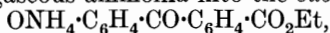
m. p. 78° ; *diamide*, colourless crystals, m. p. 224° ; *dianilide*, m. p. 283° ; δ -*truxinalic acid*, m. p. 225° . 1- δ -*Truxindiamide* has m. p. 206° , $[\alpha]_D^{25} + 33.5^{\circ}$ in acetone.

ζ -*Truxinic acid* is converted by pyridine and water at 195 – 205° into δ -*truxinic acid*, m. p. 175° . H. W.

***o*-4'-Hydroxybenzoylbenzoic Acid and some of its Derivatives.** W. K. ORNDORFF and LOUISE KELLEY (*J. Amer. Chem. Soc.*, 1922, **44**, 1518–1527).—*o*-4'-Hydroxybenzoylbenzoic acid, which in the free condition probably has the lactonic constitution, $\text{HO}\cdot\text{C}_6\text{H}_4\cdot\underset{\text{O} \text{---} \text{CO}}{\underset{|}{\text{C}}}(\text{OH})\cdot\text{C}_6\text{H}_4$, crystallises in colourless plates, m. p. 213°

(gas evolution). One hundred c.c. of water, ethyl alcohol (95%), methyl alcohol, and benzene dissolve, respectively, 0.0632, 36.00, 11.58, and 0.0121 grams of the acid at 21° . The acid exhibits an abnormal absorptive power towards dry gaseous ammonia, of which it takes up 2.5 molecular proportions; when placed in an evacuated desiccator over concentrated sulphuric acid, the product loses ammonia slowly and reaches a constant weight when only one molecular proportion of the gas remains. The *ammonium salt*, *sodium salt*, $\text{C}_{14}\text{H}_9\text{O}_4\text{Na}$, colourless needles (also +1EtOH), the *barium salt*, large, six-sided, greenish-yellow crystals, m. p. 259° (decomp.) after softening at 245° (dihydrate and anhydrous), *calcium salt*, small, pale yellow, glistening needles, m. p. 262 – 263° (decomp.) after softening at 252° (dihydrate and anhydrous), and *zinc salt*, colourless crystals, m. p. 80 – 81° (anhydrous and +7.5 H_2O), are described. The *diacetate*, $\text{OAc}\cdot\text{C}_6\text{H}_4\cdot\underset{\text{O} \text{---} \text{CO}}{\underset{|}{\text{C}}}(\text{OAc})\cdot\text{C}_6\text{H}_4$,

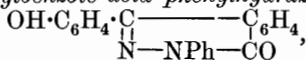
prepared by boiling the acid with acetic anhydride and sodium acetate, has m. p. 162 – 163° . *Ethyl o*-4'-hydroxybenzoylbenzoate, $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{Et}$, colourless needles, m. p. 114 – 115° , is converted by dry gaseous ammonia into the substance,



which, however, is not stable, since it loses a part of its ammonia when preserved in a vacuum over sulphuric acid. *Methyl o*-4'-hydroxybenzoylbenzoate, triclinic crystals, m. p. 149 – 150° , similarly absorbs between 1 and 1.5 molecular proportions of ammonia, forming a greenish-yellow semi-liquid mass.

o-3' : 5'-*Dibromo-4'-hydroxybenzoylbenzoic acid*, colourless crystals, m. p. 250° , is prepared by the bromination of the parent acid in glacial acetic acid solution or (m. p. 246 – 248°) by the action of boiling dilute sulphuric acid on tetrabromophenolphthaleinoxime.

o-4'-Hydroxybenzoylbenzoic acid *phenylhydrazone*,



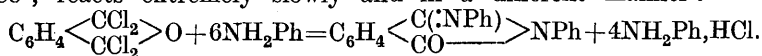
small, colourless needles, m. p. 267 – 268° , is obtained by heating the acid with an excess of phenylhydrazine at 160° .

Hydroxyphenylphthalide (cf. Bistrzycki and Oehlert, A., 1894, i, 600; Meyer, A., 1899, i, 707) crystallises in small, colourless needles, m. p. 164 – 165° ; the corresponding acetate, small, colour-

less needles, which probably belong to the triclinic system, has m. p. 125—126°.

o-4'-Methoxybenzoylbenzoic acid is prepared from phthalic anhydride and anisole (m. p. 141·5—142°) or from *o*-4'-hydroxybenzoylbenzoic acid, sodium hydroxide, and methyl sulphate (m. p. 144—145°) (cf. Nourrisson, A., 1886, 1029; Meyer and Turnau, A., 1909, i, 710). The acid absorbs one and a half molecular proportions of dry ammonia gas; the product when preserved in a vacuum over concentrated sulphuric acid ultimately retains one molecular proportion. The *sodium* salt, small, colourless needles, and the *potassium* salt, long, colourless needles (+0·5EtOH), are described. Methyl *o*-4'-methoxybenzoylbenzoate, prepared by the action of sodium hydroxide solution and methyl sulphate on *o*-4'-hydroxybenzoylbenzoic acid, has m. p. 80—81·5° (cf. Meyer and Turnau, *loc. cit.*). H. W.

The Constitution and Tautomeric Equilibrium of the Two Phthalic Acid Tetrachlorides. ERWIN OTT (*Ber.*, 1922, 55, [B], 2108—2125).—The action of phosphorus pentachloride on ordinary phthalyl chloride at a high temperature has been shown by Vongerichten (A., 1880, 473) to lead to the formation of two crystalline chlorides, $C_6H_4OCl_4$, which he designated phthalic acid tetrachlorides; the formulæ $C_6H_4<\begin{smallmatrix} Cl_2 \\ Cl_2 \end{smallmatrix}>O$ and $CCl_3\cdot C_6H_4\cdot COCl$ were proposed for the compounds, but these were not allocated to the individual substances. Subsequently, Claus and Hoch (A., 1886, 705) could only isolate the isomeride of higher melting point (88°) from phosphorus pentachloride and phthalic anhydride; a similar result was obtained by Anschütz and his pupils in the investigation of the action of phosphorus pentachloride on phthalyl chloride or phthalide. On account of its behaviour in the presence of aluminium chloride and by reason of the intermediate products from phosphorus pentachloride and phthalide, the constitution $CCl_3\cdot C_6H_4\cdot COCl$ has been assigned to the variety, m. p. 88°, by Haller and Guyot (A., 1895, i, 376) and by Anschütz, respectively. This is now shown to be incorrect. The isomeride of lower melting point reacts instantaneously with aniline in suitably concentrated benzene solution with separation of aniline hydrochloride and benzotrichloride-*o*-carboxyanilide: $(CCl_3\cdot C_6H_4\cdot COCl + 2PhNH_2 = CCl_3\cdot C_6H_4\cdot CO\cdot NHPh + NH_2Ph\cdot HCl)$, whereas the substance, m. p. 88°, reacts extremely slowly and in a different manner:



The difference in the rates of reaction is so great that the process can be utilised for the estimation of the chloride of lower melting point in mixtures containing the other isomeride also. For this purpose, the almost quantitatively precipitated mixture of aniline hydrochloride and benzotrichloride-*o*-carboxyanilide is collected, washed with benzene and ether, and weighed; the aniline hydrochloride is removed by water and the residual anilide again weighed.

Towards methyl alcohol the two chlorides do not exhibit such

marked difference in their behaviour as towards aniline. The isomeride of lower melting point reacts quantitatively in *N*/2-solution in about six hours, in accordance with the equation $\text{CCl}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{COCl} + \text{MeOH} = \text{CCl}_3 \cdot \text{C}_6\text{H}_4 \cdot \text{CO}_2\text{Me} + \text{HCl}$. Under similar conditions, the reaction with the lactone is complete in about twenty-four hours according to the scheme $\text{C}_6\text{H}_4 \begin{smallmatrix} < \text{CCl}_2 \\ \text{CCl}_2 > \end{smallmatrix} \text{O} + 4\text{MeOH} = \text{C}_6\text{H}_4(\text{CO}_2\text{Me})_2 + \text{OMe}_2 + 4\text{HCl}$.

Confirmation of the constitutions assigned to the respective chlorides is found in their absorption spectra in the ultra-violet.

Benzotrichloride-*o*-carboxyl chloride reacts much less readily with aniline or methyl alcohol than any 1:2-dicarboxyl chloride hitherto investigated. The behaviour of benzoyl, toluoyl, and mono- and di-chlorotoluoyl chlorides in this respect have therefore been subjected to a comparative examination. Benzoyl chloride reacts far less readily than an aliphatic acid chloride or a true 1:2-dicarboxyl chloride (*s-o*-phthalyl chloride). The presence of a methyl group in the ortho-position causes a somewhat unexpected and considerable increase in reactivity. The introduction of one or two chlorine atoms into the methyl radicle does not diminish the reactivity, which, however, falls far below that of benzoyl chloride when a third chlorine atom is introduced.

A tautomeric equilibrium between the two chlorides tends to become established if one of them is molten. The position of the equilibrium is a function of the temperature; it has been measured at 120°, 220°, and 286·5°. It is thus established that the two forms are mutually interconvertible by alteration of temperature, and that the lactonic cannot be converted into the acyclic form to an extent greater than 80%. The velocity of establishment of equilibrium is readily measurable at the high temperatures and very slow at lower temperatures, and the wandering of the heavier chlorine atom appears therefore to be a much slower process than that of the hydrogen atom. The nature of the equilibrium curve indicates that the acyclic chloride is incapable of existence at temperatures below 70°. This is confirmed to some extent by the observation that, whereas the solid, crystalline material appears stable, the molten substance gradually undergoes transformation at 57·5°. The rate of conversion of the acyclic into the lactonic variety is, however, very small and proceeds much more slowly than the reverse process (the latter is probably subject to catalytic influences).

The two chlorides are prepared in the following manner. Phthalide is heated with phosphorus pentachloride at 100° until reaction is complete and the phosphorus trichloride and phosphoryl chloride are removed by distillation. The residue is fractionated under 15 mm. pressure. The chloride of higher melting point solidifies from the distillates and is removed. The liquid portions of the distillates and the residues from the crystallisation of the above chloride are united and distilled fractionally in a high vacuum. The initial fractions contain the lactonic chloride, whereas those of highest boiling point are composed of almost

homogeneous acyclic chloride. Benzotrichloride-*o*-carboxyl chloride has m. p. 43° (Vongerichten 47°), b. p. (not definite) $115\text{--}120^{\circ}/0.2$ mm., whereas the lactonic form has m. p. $85\text{--}86^{\circ}$ (Vongerichten 88°), b. p. $90\text{--}105^{\circ}/0.2$ mm. Methyl benzotrichloride-*o*-carboxylate has b. p. 125° (corr.)/1 mm. Benzotrichloride-*o*-carboxyanilide has m. p. $165\text{--}170^{\circ}$ (decomp.). H. W.

Preparation of Phthalimide. BRITISH DYESTUFFS CORPORATION LTD., ARTHUR GEORGE GREEN, and STANLEY JOSEPH GREEN (Brit. Pat. 183044).— α -Nitronaphthalene is directly oxidised by air or oxygen in the presence of a suitable catalyst such as pumice impregnated with an oxide of molybdenum or vanadium and heated at $300\text{--}400^{\circ}$, the main product of the oxidation being phthalimide in a yield of upwards of 50% of that theoretically possible. The operation may be carried out by passing a large excess of hot air over nitronaphthalene heated at $120\text{--}130^{\circ}$, and thence through a heated iron tube containing the catalyst. Phthalimide condenses in small, colourless needles in a large, well cooled receiver, and a small quantity of phthalic anhydride which is formed, being more volatile, may be collected in a second receiver. G. F. M.

Conditions of Formation of Rings attached to the *o*-, *m*-, and *p*-Positions of the Benzene Nucleus. I. The Action of Sodium on *o*-Phenylenediacetic Ester. WILLIAM HENRY PERKIN, jun., and ALAN FRANCIS TITLEY (T., 1922, 121, 1562—1571).

Chemistry of Polycyclic Structures in Relation to their Homocyclic Unsaturated Isomerides. III. Intra-annular Tautomerism of α -Campholytic Acid. JUAN PEDIGE CHARLES CHANDRASENA, CHRISTOPHER KELK INGOLD, and JOCELYN FIELD THORPE (T., 1922, 121, 1542—1551).

The Dicarboxylic Acid which is Formed by Heating 1 : 5-Dihydroxynaphthalene with Potassium Hydrogen Carbonate under Pressure. FRANZ HEMMELMAYR (*Monatsh.*, 1922, 43, 61—65).—This acid (cf. A., 1917, i, 227) is probably 1 : 5-dihydroxynaphthalene-2 : 6-dicarboxylic acid, because on nitration it gives a dinitro-derivative in which the nitro-groups probably occupy α -positions. The substance forms yellow crystals which decompose on heating alone, with water, or with alkalis, and gives characteristic barium salts, $C_{12}H_4O_{10}N_2Ba \cdot 5H_2O$, and $C_{12}H_4O_{10}N_2Ba \cdot 2.5H_2O$. Bromine displaces both carboxyl groups and one nitro-group, giving a bromonitro-1 : 5-dihydroxynaphthalene, whilst acetic anhydride and sodium acetate yield a dinitro-1 : 5-diacetoxynaphthalene, m. p. 205° . Acetic anhydride and sodium acetate convert 1 : 5-dihydroxynaphthalenedicarboxylic acid into 1 : 5-diacetoxynaphthalene, m. p. $158\text{--}159^{\circ}$. C. K. I.

Formation and Stability of *spiro*-Compounds. VIII. The Dieckmann-Komppa Reaction. FRANK DICKENS, GEORGE ARMAND ROBERT KON, and JOCELYN FIELD THORPE (T., 1922, 121, 1496—1506).

Mellitic Acid, Pyromellitic Acid, and their Production from Carbon by Oxidation. ERNST PHILIPPI (*Annalen*, 1922, 428, 286—287).—A general introduction to the accompanying papers (cf. following abstracts).
C. K. I.

Mellitic Acid, Pyromellitic Acid, and their Production from Carbon by Oxidation. I. Oxidation of Carbon by Nitric Acid. ERNST PHILIPPI and GERTRUD RIE (*Annalen*, 1922, 428, 287—295).—A detailed study of this reaction and of the different methods which have been proposed for purifying the product. The preparation of pure mellitic acid by this means is a difficult matter, and the chief value of the method lies in the fact that pyromellitic acid can be obtained in 30% yield from the crude product by heating with sulphuric acid and sodium hydrogen sulphate.
C. K. I.

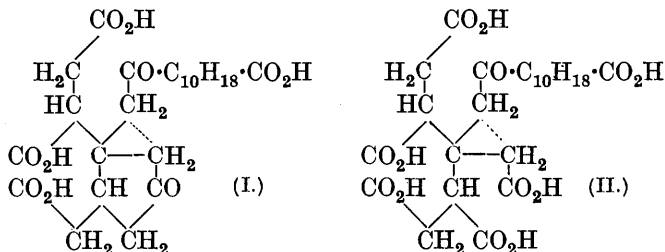
Mellitic Acid, Pyromellitic Acid, and their Production from Carbon by Oxidation. II. Oxidation of Carbon by Sulphuric Acid. ERNST PHILIPPI and RICHARD THELEN (*Annalen*, 1922, 428, 296—300).—Directions are given for the preparation of pyromellitic acid from wood charcoal by oxidation with sulphuric acid in the presence of mercury as catalyst. The yield is 6—7% of the weight of charcoal used [cf. *J. Soc. Chem. Ind.*, 1922, Sept.].
C. K. I.

Mellitic Acid, Pyromellitic Acid, and their Production from Carbon by Oxidation. III. Synthesis of Pyromellitic Acid from Commercial Xylene. ERNST PHILIPPI, REINHARD SEKA, and NORBERT FROESCHL (*Annalen*, 1922, 428, 300—306).—4-Ethyl-*m*-xylene, which is obtained by acetylating *m*-xylene by the Friedel-Crafts' method and reducing the product, gives 6-acetyl-4-ethyl-*m*-xylene, m. p. 27°, on treatment with acetyl chloride and aluminium chloride. The reduction product, 4:6-diethyl-*m*-xylene, b. p. 105°/15 mm., yields pyromellitic acid on oxidation with nitric acid. *m*-Xylene may be replaced by commercial xylene in this series of processes.
C. K. I.

Mellitic Acid, Pyromellitic Acid, and their Production from Carbon by Oxidation. IV. Synthesis of Substituted Pyromellitic Acids. ERNST PHILIPPI, REINHARD SEKA, and LILLY ROBINSON (*Annalen*, 1922, 428, 306—313).—A. Nitropyromellitic acids. Pure nitration products of 5-acetyl-2-ethyl-*p*-xylene could not be isolated, but by nitration, followed by oxidation by nitric acid, mono- and di-nitropyromellitic acids were obtained. Nitration of 2:5-diethyl-*p*-xylene gives a small yield of its 3:6-dinitro-derivative, m. p. about 100°, which can be oxidised to dinitropyromellitic acid.

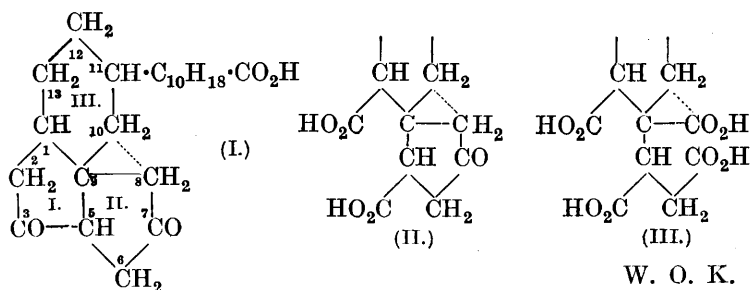
B. Bromopyromellitic acids. 2:5-Diethyl-*p*-xylene can be brominated by sulphur bromide and nitric acid. The product, 3:6-dibromo-2:5-diethyl-*p*-xylene, m. p. 81—82°, on oxidation by nitric acid (*d* 1.35) at 140°, gives 3:6-dibromo-*p*-xylylene-2:5-diacetic acid, m. p. about 180° (decomp.), 3:6-dibromo-*p*-xylylene-2:5-diglyoxylic acid, m. p. 232°, and dibromopyromellitic acid, decomp. above 170°.
C. K. I.

Bile Acids. XII. Ciloidanic Acid. HEINRICH WIELAND and OTTO SCHLICHTING (*Z. physiol. Chem.*, 1922, **120**, 227—231).—Cilidianic acid (I), although said to be very resistant to oxidising



agents (Schenck, A., 1921, i, 179), is attacked by nitric acid to form the expected *ciloidanic acid*, $\text{C}_{24}\text{H}_{34}\text{O}_{13}$, large prisms with a vitreous lustre, m. p. 248°, $[\alpha]_D^{25} + 34.55^\circ$ in alcohol, to which formula (II) is ascribed. W. O. K.

Bile Acids. XIII. The Formula of *iso*Deoxybilianic Acid. A Contribution to Orientation. HEINRICH WIELAND and FRANZ ADICKES (*Z. physiol. Chem.*, 1922, **120**, 232—243; cf. A., 1921, i, 112).—Pyroisodeoxybilianic acid (I), formed from deoxybilianic acid by distillation in a high vacuum (*loc. cit.*), is oxidised by permanganate to a *ketotricarboxylic acid*, $\text{C}_{23}\text{H}_{34}\text{O}_7$, prisms, m. p. 232—233°, $[\alpha]_D^{25} + 114.5^\circ$ in alcohol, which on heating at 270° loses carbon dioxide to only a small extent. To it has been assigned the formula (II). On further oxidation with nitric acid, *norcholoidanic acid*, $\text{C}_{23}\text{H}_{34}\text{O}_{10}$, colourless, fine needles, m. p. 246—247° (decomp.), $[\alpha]_D^{25} + 17.7^\circ$ in alcohol, is formed. It gives off carbon dioxide only slowly at 290° and so is not a derivative of malonic acid. To it has been assigned the formula (III). If the oxygen in ring II of *isodeoxybilianic acid* were attached in position 6 instead of 7, *norcholoidanic acid* could not be other than a derivative of malonic acid. This possibility is therefore excluded. *Norcholoidanic acid* can be obtained directly from *pyroisodeoxybilianic acid* by oxidation with nitric acid. It forms a *dimethyl ester*, $\text{C}_{25}\text{H}_{38}\text{O}_{10} + \text{H}_2\text{O}$, m. p. 118—119° (frothing), voluminous, fine, colourless needles, which on distillation changes into a more stable stereoisomeric form, m. p. 194°.



W. O. K.

Preparation of Piperonaldehyde from isoSafrole by the Action of Ozone. SHŌICHIRO NAGAI (*J. Chem. Ind. Japan*, 1922, 25, 631—652).—When ozonised air containing 2—3·5% ozone is introduced into a solution of isosafrole (10 grams) in a perfectly dry solvent (100—150 grams), such as carbon tetrachloride, tetrachloroethane, chloroform, glacial acetic acid, toluene, or xylene, isosafrole ozonide is easily produced. If two to three times the volume of light petroleum, having about the same boiling point as the solvent, is added, the ozonide produced is precipitated; the preparation can therefore be made continuous by adding isosafrole from time to time. The ozonide is a deep reddish-brown, viscous, oily substance having a characteristic odour; it decomposes spontaneously at the room temperature, and its solution is also decomposed by water or by heating at 40—50°. When the ozonide solution is stirred with excess of 35—36% sodium hydrogen sulphite solution, it is decomposed and piperonaldehyde separates as a crystalline additive product in 85% yield.

K. K.

6-Aminoveratraldehyde and its Derivatives. AUGUSTE RILLIET (*Helv. Chim. Acta*, 1922, 5, 547—552).—The preparation of 6-aminoveratraldehyde was accomplished by the same method as that of 6-aminopiperonaldehyde (A., 1921, i, 567), by the reduction of the condensation product of nitroveratraldehyde with an aromatic amine with subsequent hydrolysis. It was not possible, however, thus to reduce 2-nitroveratraldehyde, probably on account of steric hindrance.

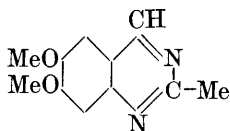
6-Nitroveratrylideneaniline, $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{OMe})_2 \cdot \text{CH} : \text{NPh}$, small, brilliant yellow spangles, m. p. 121°, which redden in air, is obtained by condensing molecular proportions of 6-nitroveratraldehyde and aniline; the corresponding *o*-toluidine compound has m. p. 123°, yellow needles; *p*-toluidine compound, 131°, *p*-anisidine compound, 133°. The yields on reduction of these nitro-compounds with sodium sulphide are from 70—80%. 6-Aminoveratrylideneaniline forms yellow spangles, m. p. 119°; of the others, the *o*-toluidine compound has m. p. 109°, *p*-toluidine compound, 115°, and *p*-anisidine compound, 114°. The hydrolysis of the anilino-compounds is somewhat difficult and the conditions have not yet been satisfactorily studied. 6-Aminoveratraldehyde crystallises from a mixture of benzene and light petroleum in long, yellow needles, m. p. 86°; it is immediately coloured red by acids. The acetyl derivative forms white needles, m. p. 176°; benzoyl derivative, yellow needles, m. p. 170°; oxime, colourless spangles, m. p. 148°; phenylhydrazone is greyish-white, m. p. 190°.

By diazotisation, etc., of the amino-aldehyde the following were prepared: 6-chloroveratraldehyde, white needles, m. p. 144°; 6-bromoveratraldehyde, small needles, m. p. 147°; 6-iodoveratraldehyde, white needles, m. p. 128°.

When condensed with acetone, 6-aminoveratraldehyde gives 6:7-dimethoxyquinaldine, yellow crystals, m. p. 103° (hydrochloride, small, white needles, m. p. 232°, mercurichloride, m. p. 250°, picrate, m. p. 217°, platinichloride, m. p. 224°, methiodide,

m. p. 241°). Condensation with methyl ethyl ketone gives 6:7-dimethoxy-2:3-dimethylquinoline, small, colourless, cubic crystals, m. p. 112° (mercurichloride, m. p. 241°, picrate, m. p. 244°, platinichloride, m. p. 226°, methiodide, m. p. 239°). With acetophenone, 6:7-dimethoxy-2-phenylquinoline is obtained, colourless needles, m. p. 131.5° (hydrochloride, m. p. 229°; mercurichloride, m. p. 231—232°; platinichloride, m. p. 208°, methiodide, m. p. 214°).

By heating 6-acetylaminoveratraldehyde with ammonia in a sealed tube at 100° for five hours, a substance was obtained, probably 6:7-dimethoxy-2-methylquinazoline (annexed formula), m. p. 165° (picrate, m. p. 230°). From 6-benzoylamino-veratraldehyde was obtained in the same way 6:7-dimethoxy-2-phenylquinazoline, long, white, silky needles, m. p. 175°; (picrate, m. p. 190°; platinichloride, m. p. 207°).
E. H. R.



The Influence of Constitution on the Rotatory Power of Optically Active Substances. XIV. Ketonic Derivatives of 1:2:2:3-Tetramethylcyclopentane and 1:2:2-Trimethylcyclopentane-3-carboxylic Acid. H. RUPE and A. JÄGGI (*Annalen*, 1922, 428, 164—188).—A number of optically active ketonic and other compounds are prepared from campholic and camphoric acids and their optical constants determined.

1:2:2:3-Tetramethylcyclopentyl phenyl ketone, obtained by the action of magnesium phenyl bromide on campholyl chloride, is a colourless, odourless, strongly refracting oil, b. p. 165°/14 mm. It has d_4^{20} 1.0050; $[\alpha]_D^{20} + 5.72^\circ$, $[\alpha]_F^{20} - 1.21^\circ$, $[\alpha]_{Hg}^{20} - 12.42^\circ$, $[\alpha]_F^{20} - 50.54^\circ$; n_D 1.52440, n_D 1.52744, n_B 1.53799, n_γ 1.54706; a 10% solution in benzene has d_4^{20} 0.8889, $[\alpha]_C^{20} - 2.70^\circ$, $[\alpha]_D^{20} - 11.47^\circ$, $[\alpha]_{Hg}^{20} - 23.96^\circ$, $[\alpha]_F^{20} - 66.49^\circ$; and a 10% solution in alcohol has d_4^{20} 0.8051, $[\alpha]_C^{20} + 21.74^\circ$, $[\alpha]_D^{20} + 21.68^\circ$, $[\alpha]_{Hg}^{20} + 17.51^\circ$, $[\alpha]_F^{20} - 3.73^\circ$. It does not react with semicarbazide, phenylhydrazine, or *p*-nitrophenylhydrazine. On reduction by sodium and alcohol, it yields, in addition to a hydrocarbon, $C_{16}H_{22}$, b. p. 136—137°/12 mm., which has not yet been completely investigated, phenyl-1:2:2:3-tetramethylcyclopentylcarbinol (Rupe and Läger, A., 1920, i, 383). 1:2:2:3-Tetramethylcyclopentyl benzyl ketone is obtained in an analogous way, using magnesium benzyl chloride, and has b. p. 175°/12 mm., d_4^{20} 0.9999, $[\alpha]_C^{20} + 26.46^\circ$, $[\alpha]_D^{20} + 32.16^\circ$, $[\alpha]_{Hg}^{20} + 36.40^\circ$, $[\alpha]_F^{20} + 42.56^\circ$, n_D 1.51649, n_D 1.51923, n_B 1.52915, n_γ 1.53706; a 10% solution in benzene has d_4^{20} 0.8878, $[\alpha]_C^{20} + 21.51^\circ$, $[\alpha]_D^{20} + 25.91^\circ$, $[\alpha]_{Hg}^{20} + 28.05^\circ$, $[\alpha]_F^{20} + 33.34^\circ$. 1:2:2:3-Tetramethylcyclopentyl β -phenylethyl ketone has b. p. 182°/13 mm., d_4^{20} 0.9681, $[\alpha]_C^{20} + 18.96^\circ$, $[\alpha]_D^{20} + 23.71^\circ$, $[\alpha]_{Hg}^{20} + 27.68^\circ$, $[\alpha]_F^{20} + 35.43^\circ$; a 10% solution in benzene has d_4^{20} 0.8870, $[\alpha]_C^{20} + 14.32^\circ$, $[\alpha]_D^{20} + 18.15^\circ$, $[\alpha]_{Hg}^{20} + 20.86^\circ$, $[\alpha]_F^{20} + 27.40^\circ$. 1:2:2:3-Tetramethylcyclopentyl α -naphthyl ketone has m. p. 78°, b. p. 229°/14 mm.; a 10% solution in benzene has d_4^{20} 0.8939, $[\alpha]_C^{20} - 41.95^\circ$, $[\alpha]_D^{20} - 60.52^\circ$, $[\alpha]_{Hg}^{20} - 80.21^\circ$, $[\alpha]_F^{20} - 132.25^\circ$; a 5% solution in alcohol has d_4^{20} 0.8012, $[\alpha]_C^{20} - 12.23^\circ$, $[\alpha]_D^{20} - 19.97^\circ$, $[\alpha]_{Hg}^{20} - 29.45^\circ$, $[\alpha]_F^{20} - 58.16^\circ$.

Methyl 1-acetyl-1:2:2-trimethylcyclopentane-3-carboxylate is obtained from α -methyl camphoryl β -chloride [$C_8H_{14}(COCl) \cdot CO_2Me$] and zinc methyl or methyl iodide and magnesium. It has b. p. $130-131^\circ/12$ mm., d_4^{20} 1.0430, $[\alpha]_D^{20} -10.53^\circ$, $[\alpha]_D^{20} -14.02^\circ$, $[\alpha]_{Hg}^{20} -14.08^\circ$, $[\alpha]_{Fe}^{20} -17.39^\circ$, $[\alpha]_F^{20} -24.99^\circ$; n_a 1.46729, n_D 1.46857, n_B 1.47554, n_γ 1.48039; a 10% solution in benzene has d_4^{20} 0.8919, $[\alpha]_D^{20} -14.46^\circ$, $[\alpha]_D^{20} -19.17^\circ$, $[\alpha]_{Hg}^{20} -20.18^\circ$, $[\alpha]_{Fe}^{20} -23.43^\circ$, $[\alpha]_F^{20} -33.41^\circ$. The *semicarbazone* crystallises in white leaflets, m. p. 194° . On attempting to condense the ketonic ester by Dieckmann's method, a substance, $C_{22}H_{32}O_4$, m. p. $221-222^\circ$, giving a silver salt, $C_{22}H_{30}O_4Ag_2$, was obtained; on treating the ketonic ester with dry hydrogen chloride, a substance, $C_{12}H_{20}O_2$, was obtained as a mobile oil, b. p. $139-141^\circ$, which solidified to needles, m. p. 85° ; definite structures are not assigned to these substances. *1-Acetyl-1:2:2-trimethylcyclopentane-3-carboxylic acid*, m. p. 90° , b. p. $177^\circ/9$ mm., is obtained by hydrolysis of the ester; a 5% solution in benzene has d_4^{20} 0.8874, $[\alpha]_D^{20} +84.29^\circ$, $[\alpha]_D^{20} +109.98^\circ$, $[\alpha]_{Hg}^{20} +116.07^\circ$, $[\alpha]_{Fe}^{20} +133.20^\circ$, $[\alpha]_F^{20} +185.71^\circ$. The *semicarbazone* forms minute nodules, m. p. 224° , and the *oxime*, needles, m. p. $165-166^\circ$. C. K. I.

Transformation Products of 1-Methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-one. K. VON AUWERS and W. JÜLICHER (*Ber.*, 1922, 55, [B], 2167-2191).—1-Methyl-1-trichloromethyl-

$\Delta^{2:5}$ -cyclohexadiene-4-one, $O:\langle \text{cyclohexadiene} \rangle \begin{smallmatrix} \text{Me} \\ \text{CCl}_3 \end{smallmatrix}$, has been prepared by Zincke and Suhl (*A.*, 1907, i, 37), and its properties have been investigated further by Zincke and Schwabe (*A.*, 1908, i, 337). In structure, it is closely similar to 1-methyl-1-dichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-one, described by von Auwers (*A.*, 1907, i, 399). The investigation of the former substance has been extended so as to permit an exact comparison of the two products. In their general behaviour, the trichloroketone and dichloroketone are very closely similar, differences being observed only in minor points. Each substance exhibits a very pronounced tendency to pass directly or indirectly into aromatic compounds, whereby either the chloromethyl or the methyl group wanders, depending on the particular reagent used and the substance under investigation.

1-Methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-one yields a *semicarbazone*, colourless, lustrous needles, m. p. $197-198^\circ$, and a *p-nitrophenylhydrazone*, yellow plates, m. p. $159-160^\circ$. The *oxime* is remarkably stable towards acids and, probably for this reason, its transformation could not be effected. The trichloroketone is converted by phosphorus pentachloride into 4-chloro-*o*-methylbenzotrichloride, which is identified by converting it into *p*-chloro-*o*-toluic acid, m. p. $166-167^\circ$.

1:4-Dimethyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol, m. p. $131-132^\circ$ (the stability of the substance when preserved appears to depend largely on the freedom of the atmosphere from acid vapours), is smoothly converted at 35° in light petroleum solution in an atmosphere of hydrogen into 1-methyl-1-trichloromethyl-4-

methylene - $\Delta^{2:5}$ - cyclohexadiene, $\text{CH}_2 \cdot \begin{array}{c} \diagup \text{---} \diagdown \\ \diagdown \text{---} \diagup \end{array} \begin{array}{c} \text{Me} \\ \text{CCl}_3 \end{array}$, a pale yellow liquid which decomposes rapidly on exposure to air, $d_4^{19.5}$ 1.2022, d_4^{20} 1.202, $n_a^{19.5}$ 1.55171, $n_D^{19.5}$ 1.55710, $n_\beta^{19.5}$ 1.56986, n_D^{20} 1.5569. Methyl-*p*- $\beta\beta$ -trichloroethylbenzene is conveniently obtained by heating the carbinol in boiling glacial acetic acid solution. The carbinol is converted by ice-cold concentrated sulphuric acid into 2:4-dimethylbenzoic acid.

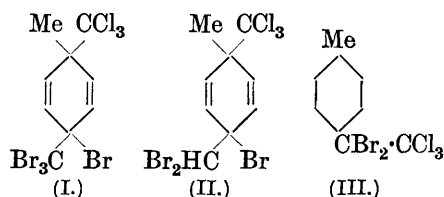
4-Phenyl-1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol, m. p. 120—121°, loses water when dissolved in ice-cold formic acid and yields a viscous, yellow liquid from which hydrogen chloride is continuously evolved at the atmospheric temperature; if the liquid is distilled under diminished pressure, it gives 4-ethyl-diphenyl, unctuous plates, m. p. 46—47°, b. p. 140°/15 mm. in small quantity (the constitution of the substance follows from its preparation by the reduction of 4-acetyldiphenyl with zinc and hydrochloric acid). The carbinol is converted by sulphuric and glacial acetic acids into 4-phenyl-2-methylbenzoic acid, m. p. 168—169°, the calcium salt of which is converted by distillation with lime into 3-methyldiphenyl, a pale yellow liquid, b. p. 272—274°, $d_4^{16.7}$ 1.0182, d_4^{20} 1.015, $n_a^{16.7}$ 1.59747, $n_D^{16.7}$ 1.60443, $n_\beta^{16.7}$ 1.62386, n_D^{20} 1.6029. 4-Phenyl-2-methylbenzoic acid is oxidised by permanganate to diphenyl-3:4-dicarboxylic acid, m. p. 194° (*anhydride*, colourless needles, m. p. 135—136°).

The trichloro-ketone is transformed by ethyl bromoacetate and zinc in the presence of benzene (which must be freed from sulphur compounds by protracted treatment with aluminium chloride) into ethyl 1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol-4-acetate, $\text{Me} \cdot \begin{array}{c} \diagup \text{---} \diagdown \\ \diagdown \text{---} \diagup \end{array} \begin{array}{c} \text{OH} \\ \text{CH}_2 \cdot \text{CO}_2\text{Et} \end{array} \cdot \text{CCl}_3$, a dark-coloured liquid containing considerable amounts of unattacked ketone, which is hydrolysed to 1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol-4-acetic acid, colourless, slender needles, m. p. 125—126° (decomp.). The ester loses water under the influence of ice-cold formic acid, but the residual hydroaromatic ester could not be purified satisfactorily. The acid is converted by being heated in xylene solution or on the water-bath into $\beta\beta$ -trichloro- α -*p*-tolylpropionic acid, small, colourless plates, m. p. 168.5—169.5°. The hydroxy-acid is converted by energetic treatment with alcoholic potassium hydroxide solution into $\beta\beta$ -dichloro-*p*-methylatropic acid, $\text{CCl}_2 \cdot \text{C}(\text{C}_6\text{H}_4\text{Me}) \cdot \text{CO}_2\text{H}$, slender, colourless needles, m. p. 118.5—120°. The action of concentrated sulphuric acid on the hydroxy-acid leads to the formation of 4-carboxy-3-methylphenylacetic acid, colourless leaflets, m. p. 198.5—199.5°.

The trichloro-ketone reacts less readily than the dichloro-ketone with chlorine. If, however, a slow stream of chlorine is passed into a solution of the former in carbon tetrachloride containing iodine, an unstable dichloride is produced which passes slowly when preserved, rapidly when boiled with acetic acid and potassium acetate, into 3-chloro-1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-

4-one, small, colourless needles, m. p. 99° (*oxime*, colourless needles, m. p. 162—164°, *p*-nitrophenylhydrazone, yellow needles, m. p. 146—148°). When dissolved in carbon disulphide and treated with chlorine in direct sunlight, the trichloro-ketone is transformed into 2 : 3 : 5 : 6-tetrachloro-1-methyl-1-trichloromethylcyclohexane-4-one, small, colourless needles, m. p. 134—136°, which is converted by cautious treatment with sodium hydroxide solution into 3 : 5-dichloro-1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-one, small, lustrous plates, m. p. 161—162°.

3 : 5-Dibromo-1-methyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-one (cf. Schwabe, *loc. cit.*), m. p. 172°, is prepared conveniently by exposing a solution of the trichloro-ketone in an excess of bromine to bright sunlight and subsequently evaporating the solution to dryness. When dissolved in benzene and treated with an ethereal solution of magnesium methyl bromide, it is converted into 3 : 5-dibromo-1 : 4-dimethyl-1-trichloromethyl- $\Delta^{2:5}$ -cyclohexadiene-4-ol, colourless needles, m. p. 88—95°, which probably consists of a mixture of stereoisomeric forms. The carbinol loses water with



some difficulty, and passes into 3 : 5-dibromo-1-methyl-1-trichloromethyl-4-methylen- $\Delta^{2:5}$ -cyclohexadiene, m. p. (indefinite) 83—100°. The dissimilarity of the latter substance and the dibromo-compound obtained by

Zincke and his co-workers by the bromination of the methylcarbinol indicates that bromine is not present in the nucleus of the latter substances. Zincke's tetra-, tri-, and di-bromo-compounds receive the formulæ I, II, and III, respectively. H. W.

The Action of Alcohols on α -Bromobenzylideneacetophenone. CH. DUFRAISSE and P. GÉRALD (*Compt. rend.*, 1922, 174, 1631—1632).—It has previously been shown (this vol., i, 39) that ethyl alcohol condenses with α -bromobenzylideneacetophenone to give a saturated compound, which with an alkali hydroxide loses hydrogen bromide to give an ethylenic compound. This is now shown to occur with other alcohols, and new compounds described are : α -bromo- α -benzoyl- β -methoxy- β -phenylethane, $\text{CHBzBr}\cdot\text{CHPh}\cdot\text{OMe}$, m. p. 76—77°; α -bromo- α -benzoyl- β -propoxy- β -phenylethane, m. p. 95—96°; α -bromo- α -benzoyl- β -butoxy- β -phenylethane, m. p. 81—82°; α -bromo- α -benzoyl- β -isobutoxy- β -phenylethane, m. p. 110—111°; α -benzoyl- β -methoxy- β -phenylethylene, $\text{CHBz}\cdot\text{CPh}\cdot\text{OMe}$, m. p. 65—66°; α -benzoyl- β -propoxy- β -phenylethylene, m. p. 59—60°; α -benzoyl- β -butoxy- β -phenylethylene; α -benzoyl- β -isobutoxy- β -phenylethylene, m. p. 55—56°, and α -benzoyl- β -isopropoxy- β -phenylethylene, m. p. 49—50°. W. G.

The Grignard Reaction. G. J. ÖSTLING (*Hyllningsskrift tillägnad Ossian Aschan*, 1920, 92—97).—An attempt was made to prepare ketones by means of the Grignard reaction. Magnesium $g\ g^* 2$

phenyl bromide reacted with benzyl chloride, giving a trace of benzophenone. All other experiments gave negative results.

CHEMICAL ABSTRACTS.

Imino-aryl Ethers. I. **N-Phenylbenziminom-*m*-hydroxyphenyl Ether and the Synthesis of 2:4-Dihydroxybenzophenone.** ARTHUR WILLIAM CHAPMAN (T., 1922, 121, 1676—1681).

Dinitrobenzil. E. DE BARRY BARNETT and L. J. KAY (*Chem. News*, 1922, 125, 57—58).—Dinitrobenzil may be obtained in almost theoretical yield and very pure by nitration of benzil with a mixture of sulphuric and nitric acids. Details of the preparation are given. Although dinitrobenzil has two carbonyl groups, it only forms a *monophenylhydrazone*, m. p. 159° (decomp.), under ordinary conditions. Attempts to prepare a tetranitro-derivative from dinitrobenzil by further nitration were unsuccessful. G. W. R.

A Double Decomposition Catalysed by Copper. EDUARD KOPETSCHNI and HERTA WIESLER (*Monatsh.*, 1922, 43, 89—92).—When 1-chloro-2-aminoanthraquinone is boiled with excess of dimethylaniline with the addition of a small amount of copper powder or cupric acetate, a good yield of 2-aminoanthraquinone is produced. The chlorine is presumed to re-enter into combination as *p*-chlorodimethylaniline, which may undergo subsequent reduction to tetramethylbenzidine. If potassium carbonate is added in addition to copper powder or cupric acetate, or if the dimethylaniline is replaced by methylaniline, 2-aminoanthraquinone is not obtained, although indanthrene and flavanthrene can be recognised amongst the products. C. K. I.

Homologues of Menthol. AKIRA OGATA and CHÛJI MIYASHITA (*J. Pharm. Soc. Japan*, 1922, 473—482).—By the action of magnesium methyl iodide, menthone is converted into *methylmenthol* (1:5-dimethyl-2-isopropylcyclohexanol), b. p. 83°/6 mm., d_4^{16} 0.8991, $[\alpha]_D +9.74^\circ$. When boiled under atmospheric pressure or warmed with zinc chloride, it loses the elements of water and changes into 5-methyl-2-isopropyl-1-methylenecyclohexane, b. p. 181—182°, d_4^{18} 0.8273, $[\alpha]_D +87.25^\circ$. By the same method, ethyl- and propyl-menthols have been prepared from menthone. When distilled under atmospheric pressure, *ethylmenthol* (5-methyl-1-ethyl-2-isopropylcyclohexanol), b. p. 84—85°/4 mm., d_4^{17} 0.9040, $[\alpha]_D +10^\circ$, was partly decomposed into menthone (semicarbazone, m. p. 186°). By warming with zinc chloride, it gave 5-methyl-2-isopropyl-1-ethylidenecyclohexane, b. p. 58—59°/4 mm., d_4^{16} 0.8304, $[\alpha]_D +34.79^\circ$. *Propylmenthol* (5-methyl-1-propyl-2-isopropylcyclohexanol) gave, on warming with zinc chloride, two isomeric hydrocarbons (1-methyl-4-isopropyl-3-propylenecyclohexane), which are differentiated by the position of the double bond: one, with an odour like that of an ethylidene derivative, has b. p. 46—50°/6 mm., $d_4^{16.5}$ 0.8124, $[\alpha]_D +3.09^\circ$, whilst the other, which is almost odourless, has b. p. 91—92.5°/11 mm., $d_4^{16.5}$ 0.8318, $[\alpha]_D +32.43^\circ$. K. K.

Hydration of Caryophyllene. YOSHIHIKO ASAHINA and TAKEO TSUKAMOTO (*J. Pharm. Soc. Japan*, 1922, 463—473).—A mixture of absolute ether and sulphuric acid monohydrate has been used for the hydration of some hydrocarbons by Aschan (Schimmel & Co. Rep., 1919, 130), and is now found to effect hydration of caryophyllene more easily and quickly than Bertram's method (*Annalen*, 1892, 271, 288). One hundred c.c. of caryophyllene were added drop by drop to a mixture of 80 c.c. of absolute ether and 30 c.c. of sulphuric acid monohydrate cooled to 0°, the temperature of the reaction mixture being maintained below 10°. After remaining for one to two hours at the room temperature, it was poured into a mixture of ice and sodium carbonate and the alkaline solution subjected to distillation with steam, when a 30% yield of caryophyllene alcohol, m. p. 94—95°, was obtained. The alcohol has always been regarded as optically inactive, but it is now found to be active, $[\alpha]_D -5.8^\circ$ in alcohol. The phenylurethane, m. p. 135°, has $[\alpha]_D +50.5^\circ$ in alcohol. An oily by-product which distilled with the alcohol was separated into two fractions:

(a) b. p. 93—98°/3 mm., d^{18}_4 0.9237, $\alpha^{18}_D -31.76^\circ$, n^{18}_D 1.5037, and

(b) b. p. 98—105°/3 mm., d^{18}_4 0.9283, $[\alpha]^{18}_D -33.68^\circ$, n^{18}_D 1.4997.

The alkaline-aqueous solution remaining in the flask in the above distillation was freed from resinous matter by shaking with ether, acidified with dilute sulphuric acid, and distilled with steam, when a substance passed over, crystallising in plates, m. p. 117°, soluble in the ordinary organic solvents, and stable towards permanganate, etc. It proved to be an *isomeride* of caryophyllene alcohol, and is optically inactive, as also is its *phenylurethane*, m. p. 180°. It is therefore regarded as the α -compound and the active one as the β -compound. Clovene was prepared from the β -compound by Wallach's method and found also to be optically active, b. p. 259—260°, d^{18}_4 0.9241, n^{18}_D 1.49985, and $\alpha_D +2.84^\circ$.

K. K.

Essential Oils. ROURE-BERTRAND FILS (*Bull. Sci. Ind.*, 1920, [iv], 1, 1—38, and 2, 1—37; from *Chem. Zentr.*, 1922, i, 359—360).—Scheih oil, from *Artemisia herba-alba* var. *genuina* of Algerian origin, has d^{15}_4 0.9432; $[\alpha]_D +2^\circ 6'$; acid number, 3.5; saponification number, 57.4; ester number, 53.9; acetyl number, 147; combined alcohols, 14.80%; free alcohols, 30.64%. A sample kept for six years gave a greater acid number and on distillation with steam yielded 70% of an oil with properties different from those of the fresh oil. Camphor, cineole, and *l*-camphor were found as constituents, also, from the odour, menthol (cf. Grimal, A., 1904, i, 605). Gouft oil, from *Artemisia campestris*, L., var. *odoratissima*, has d^{15}_4 0.8727; $[\alpha]_D -16^\circ 20'$; acid number, 0.94; saponification number, 30.81; ester number, 29.87; acetyl number, 41.07; combined alcohols, 8.21%; free alcohols, 3.44%. It does not change appreciably on keeping. The constituents found were *l*- α -pinene, nopinene (?), and geraniol (cf. Jeancard and Satie, A., 1904, i, 516). Pagoda corn oil from Annam of unknown botanical origin has d^{20}_4 0.9182, $[\alpha]_D +58^\circ 40'$; n^{20}_D 1.4870; acid

number, 1.87; saponification number, 11.20; ester number, 9.33; acetyl number, 130.67; total alcohol ($C_{10}H_{18}O$), 39.83%; combined alcohols, 2.56%. The constituents are *d*-limonene, geraniol (?), and cuminaldehyde. Rhododendron oil from *R. ferrugineum* has d^{15} 0.840; acid number, 0.0; saponification number, 63.47 (cf. Haensel, A., 1906, i, 524). Pichurim bean oil, from the seeds of *Nectandria Puchury major*, is yellowish-green in colour and has d^{17} 1.0396; $[\alpha]_D$ $-4^{\circ}54'$; n_D^{16} 1.5180; acid number, 2.8; saponification number, 2.8; acetyl number, 33.47. It contains 8% of phenols, including isoeugenol. Safrole and cineole are present. The oil obtained by extraction of the distillation water has d^{15} 1.0237; $[\alpha]_D$ $-9^{\circ}28'$; acid number, 9.33; saponification number, 9.33. *Cistus ladaniferus*, L., and *C. Monspeliensis* give an oil with $d^{17.5}$ 0.9033; $[\alpha]_D$ $-12^{\circ}10'$; $n_D^{17.5}$ 1.4800; acid number, 3.7; saponification number, 22.37. The distillation water yields on extraction with light petroleum an oil having $d^{17.5}$ 0.9755, $[\alpha]_D$ $-2^{\circ}40'$; acid number, 18.67; saponification number, 41.07. The essential oil from *Chenopodium ambrosioides* (Dutch Indies) has d^{15} 0.9763; acid number, 0.93; saponification number, 7.47. The corresponding oil from the distillation water has d^{15} 0.9843; acid number, 0.93; saponification number, 13.98. It has been found specific against ankylostomiasis. The essential oil from *Skimmia laureola* is light green in colour and has d^{18} 0.8931; $[\alpha]_D^{18}$ $+4^{\circ}28'$; saponification number, 82.13. Cinnamon oil (Annam) has d^{15} 1.051; n_D^{27} 1.690; $[\alpha]_D$ $-0^{\circ}8'$; acid number, 2.8; aldehydes, 95%.
G. W. R.

Two Indo-Chinese Oils. ROURE-BERTRAND FILS (*La Parfumerie Moderne*, 1921, 14, 151; from *Chem. Zentr.*, 1922, i, 360).—Pagoda corn oil has a similar odour to geranium and bergamot. It has d^{20} 0.920; $[\alpha]_D$ $+56^{\circ}8'$; n_D^{20} 1.4870; saponification number, 13.25; acetyl number, 139.13; free alcohol, 38.20%. Limonene and geraniol are present (cf. preceding abstract). Annam brier oil has an odour like cajuput oil. It has d^{20} 0.886; $[\alpha]_D$ -0.6° ; n_D^{20} 1.4772; ester number, 10.45; acetyl number, 50.21; free alcohols, 11.27%. It is probably obtained from *Cathetus fasciculata*, Lour.
G. W. R.

Essential Oils. ROURE-BERTRAND FILS (*Bull. Sci. Ind. Roure-Bertrand Fils.*, 1921, [iv], No. 3, 14—19; from *Chem. Zentr.*, 1922, ii, 483).—Boldo leaf oil, the essential oil from the leaves of *Peumus Boldus*, Mol., has d^{17} 0.9318, d^{15} 0.9334; $[\alpha]_D$ -0.14° ; acid number, 1.87; saponification number, 14.87: it contains 30% of cineole. The oil from the distillation water has d^{15} 0.9323; acid number, 3.73; saponification number, 26.13; acetyl number, 142.18. It has a different odour from that of the first oil and contains 15% of phenols. Patchouli oil (Sumatra) from the leaves has d^{15} 0.9689; $[\alpha]_D$ $-52^{\circ}4'$; acid number, 1.2; saponification number, 7.9; acetyl number, 26.13. Patchouli oil from the stems has d^{15} 0.9739; $[\alpha]_D$ $-54^{\circ}8'$; acid number, 8.7; saponification number, 10.0.
G. W. R.

Essential Oils. ROURE-BERTRAND FILS (*Sci. Ind. Bull.*, 1921, [iv], No. 4; cf. A., 1921, i, 797, 798).—An oil distilled from *Lavandula stoechas* resembled that ascribed by Schimmel & Co. (1905) to *L. dentata*. It had d^{15} 0.945—0.962, α +35° 30' to +47°, acid number, 0.93—5.16; saponification number, 18.26—18.67; ester number, 13.1—17.74; acetyl ester number, 47.14. The chief constituents (80%) are *d*-camphor and *d*-fenchone, probably also fenchyl alcohol, terpineol, and a phenol compound. *d*-Fenchone has d^{20} 0.9443, d^{26} 0.9402, α^{23} +54° 34', n_D^{21} 1.4625, m. p. 3—5°. Oil of angelica root, obtained by distilling the fresh root with water, had $d^{17.5}$ 0.8887, d^{15} (corr.) 0.8907, α^{18} +6° 42' (normally 16° to +41°), acid number, 7.20 (usually 1 to 4); saponification number, 52.27 (13 to 44); ester number, 45.07 (12 to 40). Madagascar cinnamon bark oil (a) from pounded bark, (b) from the separated water by extraction with light petroleum, (c) a mixture of both, had respectively d^{17} 0.9715, 1.0281, 1.0075; d^{15} 0.9731, 1.0297, 1.0091; α^{17} —5° 49', α^{16} —2° 2', α^{17} —3° 23'; acid number, 2.49; 2.49, 2.49; aldehyde content, 48%, 82%, 70%. The composition and analytical characters of French oil of lavender are discussed. Oil of *Tagetes anisata*, Lillo, which has an odour of anise, has d^{15} 0.9862, b. p. 214—218°, f. p. —6°, n_D 1.5432, α —1° 10', saponification number, 3.1.

The table of structural formulæ, physical constants, and characteristic derivatives of essential oil constituents is continued.

CHEMICAL ABSTRACTS.

Oil of *Bystropogon Canus*. JULIA WHELAN (*J. Amer. Pharm. Assoc.*, 1922, 11, 337—338).—The total oil obtained by distillation in steam was 0.3%. The colour is green, somewhat like that of bergamot oil, and the odour more like that of fatty acid esters than of menthol; d^{20} 0.910; $[\alpha]_D$ —0.59°; n_D^{25} 1.563. Tests for pulegone, menthol, thymol, and carvacrol were negative.

CHEMICAL ABSTRACTS.

Essential Oil of the Leaves of *Doryphora sassafras*. A. R. PENFOLD (*Perf. Essent. Oil Rec.*, 1922, 13, 273—275).—The leaves of *Doryphora sassafras*, the New South Wales variety of the sassafras tree, yield, according to season, 0.1—1.05% of essential oil, the former quantity being obtained in May and the latter in November. The oil varies considerably in composition according to the districts from which it is obtained. Leaves from the Monga district gave an oil having the following constants: d 1.01—1.02; n 1.506—1.509; α +16.2° to +22.2°; ester value, 4.6 (after acetylation, 32.97); solubility in 70% alcohol, 1 in 8. The principal constituents so far identified are safrole, 60—65%; camphor, 10—15%; *d*- α -pinene, 10%; sesquiterpenes, 10%; eugenol, 1%. Another sample of oil from the Currowan district was lighter than water (d 0.9808) and contained about 30% only of safrole, together with a considerable quantity of a substance which was apparently eugenol methyl ether, but which has not yet been satisfactorily separated from admixed sesquiterpenes and alcoholic substances.

The proportion of camphor in this oil was also greater, amounting to about 30%.

G. F. M.

The Volatile Oil of *Mentha aquatica*, Linné, and a Note on the Occurrence of Pulegone. ROLAND E. KREMERS (*J. Biol. Chem.*, 1922, **52**, 439—443).—The distilled oil of *Mentha aquatica*, Linné, has d^{24}_D 0.916; n^{24}_D 1.4582; $[\alpha]^{24}_D$ -7.48° ; acid number, 7.84; ester number, 210.93; ester number after acetylation, 224.0; and contains 73.82% of ester, 61.6% of total alcohol, 3.6% of free alcohol. The ester consists mainly of linalool acetate. There are also present small quantities of another ester, free linalool, a free acid, and an unstable aldehyde.

Pulegone is a constituent of the cohobated oil of peppermint (cf. this vol., i, 357).

E. S.

Essential Oil of Violet Roots. A. GORIS and CH. VISCHNIAC (*Bull. Sci. Ind. Roure-Bertrand Fils*, 1921, [iv], **3**, 1—8; from *Chem. Zentr.*, 1922, i, 360).—The roots of violet (*Viola odorata*) contain an essential oil and a glucoside. The ethereal oil is a salicylic ester. The amount of glucoside is small. It is acted on by an enzyme contained in the root with the formation of an essential oil of strong odour.

G. W. R.

The Vulcanisation of Caoutchouc in Solution. F. BOIRY (*Compt. rend.*, 1922, **175**, 102—104).—If caoutchouc is heated, in colloidal solution, with sulphur at 120° the product depends on the concentration of the solution and the nature of the solvent. With dilute solutions (1—2%), and with solvents such as nitrobenzene, petrol, phenetole, etc., a gelatinous deposit is obtained which, when dried, is a hard, elastic mass with a black fracture. After extraction with acetone, it contains 15—30% of "combined" sulphur. With solvents such as aniline, xylene, thymol, etc., no precipitate is obtained even after several weeks' boiling. With 10% solutions in solvents of the first group, the viscosity of the solution at first diminishes on heating, then reaches a minimum, and increases rapidly until the liquid forms a gel. These gels show the phenomenon of syneresis. The sulphur content of the products obtained, after extracting the gels with acetone, varies between 20 and 30%.

W. G.

The Glucosides. I. The Constitution of Indican. ALEXANDER KILLEN MACBETH and JOHN PRYDE (*T.*, 1922, **121**, 1660—1668).

Digitonin and its Derivatives. A. WINDAUS and K. WEIL (*Z. physiol. Chem.*, 1922, **121**, 62—79; cf. Kiliani, A., 1890, i, 996; 1891, i, 576; 1919, i, 90).—Digitonin has the formula $C_{55}H_{90}O_{29}$. On hydrolysis by alkali, the products are (i) digitogenin, $C_{26}H_{42}O_5$, a neutral material containing three hydroxyl groups, and forming a triacetyl derivative, $C_{26}H_{39}O_5Ac_3$, needles, m. p. 190° , (ii) a hexose, (iii) a pentose, according to the equation $C_{55}H_{90}O_{29} + 5H_2O = C_{26}H_{42}O_5 + 4C_6H_{12}O_6 + C_5H_{10}O_5$. Digitogenin, which does not possess lactone, methoxyl, aldehyde, or ketone groups, is oxidised

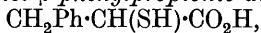
by chromic acid to digitogenic acid, which is now shown to have the formula $C_{26}H_{38}O_7$, to yield a dimethyl ester, $C_{26}H_{36}O_7Me_2$, m. p. 146° , and a diethyl ester, $C_{26}H_{36}O_7Et_2$. Gitonic acid, deoxy-digitogenic acid, and hydrodigitonic acid, described by Kiliani, are all really impure forms of digitogenic acid. Digoitic acid and β -digitogenic acid, isomeric with digitogenic acid, from which they are formed on warming with alkali, both yield the same *dimethyl* ester, $C_{28}H_{42}O_7$, m. p. 140° . On boiling with potassium hydroxide solution, the dimethyl esters of digitoic acid, digitogenic acid, and β -digitogenic acid all yield digitoic acid. Oxydigitogenic acid, from the oxidation of digitoic acid, digitogenic acid, or β -digitogenic acid, has the formula $C_{26}H_{38}O_9$ (*trimethyl* ester, $C_{29}H_{44}O_9$, m. p. 153°). It loses carbon dioxide easily on boiling with acetic acid and some mineral acid, indicating a β -ketonic acid or a derivative of malonic acid. Further oxidation yields digitic acid, $C_{26}H_{38}O_{10}$ (*dimethyl* ester, $C_{29}H_{44}O_{10}$, m. p. $137-138^\circ$). This ester differs from the previously described esters in that it contains a hydroxyl group. On treatment with acetic acid and hydrogen chloride at 0° , it loses 1 molecule each of carbon dioxide and of water to form anhydrodigitic acid, which presumably has the formula $C_{25}H_{36}O_7$. W. O. K.

Hyssopin. O. A. OESTERLE (*Schweiz. Apoth. Ztg.*, 1921, 59, 548—553; from *Chem. Zentr.*, 1922, i, 579).—*Hyssopin*, $C_{50}H_{66}O_{30} \cdot 3H_2O$, which occurs as crystals in hyssop plants attacked by fungi, is a rhamnoglucoside similar to hesperidin; it forms spherulitic crystals, m. p. $275-276^\circ$. *Hyssopinglycone*, $C_{16}H_{14}O_6$, forms bright ochre-yellow platelets, m. p. $262-263^\circ$. *Hyssopinglycone acetate*, $C_{16}H_{11}O_6Ac_3$ or $C_{16}H_{10}O_6Ac_4$, forms white needles.

G. W. R.

The Use of Rhodanine in Organic Syntheses. I. Furylalanine. CH. GRÄNACHER (*Helv. Chim. Acta*, 1922, 5, 610—624).—The condensation products of rhodanine with aldehydes are readily decomposed by alkalis, and a study of their decomposition has shown that by this means many organic compounds not otherwise readily accessible may be synthesised. It has been previously observed by several authors that the condensation product of rhodanine with benzaldehyde breaks up, forming α -thiolcinnamic acid. This reaction is found to occur readily on warming with 10—15% sodium hydroxide solution. α -Thiolcinnamic acid is found to behave in many respects as the α -thio-keto-carboxylic acid, $CH_2Ph \cdot CS \cdot CO_2H$, and is therefore to be considered a tautomeric substance. It gives phenylpyruvic acid oxime, which melts with decomposition at $173-174^\circ$, not at $159-160^\circ$, as has been stated. It also reacts with other amines, giving derivatives of pyruvic acid with loss of sulphur. The oxime can be readily hydrolysed to pyruvic acid or reduced to an α -amino acid. It is thus possible to pass from benzaldehyde directly to pyruvic acid or phenylalanine, and in the same way from furfuraldehyde to furylalanine. The α -thio-ketonic acids may also be converted into the α -ketonic acids by simply boiling with ammonia.

The oxime can also be reduced to give a nitrile containing one carbon atom more than the original aldehyde. Further, α -thiolcinnamic acid can be reduced to β -phenylpropionic acid, a saturated acid containing two carbon atoms more than the original aldehyde. By reduction of α -thioleinnamic acid in alkaline solution with sodium amalgam, α -thiol- β -phenylpropionic acid,



was obtained. It forms a thick syrup with an unpleasant odour, cannot be distilled, and gives with ferric chloride and a trace of ammonia a fugitive blue coloration.

α -Thiol- β -2-furylacrylic acid (Andreassch, A., 1919, i, 97) forms with hydroxylamine α -oximino- β -2-furylpyruvic acid, white needles, m. p. 145° . By reduction with sodium amalgam in alcohol in presence of lactic acid to give the necessary acidity, this is reduced to 2-furylalanine, a coarse, crystalline powder decomposing at 252° . With phenylcarbimide in alkaline solution, this is condensed to α -phenylcarbamido- β -2-furylpropionic acid, m. p. 177 — 178° , not 162 — 163° as given by Sasaki (A., 1921, i, 808). E. H. R.

A Synthesis of Pyrylium Salts of Anthocyanidin Type.

DAVID DOIG PRATT and ROBERT ROBINSON (T., 1922, 121, 1577—1585).

The Coumaranone Series. II. The Preparation of 4- and 6-Chlorocoumaran-2-ones and their Conversion into 2- and 4-Chloroflavonols respectively, and some Derivatives of *o*- and *p*-Chlorophenoxyacetic Acids. THOMAS HOSKER MINTON and HENRY STEPHEN (T., 1922, 121, 1598—1603).

The Thiophen Series. XIII. The Action of Acetylene on Pyrites. WILHELM STEINKOPF and JULIUS HEROLD (*Annalen*, 1922, 428, 123—153; cf. A., 1914, i, 425).—The product of the action of acetylene on finely divided pyrites at 300° contains the following substances: carbon, hydrogen, carbon disulphide, methane, butadiene, acetaldehyde, hydrogen sulphide, acetone, benzene, thiophen (about 40%), 2-thiotolen, 3-thiotolen, 2:3-thioxen, 2-ethylthiophen, and 3-ethylthiophen, and probably, in addition, butane, Δ^2 -butinene, toluene, and xylene, as well as higher homologues of acetylene.

The thiophen homologues were identified for the most part by means of their mercury compounds, many of which had previously been prepared from synthetic specimens of the alkylthiophens (A., 1921, i, 630). 2- and 3-Ethylthiophen, however, had not been fully characterised previously and the following facts relating to these substances had to be ascertained in order to establish their presence in the mixture.

3-Ethylthiophen, on treatment with mercuric chloride, yields 3-ethylthiophen-2(or 5)-mercurichloride, which forms colourless crystals, m. p. 67 — 68° , and 3-ethylthiophen-2:5-dimercurichloride, microscopic, filamental needles, m. p. 295 — 297° (decomp.). The former, on treatment with 2 molecules of sodium thiocyanate, gives mercury 3:3'-diethylthiophenyl, needles, m. p. 68° , but no mercurithiocyanate.

2-Ethyl-5-thienyl methyl ketone, prepared from 2-ethylthiophen by the phosphoric oxide method (A., 1921, i, 579), gives a *semi-carbazone* which crystallises from alcohol in leaflets, m. p. 215°, with previous sintering. C. K. I.

Thiophen Series. XIV. The Condensation of Diazoacetic Ester with Thiophen. WILHELM STEINKOPF and HALVARD AUGESTAD-JENSEN (*Annalen*, 1922, 428, 154—163).—Condensation between ethyl diazoacetate and thiophen takes place at 127°, giving a poor yield of an ester, b. p. 113·5—114·5°/13 mm., which is believed to be *ethyl dicyclo-Δ²-α-penthiophen-5-carboxylate*, $\begin{array}{c} \text{CH} \text{---} \text{CH} \\ | \quad | \\ \text{CH} \cdot \text{S} \cdot \text{CH} \end{array} > \text{CH} \cdot \text{CO}_2\text{Et}$, rather than any of the possible monocyclic isomerides, because the ease with which it forms an *amide*, long needles, m. p. 165°, on treatment with ammonia, suggests that the carbethoxy-group is not attached to a quaternary carbon atom. Both the ester and the amide yield an *acid*, C₆H₆O₂S, on hydrolysis with sodium hydroxide, but, as it is not clear whether or no isomerisation occurs during hydrolysis, a definite structure is not assigned to this substance. C. K. I.

Preparation of the Alkaloidal Mercuri-iodides in Crystalline Form. MAURICE FRANÇOIS and LOUIS GASTON BLANC (*Compt. rend.*, 1922, 175, 169—171).—The amorphous precipitate obtained by adding potassium mercuric iodide to a solution of an alkaloidal salt can be brought into solution by warming it in suspension in the mother-liquor with a large excess of hydrochloric acid, and on allowing to cool slowly it is usually redeposited in a crystalline form. In the actual preparation of these crystals the initial precipitation may be avoided by slowly mixing equal volumes of warm solutions of the alkaloidal salt containing a large amount of hydrochloric acid, and of potassium mercuric iodide, of suitable concentrations. Clear solutions are thus obtained from which the alkaloidal mercuri-iodides are deposited in crystals on slowly cooling. In this way, the mercuri-iodides of caffeine, theobromine, quinine, morphine, codeine, cocaine, strychnine, pilocarpine, and sparteine, and also of quinoline, were prepared. They form brilliant yellow crystals, containing neither chlorine nor water of crystallisation. They show a tendency, well marked in the case of the caffeine compound but scarcely perceptible with the less soluble compounds such as that of quinine, to be decomposed by water into mercuric iodide and the alkaloidal hydriodide.

G. F. M.

Preparation of the Alkaloidal Bismuthic Iodides in a Crystalline Form. MAURICE FRANÇOIS and LOUIS GASTON BLANC (*Compt. rend.*, 1922, 175, 273—274).—Crystalline bismuthic iodides of caffeine, theobromine, morphine, codeine, quinine, atropine, arecoline, pilocarpine, sparteine, nicotine, aniline, pyridine, and quinoline were prepared from potassium bismuthic iodide and acid solutions of the hydrochlorides of the bases by methods precisely analogous to those employed for the preparation of the

double mercuric iodides (preceding abstract). These compounds form extremely well-defined microscopic crystals, and in the bulk are considerably darker in colour than the corresponding amorphous substances. They contain no water of crystallisation, and have the general formula $(\text{BiI}_3)_x(\text{AlkHI})_y$. They appear to be adapted for the microchemical characterisation of the alkaloids.

G. F. M.

Anhalonium Alkaloids. IV. Synthesis of Anhalamine.

ERNST SPÄTH and HANS RÖDER (*Monatsh.*, 1922, **43**, 93—111).—6-Hydroxy-7 : 8-dimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline has been prepared synthetically, and shown to be identical with anhalamine.

At the outset it was supposed that anhalamine might be 7-hydroxy-6 : 8-dimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline, and therefore this substance was synthesised. It was necessary, in the first place, to prepare β -4-ethylcarbonato-3 : 5-dimethoxyphenylethylamine, and two methods were attempted. The starting point of the first was carbethoxysinapic acid (4-ethylcarbonato-3 : 5-dimethoxycinnamic acid), which was reduced by hydrogen in the presence of palladium and platinum to carbethoxydihydrosinapic acid (β -4-ethylcarbonato-3 : 5-dimethoxyphenylpropionic acid), m. p. 167—169°. The same end-product was obtained by reducing carbethoxysyringylidenemalonic acid (4-ethylcarbonato-3 : 5-dimethoxybenzylidenemalonic acid) under similar conditions to 4-ethylcarbonato-3 : 5-dimethoxybenzylmalonic acid, m. p. 122—123° (decomp.), and effecting the elimination of a carboxyl group from this substance by heating. The carbethoxydihydrosinapic acid was converted into its *chloride*, and thence into its *amide*, m. p. 122—123°, from which it was hoped to obtain the required ethylamine by the action of bromine and alkali. The sole isolable product, however, was β -4-hydroxy-3 : 5-dimethoxyphenylpropionamide, m. p. 153—154°, hydrolysis of the carbonato-group having taken place.

Carbethoxysyringaldehyde (4-ethylcarbonato-3 : 5-dimethoxybenzaldehyde) was therefore condensed with nitromethane to give ω -nitro-4-ethylcarbonato-3 : 5-dimethoxystyrene, yellow crystals, m. p. 167°, which was reduced by zinc dust and acetic acid to 4-ethylcarbonato-3 : 5-dimethoxyphenylacetaldoxime. This was reduced, without purification, by means of sodium amalgam to β -4-ethylcarbonato-3 : 5-dimethoxyphenylethylamine, an oil which gave a crystalline *hydrochloride*, *platinichloride*, and *picrate*, m. p. 200° (decomp.).

The base was now condensed with formaldehyde to give 7-ethylcarbonato-6 : 8-dimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline. This base gave a crystalline *hydrochloride*; on removal of the carbethoxy-group and methylation by means of methyl sulphate and alkali, it yielded 6 : 7 : 8-trimethoxy-2-methyl-1 : 2 : 3 : 4-tetrahydroisoquinoline methiodide, and on hydrolysis it gave 7-hydroxy-6 : 8-dimethoxy-1 : 2 : 3 : 4-tetrahydroisoquinoline, m. p. 166—167°, which was different from anhalamine.

A similar series of experiments was therefore instituted with

the isomeric aldehyde, 5-ethylcarbonato-3:4-dimethoxybenzaldehyde, but, at the outset, difficulties were encountered in the preparation of this substance. 5-Nitroveratraldehyde was reduced to 5-aminoveratraldehyde, which was isolated as the tin double salt and diazotised. The hydrolysis product of the diazonium salt was not 5-hydroxyveratraldehyde, however, but 4:5-dihydroxy-3-methoxybenzaldehyde, a methyl group having been eliminated. Methylation of this gave 3:4:5-trimethoxybenzaldehyde, so that this way to the desired substance appeared to be closed. The methylation of gallic acid was therefore investigated. Methyl sulphate gave a mixture of methyl 4:5-dihydroxy-3-methoxybenzoate, methyl 5-hydroxy-3:4-dimethoxybenzoate, and methyl 3:4:5-trimethoxybenzoate, and by further methylation of the first of these a mixture of the second and third could be obtained. The methyl 5-hydroxy-3:4-dimethoxybenzoate was hydrolysed with alkali to 5-hydroxy-3:4-dimethoxybenzoic acid, which was condensed with ethyl chlorocarbonate to give 5-ethylcarbonato-3:4-dimethoxybenzoic acid, m. p. 117—118°. This substance was converted into its chloride, m. p. 45—46°, by means of phosphorus pentachloride, and the chloride reduced by hydrogen to 5-ethylcarbonato-3:4-dimethoxybenzaldehyde, m. p. 60—60·5°. This on hydrolysis gave 5-hydroxy-3:4-dimethoxybenzaldehyde, m. p. 62—63°.

The carbonato-aldehyde was now condensed with nitromethane to give ω -nitro-5-ethylcarbonato-3:4-dimethoxystyrene, m. p. 96°, which on reduction gave β -5-hydroxy-3:4-dimethoxyphenylethylamine, a brown, amorphous mass. This yielded anhalamine on condensation with formaldehyde.

As the yield in this last condensation was not good, the method was modified. 5-Hydroxy-3:4-dimethoxybenzoic acid was benzylated, but the 5-benzyloxy-3:4-dimethoxybenzoic acid so obtained, m. p. 170—172°, could not be reduced to the aldehyde. 5-Hydroxy-3:4-dimethoxybenzaldehyde was therefore directly benzylated. 5-Benzyloxy-3:4-dimethoxybenzaldehyde, m. p. 54°, on condensation with nitromethane, gave ω -nitro-5-benzyloxy-3:4-dimethoxystyrene, m. p. 104—105°, which, on reduction, yielded β -5-benzyloxy-3:4-dimethoxyphenylethylamine (picrate, m. p. 163°). This, on condensation with formaldehyde and subsequent digestion with hydrochloric acid (to remove the benzyl group), gave anhalamine.

C. K. I.

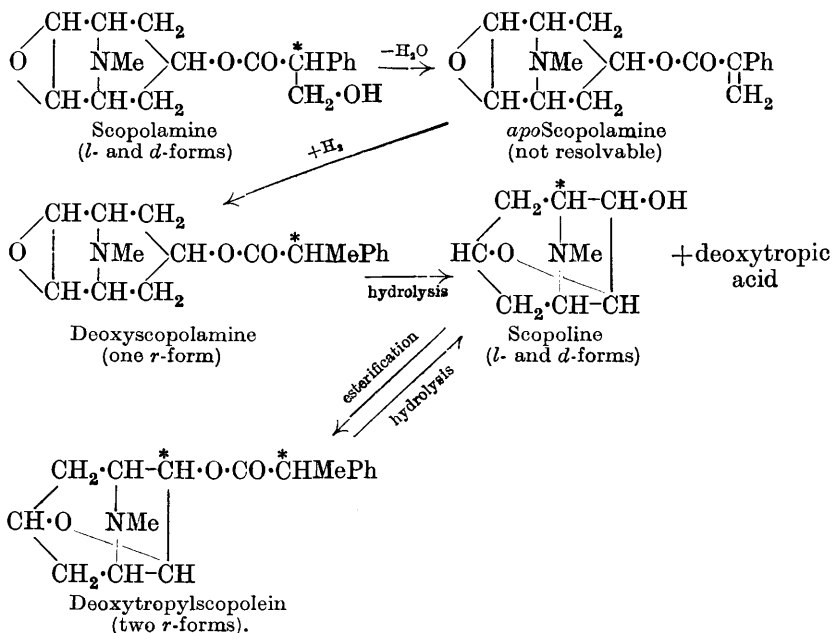
Preparation of Amino-derivatives of Hydrogenated Cinchona Alkaloids and their Derivatives. HOWARD & SONS, LTD., JOHN WILLIAM BLAGDEN, and MAXIMILIAN NIERENSTEIN (Brit. Pat. 182986).—Good yields of the amino-derivatives of hydrogenated cinchona alkaloids are obtained by reducing the nitro-derivatives in neutral or nearly neutral solution with suitable reducing agents such as zinc or iron in conjunction with a neutral salt. Thus nitrohydroquinine, dissolved in alcohol, or in water in the form of a salt, is heated at 50° or more, and zinc dust and aqueous ammonium sulphate solution are added. After stirring for some hours at this temperature, the filtered solution is concentrated in a vacuum to crystallise the product.

G. F. M.

Preparation of Morphine Allyl Ether. GEORG VON KERESZTY and EMIL WOLF (D.R.-P. 343055; from *Chem. Zentr.*, 1922, ii, 147).—A solution of an alkali metal compound of morphine is allowed to react with an alcoholic solution of an allyl arylsulphonate. By the action of sodium morphine on allyl benzenesulphonate, *allyl morphine ether* is obtained; it forms a *hydrochloride* ($+1\text{H}_2\text{O}$), which has m. p. 129—131° when heated quickly, or 130—132° if heated slowly. The free base has m. p. 67—68°. It has therapeutic uses.
G. W. R.

Scopoline. VI. The Constitutions of Scopolamine and Scopoline. The Hofmann Degradation of Scopoline. KURT HESS and OTTMAR WAHL (*Ber.*, 1922, 55, [B], 1979—2025).—Inactive scopoline, obtained by the hydrolysis of *l*-scopolamine with acids or alkalis, has been shown by King (T., 1919, 115, 476, 974; cf. Tutin, T., 1910, 97, 1793) to be a racemic form of *d*- and *l*-scopoline and, since the active scopolines are not racemised under such conditions as are used in the hydrolysis of scopolamine, he has drawn the conclusion that *r*-scopoline is present initially in *l*-scopolamine and that the optically asymmetric character of the latter is due to the presence of the optically active tropanyl group. The conception of *l*-scopolamine as a partial racemate appears to the authors improbable on theoretical grounds, and also on account of the non-observation of a transition temperature for *l*-scopolamine and the failure of attempts to resolve *dl*-*aposcopolamine*. More conclusive evidence has been sought by attempts to synthesise *l*-scopolamine from *dl*-scopoline and *l*-tropic acid, the initial experiments being conducted with optically inactive material. Direct attempts were unsuccessful by reason of the reactivity of the hydroxyl group of tropic acid, whilst acetyltropanyl bromide and scopoline gave acetylscopoline. Esterification of *dl*-scopoline with atropic acid was rendered impossible by reason of the polymerisation of the latter. Greater success was encountered with deoxytropic (α -phenylpropionic) acid. From the *r*-acid and *dl*-scopoline, two racemic products are derived, whereas, according to King's conception, the formation of a single partial racemate is more probable. It must therefore be assumed that either this conception is incorrect or that the ester differs in its behaviour from scopolamine and *aposcopolamine*. If the latter hypothesis is correct, the compound derived from the partly racemic scopolamine by hydrogenation of the corresponding *apo*-derivative must be a separable mixture of racemates which are identical with the compounds just described. Experiment, however, shows that the deoxyscopolamine which is prepared readily from *aposcopolamine* is a single racemic form which is not identical with either of the products derived from scopoline and deoxytropic acid. Since the acid component of the three esters is the same, the difference must be caused by the alcoholic component; hence the alcoholic component of deoxyscopolamine, and therefore of scopolamine itself, cannot be identical with scopoline. It follows also that only one asymmetric carbon atom is present in deoxy-

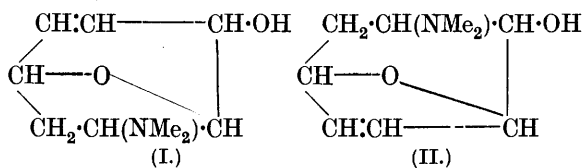
scopolamine, and hence in scopolamine; since this is located in the trotyl residue, a symmetrical structure must be assigned to the basic portion of scopolamine. As, however, an asymmetric carbon atom has been proved to be present in scopoline, it must be assumed that it is developed during the hydrolysis, which thus causes a structural change in the basic component of scopolamine. Further confirmation of this hypothesis is derived from the observation that the three isomeric deoxyscopolamines and the two racemates of deoxytrotylscopolein yield the same products (scopoline and deoxytropic acid) when hydrolysed. The constitution assigned previously to scopolamine and its derivatives therefore requires revision; the reactions are interpreted satisfactorily by the following formulæ:—



Deoxytropic acid is prepared conveniently by the hydrogenation of atropic acid in glacial acetic acid solution in the presence of platinum and is converted by thionyl bromide (obtained by saturating boiling thionyl chloride with hydrogen bromide) into *deoxytrotyl bromide*, a pale yellow liquid, b. p. 106–107°/13 mm. The latter reacts with scopoline hydrobromide in the presence of xylene at 140° with the formation of α - and β -deoxytrotylscopolein bromides in approximately equal amount, which can be separated from one another mechanically or by seeding the solution of the mixture with one variety. α -*Deoxytrotylscopolein* crystallises in large, thick rhombohedra, m. p. 66–67° (the *hydrobromide*, aggregates of needles, m. p. 205°; *picrate*, quadratic leaflets, m. p. 172°; *methiodide*, m. p. 195°, and *platinichloride*, yellow crystals, decomp.

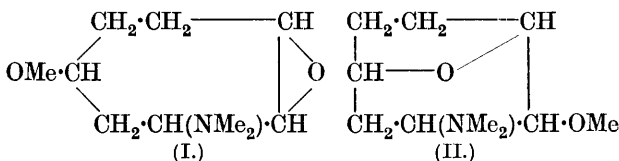
155—157°, are described). β -*Deoxytropylscopolein* forms large prisms, m. p. 63—64° [the *hydrobromide*, m. p. 176—177°; *picrate*, small cubes, m. p. 130°; *methiodide*, long, slender needles, m. p. 183°; *platinichloride*, m. p. 215° (decomp.), and oily *aurichloride* are described]. *apoScopolamine* is converted by hydrogen in the presence of spongy platinum and glacial acetic acid into *deoxy-scopolamine*, long, slender needles, m. p. 69°; the *hydrobromide*, m. p. 182—183°; *picrate*, thin leaflets, m. p. 209—210°; *methiodide*, leaflets, m. p. 219° (decomp.), and *platinichloride*, m. p. 220°, were analysed.

The new conception of the constitution of scopolamine permits a more definite hypothesis with regard to the Hofmann degradation of scopoline (cf. Hess, A., 1921, i, 683; Gadamer and Hammer, A., 1921, i, 588). The process has been shown to give rise to products which contain two double bonds but, under definite conditions which are now described, it can be so regulated that only compounds containing one double bond are formed. The product of the reaction consists of a mixture of four isomeric bases, $C_9H_{15}O_2N$, from which α -demethylscopoline (annexed formula I or



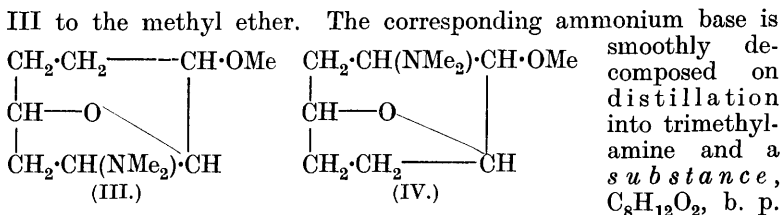
II) separates on cooling; the product is identical with that described previously as α - ψ -demethyl-

scopoline. The remaining bases are only separable from one another after hydrogenation. Under these conditions α -demethylscopoline gives α -*dihydrodemethylscopoline*, colourless, lustrous needles, m. p. 53° (the *picrate*, m. p. 183°, and *methiodide*, m. p. 209—210°, have been prepared previously from non-homogeneous material; the *benzoyl* compound has m. p. 219°). Distillation of the quaternary ammonium base of α -*dihydrodemethylscopoline* leads to the formation of *O-methyliso- α -dihydrodemethylscopoline*, b. p. 116—120°/13 mm. (*picrate*, rhombic crystals, m. p. 185°; *methiodide*, m. p. 240—241°), for which the annexed formulæ I and



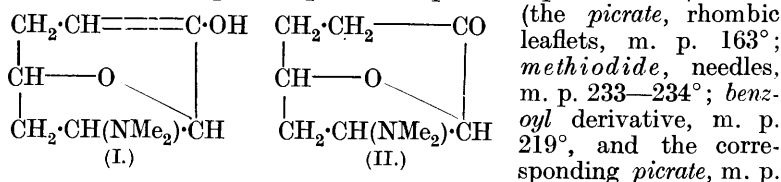
II are possible. The second formula is, however, practically excluded

by the following series of observations. α -*Dihydrodemethylscopoline* is converted by thionyl chloride into α -*dihydrodemethylscopoline chloride*, b. p. 115—118°/13 mm., m. p. 45° [*picrate*, m. p. 228° (decomp.)], which is transformed by sodium methoxide into the *methyl ether* of α -*dihydrodemethylscopoline*, b. p. 110—115°/14 mm. (*methiodide*, m. p. 174—175°). (α -*Dihydrodemethylscopoline* is unaffected by sodium methoxide under the experimental conditions adopted.) It therefore appears valid to assign the formula



70—71°/13 mm. In a similar manner, β -dihydrodemethylscopoline (see later) is converted successively into β -dihydrodemethylscopoline chloride, b. p. 122—125°/13 mm., m. p. 38—39°, and the methyl ether of β -dihydrodemethylscopoline (formula IV) (methiodide, lustrous leaflets, m. p. 225·5°). The degradation of the ammonium base of the latter gives trimethylamine and a nitrogen-free product, b. p. about 80°/15 mm. The smooth Hofmann degradation of these substances is in such striking contrast to the stability of *O*-methyliso- α -dihydrodemethylscopoline under similar conditions that the substances cannot be constituted similarly.

The liquid residue obtained after the removal of α -demethylscopoline is submitted to hydrogenation and the dihydro-products are separated by fractional crystallisation of the corresponding picrates. The following substances are thereby obtained: β -Dihydrodemethylscopoline, colourless, lustrous needles, m. p. 78°, b. p. 128—131°/13 mm. (picrate, large cubes, m. p. 153°; methiodide, rectangular leaflets, m. p. 249°); γ -Dihydrodemethylscopoline, b. p. 120—123°/13 mm. (picrate, large crystals, m. p. 194°; methiodide, m. p. 171°); demethylscopolinone (annexed formula I or II), lustrous, pointed prisms, m. p. 42°, b. p. 117—119°/13 mm.



(the picrate, rhombic leaflets, m. p. 163°; methiodide, needles, m. p. 233—234°; benzoyl derivative, m. p. 219°, and the corresponding picrate, m. p.

213—214°, are described; the compound does not react with hydroxylamine or hydrazine hydrate).

α -, β -, and γ -Dihydrodemethylscopolines are reduced with comparative readiness by hydriodic acid and phosphorus to the amine, $C_9H_{17}N$, b. p. 59°/17 mm., 170—172°/756 mm. (picrate, needles, 157—158°), which contains two atoms of hydrogen less than the expected dimethylsuberyllamine. H. W.

Cevadine. I. ALEXANDER KILLEN MACBETH and ROBERT ROBINSON (T., 1922, **121**, 1571—1577).

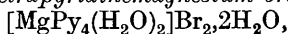
Derivatives of Pyrrole. WILLIAM KÜSTER [with W. WEBER, H. MAURER, W. NIEMANN, P. SCHLACK, SCHLAYERBACH, and WILLIG] (Z. physiol. Chem., 1922, **121**, 135—163).—By the reduction of a mixture of methyl acetoacetate and methyl oximinoacetoacetate, methyl 2 : 4 - dimethylpyrrole - 3 : 5 - dicarboxylate,

needles, m. p. 174—175°, is obtained. From methyl acetoacetate and ethyl oximinoacetoacetate is obtained 3-ethyl 5-methyl 2:4-dimethylpyrrole-3:5-dicarboxylate, colourless needles, m. p. 158°, and in an analogous way, the 3-methyl 5-ethyl ester, colourless needles, m. p. 119—120°, can be prepared. On partial hydrolysis, these give respectively 2:4-dimethylpyrrole-3:5-dicarboxylic acid 3-ethyl ester, colourless needles, m. p. 202° (decomp.), and 2:4-dimethylpyrrole-3:5-dicarboxylic acid 3-methyl ester, colourless needles, m. p. 182° (decomp.). 2:4-Dimethylpyrrole-3:5-dicarboxylic acid 3-ethyl ester, when boiled with acetic anhydride, yields ethyl 2:4:2':4'-tetramethylpyrocoll-3:3'-dicarboxylate, colourless needles, m. p. 257—258°, and over a free flame it loses carbon dioxide to form methyl 2:4-dimethylpyrrole-3-carboxylate. This and the analogous ethyl 2:4-dimethylpyrrole-3-carboxylate, when coupled with diazobenzenesulphonic acid, yield respectively methyl and ethyl 5-sulphobenzeneazo-2:4-dimethylpyrrole-3-carboxylate as red powders, unstable in the air. Ethyl 2:4-dimethylpyrrole-3-carboxylate condenses with formaldehyde, *m*-nitrobenzaldehyde, and furfuraldehyde to give bis(3-carbethoxy-2:4-dimethylpyrrol)-methane, bis(3-carbethoxy-2:4-dimethylpyrrol)-*m*-nitrophenylmethane, colourless needles, m. p. 180°, and bis(3-carbethoxy-2:4-dimethylpyrrol)-furylmethane, colourless needles, m. p. 176°. The first of these compounds on oxidation with chloranil yields bis(3-carbethoxy-2:4-dimethylpyrrol)-methene hydrochloride, a red dye, m. p. 215°. Bis(3-carbethoxy-2:5-dimethylpyrrol)-furylmethane, colourless needles, m. p. 198°, has also been prepared. Ethyl 3-hydroxy-5-methylpyrrole-4-carboxylate yields the following compounds: with anisaldehyde in presence of potassium hydrogen sulphate, 3-hydroxy-4-carbethoxy-5-methylpyrrolenyl-3-*p*-methoxyphenylmethane, yellow needles, m. p. 210°; with *p*-dimethylaminobenzaldehyde, 3-hydroxy-4-carbethoxy-5-methylpyrrolenyl-3-*p*-dimethylaminophenylmethane, red crystals; with furfuraldehyde, 3-hydroxy-4-carbethoxy-5-methylpyrrolenyl-3-furylmethane, yellow needles, m. p. 117° (decomp.); with acetone, in presence of sodium hydroxide and acetyl chloride, ethyl 3-hydroxy-5-methyl-2-isopropylidenepyrrolenine-4-carboxylate, short, pale yellow needles, which slowly decompose at 180—200°; with acetic anhydride and potassium acetate, ethyl 3-acetoxy-5-methylpyrrole-4-carboxylate, m. p. 120°; with acetic anhydride and sulphuric acid, ethyl 3-acetoxy-2-acetyl-5-methylpyrrole-4-carboxylate, light yellow needles, m. p. 167°, which on hydrolysis with alcoholic sodium ethoxide yields ethyl 3-hydroxy-2-acetyl-5-methylpyrrole-4-carboxylate, colourless, fine needles, m. p. 199° (semicarbazone, $C_{11}H_{16}O_3N_4$). 5-Acetyl-2:4-dimethylpyrrole forms a nitroso-derivative, small, deep green needles, m. p. 148—149°, and it couples with diazobenzenesulphonic acid to yield 5-acetyl-2:4-dimethylpyrrole-3-azobenzenesulphonic acid, greenish-black needles. Similarly, with diazonaphthalenesulphonic acid is obtained 5-acetyl-2:4-dimethylpyrrole-3-azonaphthalenesulphonic acid, dark blue, six-sided leaflets, which decompose at 210—212°. From methyl acetonedicarboxylate, acetic acid, sodium nitrite, and zinc dust is obtained methyl pyrrole-

3 : 5-diacetate-2 : 4-dicarboxylate, tufted crystals, m. p. 98—99°, which on partial hydrolysis yields a dibasic acid, $C_{12}H_{13}O_8N$.

W. O. K.

Complex Magnesium Salts. G. SPACU (*Bull. Soc. Stiințe Cluj*, 1921, 1, 72—91; from *Chem. Zentr.*, 1922, i, 313—314).—A number of complex pyridine compounds of magnesium containing combined water are described. *Tetra-aquodipyridinemagnesium chloride*, $[MgPy_2(H_2O)_4]Cl_2$, is obtained by the action of anhydrous pyridine on carnallite; it crystallises in colourless needles which deliquesce on exposure to air with liberation of pyridine. It gives magnesium hydroxide on treatment with ammonia, and silver chloride with silver nitrate. *Triaquotripyridinemagnesium chloride*, $[MgPy_3(H_2O)_3]Cl_2 \cdot H_2O$, is similar to the preceding compound. *Diaquotetrapyridinemagnesium bromide*,



forms very hygroscopic crystals which give up their water of crystallisation in a vacuum over phosphoric oxide. *Aquopentapyridinemagnesium iodide*, $[MgPy_5H_2O]I_2 \cdot 2H_2O$, forms crystals from which iodine separates on exposure to air; it is less hygroscopic than the preceding compounds: *Tetra-aquodipyridinemagnesium nitrate*, $[MgPy_2(H_2O)_4](NO_3)_2 \cdot 2H_2O$, forms nacreous lamellæ. The anhydrous salt has similar properties. *Hexapyridinemagnesium bromide*, $[MgPy_6]Br_2$, is prepared by the Tissier-Grignard reaction by way of the ether compound, $[MgPy_4(Et_2O)_2]Br_2$. The latter is a light yellow, unstable powder which gives with anhydrous pyridine at 100° the hexapyridinemagnesium bromide: the latter forms colourless platelets and is very hygroscopic and unstable. *Hexapyridinemagnesium iodide* is similarly prepared and resembles the corresponding bromide.

G. W. R.

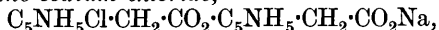
Complex Iridium Compounds. M. DELÉPINE (*Rev. gen. sci. pures appl.*, 1921, 32, 607—615; from *Chem. Zentr.*, 1922, i, 411).—A number of complex pyridine compounds are described in connexion with a study of Werner's valency theory. *Potassium pentachloropyridineiridiate*, $K_2[Ir^{III}PyCl_5]$, is prepared from the corresponding aquo-salt or potassium iridichloride and pyridine at 100°. The alkali salts are reddish-brown, giving orange solutions; the silver and thallium salts are violet or blue. By chlorination of the above salt, *pentachloropyridineiridic acid*, $H[Ir^{IV}PyCl_5]$, is obtained: it is crystalline and gives a violet solution in amyl alcohol. *Potassium tetrachlorodipyridineiridiate*, $K[Ir^{III}Py_2Cl_4]$, is prepared similarly to the pentachloropyridine compound by longer heating. Two isomerides occur of orange-yellow and red colour respectively. The alkali, thallium, silver, and pyridine salts are similar. By oxidation with chlorine or nitric acid, *tetrachlorodipyridineiridium*, $Ir^{IV}Py_2Cl_4$, is obtained; it is crystalline, and with potassium iodide it gives potassium tetrachlorodipyridineiridiate and iodine. By the action of ammonia, a mixture of a compound, $[Ir^{III}Py_2(NH_3)_2Cl_2]$, $[Ir^{III}Py_2Cl_4]$, and a compound, $[Ir^{III}Py_2(NH_3)_3Cl]$, $[Ir^{III}Py_2Cl_4]_2$, is obtained. Tetrachlorodipyridineiridium, prepared from orange-coloured salts,

shows green and reddish-violet dichroism in polarised light and is the *cis*-form, isomorphous with the corresponding platinum compound. *Potassium dioxalodipyridineiridiate*, $K[\text{Ir}^{\text{III}}\text{Py}_2(\text{C}_2\text{O}_4)_2]$, is prepared from pyridine and potassium trioxaloiridate or potassium dichlorodioxaloiridate at 130° . It is crystalline and gives with hydrogen chloride at 130° a compound, $[\text{Ir}^{\text{III}}\text{Py}_2(\text{H}_2\text{O})\text{Cl}(\text{C}_2\text{O}_4)]$, yellow needles, and a compound, $[\text{Ir}^{\text{III}}\text{Py}_2(\text{H}_2\text{O})_2\text{Cl}_2][\text{Ir}^{\text{III}}\text{Py}_2\text{Cl}_4]$, orange-yellow prisms. The latter compound gives with ammonia, ammonium tetrachlorodipyridineiridate, $\text{NH}_4[\text{Ir}^{\text{III}}\text{Py}_2\text{Cl}_4]$, and a compound, $[\text{Ir}^{\text{III}}\text{Py}_2(\text{H}_2\text{O})(\text{OH})\text{Cl}_2]$, forming yellow crystals. The dioxalodipyridine compound cannot be resolved into optical isomerides. The *cis*-form of the compound, $\text{K}_3[\text{Ir}^{\text{III}}\text{Cl}_2(\text{C}_2\text{O}_4)_2]$, can be resolved into optically active constituents by way of the strychnine compounds. The *cis*-form is changed into the *trans*-form by heating at 130° . The *trans*-form is also obtained by way of potassium hexachloroiridate and potassium oxalate.

Trichlorotripyridineiridium, $[\text{Ir}^{\text{III}}\text{Py}_3\text{Cl}_3]$, is obtained from potassium tetrachlorodipyridineiridate by heating at 130° . From the orange-coloured modification two isomerides can be isolated, whilst from the red modification only one compound is obtainable. The orange-coloured salts and their products correspond throughout with the *cis*-form, and may give optical isomerides, whilst the red salts correspond with optically inactive *trans*-forms.

G. W. R.

Preparation of Compounds of Pyridinebetaine with Metallic Salts. LEOPOLD CASSELLA & Co., G. M. B. H. (D.R.-P. 343148; from *Chem. Zentr.*, 1922, ii, 146).—By the action of metallic salts on pyridinebetaine in concentrated aqueous solution, compounds are obtained which serve as glycerol substitutes. *Dipyridinebetaine sodium chloride*,



is obtained by the action of sodium carbonate on dipyridinebetaine hydrochloride; it is a viscid liquid, d^{15}_4 1.26. *Dipyridinebetaine calcium chloride* has d^{15}_4 1.28. *Dipyridinebetaine potassium iodide* is a light yellow liquid, d^{15}_4 1.475. *Dipyridinebetaine mercuric chloride* forms long needles. *Dipyridinebetaine sodium salicylate* is also mentioned. The alkali and alkaline-earth metallic compounds are strongly hygroscopic and with the addition of small quantities of water form viscous liquids having many of the properties of glycerol. They may be crystallised by concentration and cooling.

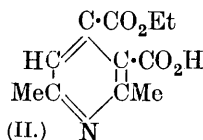
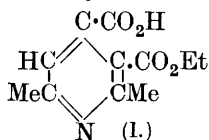
G. W. R.

Preparation of a Derivative of Pyridine-3-carboxylic Acid (Nicotinic Acid). SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 90807; from *Chem. Zentr.*, 1922, ii, 324—325).—Compounds containing a pyridine-3-carboxylic acid residue are treated with diethylamine. For example, the acid chloride is treated with diethylamine hydrochloride for two hours at 160° . From the product of the reaction, *pyridine-3-carboxylodiethylamide* is obtained as a yellow oil, b. p. $175^\circ/25$ mm. It has therapeutic uses.

G. W. R.

Preparation of Quaternary Ammonium Salts of Pyridine-3-carboxylic Acid Alkyl Esters. RICHARD WOLFFENSTEIN (D.R.-P. 343054; from *Chem. Zentr.*, 1922, ii, 145—146).—Alkyl pyridine-3-carboxylates are treated with alkyl salts, excepting alkyl haloids. *Methyl 1-methylpyridine-3-carboxylate methosulphate*, obtained by the action of methyl sulphate on methyl pyridine-3-carboxylate, is a light yellow, uncrystallisable oil. The quaternary compound from the action of ethyl nitrate on *ethyl pyridine-3-carboxylate* is a thick, light brown oil. *Amyl pyridine-3-carboxylate* and methyl sulphate give similarly a quaternary compound, which is an almost colourless oil. G. W. R.

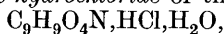
The Hydrogen Esters of 2:6-Dimethylcinchomeronic Acid. OTTO MUMM and ELSE GOTTSCHALDT (*Ber.*, 1922, 55, [B], 2064—2075).—In a previous communication, the ethyl hydrogen ester obtained by the partial hydrolysis of ethyl 2:6-dimethylcinchomerionate has been regarded as the 3-ester (I),



whereas that prepared by the action of ethyl alcohol on the acid anhydride has been considered to be the 4-compound (II), the formulæ assigned resting mainly on considerations of the possibility of steric hindrance (Mumm and Hüneke, A., 1918, i, 184). Since, however, Wegscheider (A., 1920, ii, 761) has more recently pointed out that such considerations are frequently not applicable to esters containing nitrogen, further confirmation appeared to be necessary. Conclusive evidence of the correctness of the previously assigned formulæ is now obtained by investigation of the behaviour of the synthetic methyl ethyl dimethylcinchomerionates.

3-Methyl 4-ethyl 2:6-dimethylcinchomerionate, b. p. 158°/13 mm., m. p. 22°, is prepared by the condensation of ethyl acetoneoxalate with methyl β-aminocrotonate; the corresponding *picrate* has m. p. 143—144°. Conversely, methyl acetoneoxalate and ethyl β-aminocrotonate give 4-methyl 3-ethyl 2:6-dimethylcinchomerionate, prisms, m. p. 52°, b. p. 115°/0.45 mm. (*picrate*, needles, m. p. 137°), whereas methyl β-aminocrotonate and methyl acetoneoxalate yield methyl 2:6-dimethylcinchomerionate, colourless needles, m. p. 48°.

3-Methyl 4-ethyl dimethylcinchomerionate is completely hydrolysed by boiling concentrated hydrochloric acid to dimethylcinchomeronic acid (the *hydrochloride* of the latter,



long prisms, which do not melt below 330°, is described). It is converted by the calculated quantity of potassium hydroxide in alcoholic solution into 3-methyl hydrogen dimethylcinchomerionate, needles, m. p. 198—199°. (4-Methyl hydrogen 2:6-dimethylcinchomerionate, colourless, rhombic plates, m. p. 165°, is prepared by the action of absolute methyl alcohol on 2:6-dimethylcinchomeronic anhydride.) Similarly, 4-methyl 3-ethyl 2:6-dimethyl-

cinchomerone is transformed by partial hydrolysis into 3-ethyl hydrogen 2:6-dimethylcinchomerone, slender needles, m. p. 165°, which is identical with the substance described previously (Mumm and Hüneke, *loc. cit.*).

3-Ethyl silver 2:6-dimethylcinchomerone is converted by distillation in a vacuum into ethyl dimethylnicotinate, b. p. 118°/18 mm. (picrate, m. p. 139°).

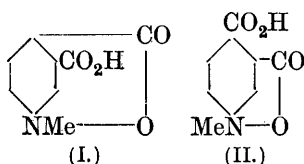
2:6-Dimethylcinchomeronic acid is transformed by ethyl alcohol and hydrogen chloride into 4-ethyl hydrogen 2:6-dimethylcinchomerone, m. p. 151—152°. The action of potassium methyl sulphate on potassium 2:6-dimethylcinchomerone at 135° gives the dimethyl ester, m. p. 48°.

The following data are recorded for the affinity constants: 2:6-dimethylcinchomeronic acid, 0.1666 (in about 0.01*N*-solution); 3-ethyl hydrogen ester, 0.0019; 4-ethyl hydrogen ester, 0.0021.

H. W.

Apophyllenic Acid and $\alpha\alpha'$ -Dimethylapophyllenic Acid.

OTTO MUMM and ELSE GOTTSCHALDT (*Ber.*, 1922, 55, [B], 2075—2082).—Apophyllenic acid was isolated by Wöhler (1844) as a product of the degradation of narcotine, and has subsequently been shown to have the constitution indicated by the annexed



formula I or II. The authors have attempted to decide between the two alternatives in the following manner. Ethyl 2:6-dimethylcinchomerone is converted by successive treatment with methyl iodide and moist silver oxide into ethyl dimethylapophyllenate, from

which the corresponding free acid is readily obtained. If this reaction is applied to 3-methyl 4-ethyl 2:6-dimethylcinchomerone, ethyl dimethylapophyllenate (identical with the product derived from the diethyl ester) must be obtained if the compound is a 3-betaine, whereas if it is a 4-betaine it must yield methyl dimethylapophyllenate (identical with the substance derived from the dimethyl ester). The latter is, however, exclusively produced, so that free 2:6-dimethylapophyllenic acid must be regarded as a 4-betaine, and this, by analogy, is true also for apophyllenic acid itself. In each case the more powerfully acidic carboxyl group takes part in the internal salt formation. The conception of apophyllenic acid as a 4-betaine is in harmony with its properties, except that its silver salt is converted by methyl iodide into the 4-methyl ester of cinchomeronic acid 3-betaine. The apparent exception may possibly be explained on the basis of Pfeiffer's hypothesis (this vol., i, 720), according to which the betaines, like true salts, are completely ionised even in the solid state. The formation of the silver salt is therefore a purely ionic reaction, and it is immaterial whether it is a 3- or a 4-betaine, since either would give initially the same ion.

The following substances are described: *Ethyl 2:6-dimethylcinchomerone methiodide*, yellow needles, m. p. 139°; *ethyl*

2:6-dimethylapophyllenate, short, colourless needles (+H₂O), m. p. 112°, m. p. (anhydrous) 185°; methyl 2:6-dimethylcinchomerionate methiodide, slender, yellow needles, m. p. 188—189°; methyl dimethylapophyllenate (trihydrate and anhydrous), colourless needles, decomp. about 255° after darkening at 205°; 3-methyl 4-ethyl 2:6-dimethylcinchomerionate methiodide, slender matted needles, m. p. 169—170° (decomp.); 2:6-dimethylapophyllenic acid (monohydrate and anhydrous), slender needles, m. p. 237—238°.

H. W.

The Mechanism of the Fischer Indole Synthesis. CECIL HOLLINS (*J. Amer. Chem. Soc.*, 1922, **44**, 1598—1600).—The explanations of the Fischer synthesis advanced by Robinson and Robinson (T., 1918, **113**, 639), Cohn ("Die Carbazolgruppe," 1919, p. 12), Bamberger and Landau (A., 1919, i, 395), and Reddelien (A., 1912, i, 363) are criticised. The last-named appears to be the most satisfactory, and its apparent failure in the case of phenylmethylhydrazones disappears if the ketone imide is supposed to react in its tautomeric form: $\text{NH}:\text{CR}\cdot\text{CH}_2\text{R} \rightleftharpoons \text{NH}_2\cdot\text{CR}:\text{CHR} \xrightarrow{+\text{NHMePh}} \text{NMePh}\cdot\text{CR}:\text{CHR} \xrightarrow{-\text{H}_2} \text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CR} \\ \text{NMe} \end{smallmatrix}\rangle\text{CR}$. Thus modified, Reddelien's theory fulfils all the conditions required: (a) an indolenine is the primary product where this is possible; (b) isobutyraldehyde and ketones of the type $\text{CHMe}_2\cdot\text{CO}\cdot\text{R}$ are converted into indolenines with extraordinary ease (due to the ready oxidisability of the $\cdot\text{CHMe}_2$ group); (c) the reaction succeeds with phenylmethylhydrazones; (d) the tertiary nitrogen atom, that is, that remote from the benzene nucleus, is the one removed; (e) acid hydrazides undergo a similar condensation to oxindoles.

H. W.

Preparation of Dihydroisindole. JULIUS VON BRAUN and ANNEMARIE NELKEN (*Ber.*, 1922, **55**, [B], 2059—2063).—The preparation of dihydroisindole, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{NH}$, has hitherto been a matter of considerable difficulty. It has been shown, however, by Scholtz (A., 1898, i, 567) that dixylenium bromide, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{NBr}\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{C}_6\text{H}_4$, and *N*-xylylenepiperidinium bromide, $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{NBr}\langle\begin{smallmatrix} \text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\rangle\text{CH}_2$, are converted in a remarkable manner by ammonia into the compounds $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2\cdot\text{NH}\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{NH}\cdot\text{CH}_2 \end{smallmatrix}\rangle\text{C}_6\text{H}_4$ and $\text{C}_6\text{H}_4\langle\begin{smallmatrix} \text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2 \end{smallmatrix}\rangle\text{CH}_2$, respectively. Since many-membered rings containing nitrogen are not generally stable, it appeared probable that these compounds would be decomposed when further heated, with the formation of dihydroisindole, on the one hand, and dihydroisindole and piperidine on the other. This is found to be the case, and a convenient method of preparing dihydroisindole is thus afforded; the intermediate isolation of the complex ring compounds is unnecessary.

N-Xylylenepiperidinium bromide is obtained in nearly 90% yield by the method of Scholtz; a greatly improved mode of obtaining dixylenium bromide is described. The conversion of the bromides into the cyclic imines has been examined in detail, as has also the action of heat on the latter. For the preparation of dihydroisoindole, however, it is preferable to neat xylylenepiperidinium bromide with one and a half times its quantity of ammonia (25%) during twenty-four hours at 200°; fractionation of the product gives piperidine, dihydroisoindole (yield 30%), and a complex residue. Di-*o*-xylyleneammonium bromide is heated with twice its quantity of ammonia (25%) for three to four hours at 250°; fractional distillation of the product gives dihydroisoindole, b. p. 90°/14 mm., in 25% yield, di-*o*-xylyleneimine in 22% yield, and a complex residue.

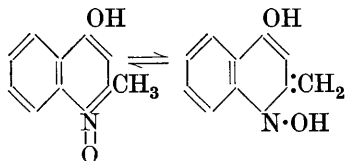
Di-*o*-xylyleneimine is conveniently identified as its *p*-nitrobenzoyl derivative, m. p. 167°; dihydroisoindole gives a characteristic benzoate, m. p. 100°.

N-Phenyldihydroisoindole, $C_6H_4\langle\begin{smallmatrix} CH_2 \\ CH_2 \end{smallmatrix}\rangle NPh$, is readily prepared from *o*-xylylene bromide and aniline; it is converted by amyl nitrite in alcoholic solution in the presence of hydrochloric acid into the nitroso-compound, a green powder, m. p. 286—287°, from which dihydroisoindole could only be obtained in small yield by the action of sodium hydroxide or sodium hydrogen sulphite.

H. W.

Some New Derivatives of 2-Methylquinoline. K. LUCILLE MCCLUSKEY (*J. Amer. Chem. Soc.*, 1922, **44**, 1573—1577).—

4-Hydroxy-2-methylquinoline oxide, described recently by Gabriel and Gerhard (A., 1921, i, 441, 687), has been obtained independently by a rather different method, and several of its derivatives are described. The isolation of a dibenzoyl derivative of the compound necessitates a partial modification



of the structure previously assigned to it, the most probable suggestion being that it is an equilibrium mixture (annexed formulæ).

Ethyl *o*-nitrobenzoylacetate is reduced by stannous chloride and hydrogen chloride in glacial acetic acid solution to ethyl 4-hydroxy-2-methylquinoline-3-carboxylate oxide, a colourless, crystalline substance, m. p. 174° [platinichloride, m. p. 203° (decomp.)]. It is hydrolysed by alkali hydroxide to 4-hydroxy-2-methylquinoline-3-carboxylic acid oxide, decomp. 209°, which passes by loss of carbon dioxide into 4-hydroxy-2-methylquinoline oxide, m. p. 247° (decomp.) after softening at 245° (platinichloride, m. p. 229—230° after darkening at about 200°; picrate, m. p. 171°; monobenzoyl derivative, m. p. 236°; dibenzoyl derivative, prepared by the action of benzoyl chloride and benzene on an alkaline solution of 4-hydroxy-2-methylquinoline oxide, a colourless, crystalline substance, m. p.

171°). 4-Hydroxy-2-methylquinoline oxide is reduced by zinc dust and hydrochloric acid to 4-hydroxy-2-methylquinoline.

o-Nitrobenzoylacetone is reduced in a similar manner to 4-hydroxy-2-methylquinoline oxide. H. W.

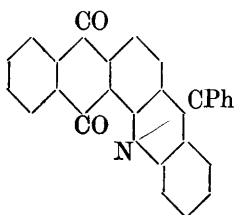
2 : 8-Tetramethyldiaminoacridine. KISHORI LAL MOUDGILL (T., 1922, 121, 1506—1509).

The Reaction of *o*-Halogenated Ketones with Feebly Basic Amines and Synthesis of Derivatives of *ms*-Phenylacridine. FRITZ MAYER and WALTER FREUND [with KASPAR PFAFF and HERMANN WERNECKE] (*Ber.*, 1922, 55, [B], 2049—2058).—The condensation of *o*-chlorobenzaldehyde with feebly basic amines has been described in a series of communications by Mayer and his co-workers (A., 1916, i, 843; 1918, i, 36; 1921, i, 175). The experiments have now been extended to *o*-halogenated ketones. Reaction occurs in accordance with the scheme: $R' \cdot CO \cdot C_6H_4Cl + NH_2R \rightarrow R' \cdot CO \cdot C_6H_4 \cdot NHR + HCl$. *o*-Nitroamines of the benzene series, 2-nitro- α -naphthylamine, and anthraquinone derivatives which contain the amino-group in the α -position may be used. *R'* may be the methyl or phenyl group; in the latter case, ring closure may be effected with production of derivatives of *ms*-phenylacridine. Full directions are given for the preparation of *o*-chlorobenzophenone (cf. Overton, A., 1893, i, 208; Graebe and Keller, A., 1899, i, 703) and *o*-bromobenzophenone. 4-Chloro-3-acetyltoiuene (cf. Claus, A., 1891, 1222; 1892, 985) has b. p. 239—240°; it yields an oxime, m. p. 100—101° (Claus, m. p. 94°), and condensation *products* with *p*-chlorobenzaldehyde and anisaldehyde, m. p. 105—106° and 83—84°, respectively. The action of acetyl chloride on *p*-bromotoluene gives a ketone, b. p. 257—258° [oxime, m. p. 112—114° (Claus, m. p. 109°); *semicarbazone*, m. p. 224°; *p*-nitrophenylhydrazone, m. p. 173°], whereas *o*-bromotoluene yields a ketone, b. p. 262—264°/760 mm., 132—137°/12 mm. (oxime, m. p. 104°; *semicarbazone*, m. p. 224°; *p*-nitrophenylhydrazone, m. p. 203°); the *semicarbazones* of the two compounds are identical, whereas the oximes and *p*-nitrophenylhydrazones differ from one another. An unexplained abnormality in the course of the Friedel-Crafts' reaction is therefore indicated, but since the imino-ketones derived from the two ketones are identical, it follows, at any rate, that each contains 3-bromo-4-acetyltoiuene. Benzoylation of *p*-bromotoluene gives a *ketone*, b. p. 204°/12—13 mm. (*oxime*, m. p. 143—145°, and also a *variety*, m. p. 100°; *semicarbazone*, m. p. 168—172° after softening at 156°). *o*-Bromotoluene yields a ketone, b. p. 206°/15—16 mm. (oxime, m. p. 143—145°, and a *variety*, m. p. 79—80°, which is possibly not homogeneous; *semicarbazone*, m. p. 168—172° after softening at 164°). In this instance, the *semicarbazones* and oximes appear to be identical. It is possible that the ketones exist in stereoisomeric forms, but the greater probability appears to be that they are mixtures. Oxidation of either dibrominated ketone gives *p*-benzoylbenzoic acid.

The imino-ketones are generally prepared by heating a solution of the halogenated ketone and the requisite base in naphthalene

or nitrobenzene at 220° with dry sodium carbonate and a little copper powder. The acridines are obtained by heating the imino-ketones with concentrated sulphuric acid on the water-bath.

The following substances are derived from *o*-chlorobenzophenone: with *o*-nitroaniline, 1-nitro-5-phenylacridine, brownish-yellow leaflets, m. p. 218°; with 2:4-dinitroaniline, *o*-2':4'-dinitroanilinobenzoylbenzene, $C_6H_3(NO_2)_2 \cdot NH \cdot C_6H_4 \cdot COPh$, yellow needles, m. p. 161—162°; 1:3-dinitro-5-phenylacridine, m. p. 240°; with 3-nitro-*p*-toluidine, *o*-2'-nitro-*p*-toluidinobenzoylbenzene, golden-yellow needles, m. p. 125—126°, and 1-nitro-5-phenyl-3-methylacridine, yellow needles, m. p. 202° (1-amino-5-phenyl-3-methylacridine, brown crystals); with 4-chloro-*o*-nitroaniline, *o*-2':4'-chloronitroanilinobenzoylbenzene, brownish-yellow needles, m. p. 124—125°, and 3-chloro-1-nitro-5-phenylacridine, golden-yellow needles, m. p. 251—252°; with 2-nitro- α -naphthylamine, *o*-2'-nitro- α -naphthylaminobenzoylbenzene, pale yellow needles, m. p. 273° (this is the only derivative of naphthalene which could be caused to react); with 1-aminoanthraquinone, *o*-anthraquinonyl-1'-aminobenzoylbenzene, brown crystals, m. p. 146° (also prepared from *o*-aminobenzophenone and 1-chloro-



anthraquinone) and anthraquinone-2:1-*ms*-phenylacridine (annexed formula), yellowish-brown crystals, m. p. 273—274° (the sulphonic acid and a mononitro-derivative, reddish-brown crystals, m. p. 284—285°, are described); from 1-amino-2-methylantraquinone, *o*-2'-methylantraquinonyl-1'-aminobenzoylbenzene, dark red crystals, m. p. 173°; with 1:5-diaminoanthraquinone, bis-2'-benzoylanilino-1:5-anthraquinone, $C_{14}H_6O_2(NH \cdot C_6H_4 \cdot COPh)_2$, dark red crystals, m. p. 248°, and anthraquinone-2:1:6:5-di-*ms*-phenylacridine, bluish-black crystals; with 1-nitro-2-aminoanthraquinone, 1-nitroanthraquinone-3:2-*ms*-phenylacridine, a pale brown powder.

o-Aminobenzophenone gives 5-phenylacridine, m. p. 179—180°, with iodobenzene; 5-phenyl-2:1-benzoacridine, yellow needles, m. p. (indefinite) 129°, with α -bromonaphthalene; and 5-phenyl-4:3-benzoacridine, m. p. 198°, with β -bromonaphthalene.

The following compounds are derived from 4-chloro-3-acetyl-toluene: with 2:4-dinitroaniline, *o*-2':4'-dinitroanilino-5-methylacetophenone, orange-coloured leaflets, m. p. 177—178°; with 1-aminoanthraquinone, *o*-anthraquinonyl-1'-amino-5-methylacetophenone, black needles, m. p. 209—210°; with 1-amino-4-hydroxyanthraquinone, *o*-4'-hydroxyanthraquinonyl-1'-amino-5-methylacetophenone, blackish-violet needles, m. p. 237—238°.

The action of 2:4-dinitroaniline on acetylated *o*- and *p*-bromotoluene gives *o*-2':4'-dinitroanilino-*p*-methylacetophenone, brownish-yellow, lustrous leaflets (m. p. 236° and 240°, respectively, mixed m. p. 237°).

Benzoylated *o*- and *p*-bromotoluenes are transformed by 2:4-dinitroaniline into *o*-2':4'-dinitroanilino-*p*-methylbenzophenone, orange-coloured needles or leaflets (m. p. 143° and 141—142°, respectively,

m.p. of mixture, 142—143°), from which 7:9-dinitro-5-phenyl-3-methylacridine, pale yellow crystals, m. p. 273°, is derived. With 3-nitro-*p*-toluidine they give o-2'-nitro-4'-methylanilino-*p*-methylbenzophenone, reddish-yellow crystals, m. p. 133·5°, which is converted into 9-nitro-5-phenyl-2:7-dimethylacridine, a pale yellow, microcrystalline powder, decomp. 241°.

2-Chloro-5-methylbenzophenone is transformed by 2:4-dinitroaniline into o-2':4'-dinitroanilino-5-methylbenzophenone, yellow needles, m. p. 136—137°. 7:9-Dinitro-5-phenyl-3-methylacridine crystallises in needles, m. p. 285—287°; the corresponding diamino-compound forms reddish-brown needles, m. p. 151°. H. W.

Preparation of Ring Ketones of the Quinoline Series.

FARBWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 343322; from *Chem. Zentr.*, 1922, ii, 146—147).—Ring ketones of the quinoline series are prepared by the action of sulphuric acid on derivatives of 3-phenylquinoline-4-carboxylic acid, which thereby pass into ring ketones of the general formula (annexed). 2-Hydroxy-3-phenylquinoline-4-carboxylic acid when heated with concentrated sulphuric acid for two hours at 100° yields a ring ketone in the form of orange-red crystals, m. p. much above 300°: it may be sublimed at higher temperatures.

2-Hydroxy-3-phenylquinoline-4-carboxylic acid is obtained by condensation, in the presence of alkali, of isatin with phenylacetyl chloride or anhydride, phenylacetyl- ψ -isatin being formed as an intermediate product. It forms light yellow needles which decompose on melting. 2:3-Diphenylquinoline-4-carboxylic acid gives similarly a yellow ring ketone. G. W. R.

Preparation of Diaminodinaphthyl- and Dinaphthacarbazole-sulphonic Acids. KALLE & Co., AKT.-GES. (D.R.-P. 343149; from *Chem. Zentr.*, 1922, ii, 144).—1:1'- or 2:2'-Azonaphthalenesulphonic acids are treated with acid or alkaline reducing agents. For example, 1:1'-azonaphthalene-5:5'-disulphonic acid by reduction with tin and hydrochloric acid gives 1:1'-diamino-2:2'-dinaphthyl-5:5'-disulphonic acid. It forms colourless needles and gives a yellow diazo-compound with nitrous acid. By the action of sodium amalgam in weak alkaline solution, 1:1'-diamino-2:2'-dinaphthyl is formed, which by heating with hydrochloric acid readily gives dinaphthaimine [*di- $\alpha\beta$ -naphthacarbazole*]. On heating the acid with hydrochloric acid at 140°, ammonia is eliminated. 1:1'-Azonaphthalene-4:4'-disulphonic acid gives, by reduction with a hot alkaline sodium thiosulphate, an acid crystallising in fine needles which cannot be diazotised, and on heating with mineral acids at 130° gives di- $\alpha\beta$ -naphthacarbazole. It is therefore supposed to be di- $\alpha\beta$ -naphthacarbazole-5:8-disulphonic acid. The reduction product from 2:2'-azonaphthalene-7:7'-disulphonic acid crystallises in compact, colourless needles and gives with nitrous acid a yellow tetra-azo-compound. On heating with mineral acids at 130°, the 2:2'-diamino-1:1'-dinaphthyl-7:7'-disulphonic acid gives di- $\beta\alpha$ -naphthacarbazole with intermediate

formation of di- $\beta\alpha$ -naphthacarbazole-2 : 12-disulphonic acid. The products are used in the preparation of colouring matters.

G. W. R.

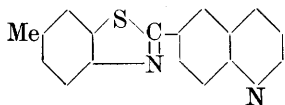
A New Mode of Formation of Thiazole Derivatives of the Anthraquinone Series. EDUARD KOPETSCHNI and HERTA WIESLER (*Monatsh.*, 1922, **43**, 81—87).—When heated with aqueous or alcoholic ammonia, 2-amino-1-thiolanthraquinone is converted into 2-aminoanthraquino-1-thiazole (cf. Gattermann, A., 1912, i, 1004), which forms microscopic needles, m. p. 285° (not sharp), and gives an *acetyl* derivative, which forms olive-yellow needles, m. p. 294°. Oxygen must enter at some stage in the formation of the thiazole, and it is probable that the first step consists in the oxidation of the mercaptan to 2 : 2'-diaminodianthraquinone 1 : 1'-disulphide, since this substance also is converted into the thiazole on treatment with ammonia. Dianthraquinonyl 1 : 1'-disulphide behaves similarly, giving the thiazole previously obtained by Gattermann (*loc. cit.*). 3 : 3'-Dichloro-2 : 2'-diaminoanthraquinone 1 : 1'-disulphide yields 3-chloro-2-aminoanthraquino-1-thiazole, blue needles, m. p. 322—324° (decomp.), which, in contrast with 2-aminoanthraquino-1-thiazole, is sulphonated with difficulty.

C. K. I.

Thiazoles. II. 1-*p*-Tolylbenzothiazole, Dehydrothio-*p*-toluidine and some Related Compounds. MARSTON TAYLOR BOGERT and MARTIN MEYER (*J. Amer. Chem. Soc.*, 1922, **44**, 1568—1572).—1-*p*-Tolylbenzothiazole, $C_6H_4 < \begin{smallmatrix} S \\ N \end{smallmatrix} \geq C \cdot C_6H_4Me$, colourless needles, m. p. 85° (corr.), is prepared in 60—75% yield by the oxidation of thio-*p*-toluanilide, m. p. 142° (corr.), by aqueous potassium ferricyanide; it cannot be obtained satisfactorily by fusing *p*-toluanilide with sulphur in the presence or absence of naphthalene. It is practically odourless when dry (in striking contrast to the corresponding phenyl derivative), but has a faint odour of roses when moistened with alcohol. It is converted by nitric and sulphuric acids into the *mononitro*-derivative, $NO_2 \cdot C_{14}H_{10}NS$, pale, cream-coloured needles, m. p. 219·5° (corr.), which is reduced by zinc or tin and hydrochloric acid to the *amino*-compound, $NH_2 \cdot C_{14}H_{10}NS$, pale brown crystals, m. p. 229° (corr.). The diazotised amine couples on the fibre with a considerable variety of the commoner azo-couplers, and thus yields mono- and bis-azo-dyes which compare very favourably with the corresponding dyes from the isomeric dehydrothio-*p*-toluidine in fastness to light, to soaping, to bleaching, etc., and are in some case superior in tinctorial power. 1-*p*-Tolylbenzothiazole is oxidised by potassium permanganate in neutral or alkaline solution to (?) *benzothiazolyl-1-*p*-benzoic acid*, microscopic, colourless needles, which darken but do not melt at 270°.

Diazotised primuline couples on the fibre with benzoylenecarbamide, giving a *product* which dyes unmordanted cotton a direct yellowish-brown of good fastness to acids, alkalis, or bleach, but quite fugitive to daylight.

Dehydrothio-*p*-toluidine [1-*p*-aminophenyl-5-methylbenzothiazole] is readily converted into the corresponding *benzylidene* derivative, $\text{C}_6\text{H}_3\text{Me} \begin{smallmatrix} \text{S} \\ \diagup \diagdown \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{C}_6\text{H}_4 \cdot \text{N} : \text{CHPh}$, almost colourless, glistening leaflets, m. p. 193° (corr.). *p*-Nitrobenzylidene-*p*-toluidine, $\text{C}_6\text{H}_4\text{Me} \cdot \text{N} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2$, pale yellow needles, m. p. 123° (corr.), could not be converted into dehydrothio-*p*-toluidine by fusion with sulphur. The conversion of dehydrothio-*p*-toluidine into the corresponding atophan could not be effected.



6-(5-*Methylbenzothiazolyl*)quinoline, microscopic, pale brown crystals, m. p. 147° (corr.), is prepared by the action of concentrated sulphuric acid, glycerol, and arsenic acid on dehydrothio-*p*-toluidine. (See also *Chem. News*, 1922, **124**, 319—323, 328—330, 344—346, 360—361, 376—381, 391—395; **125**, 2—5, 19—22.) H. W.

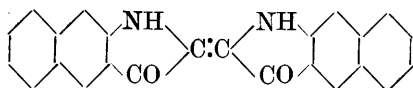
The Iron Salts of Dipyrrolylphenylmethane Dyes and Triphenylpyrrolylmethane. II. Diphenylpyrrolylcarbinol and its Derivatives. HANS FISCHER and MARIA KAAH (Z. physiol. Chem., 1922, **120**, 267—276; cf. this vol., i, 276).—Ethyl 2:4-dimethylpyrrole-3:5-dicarboxylate reacts with magnesium phenyl bromide in ethereal solution to form 3-carbethoxy-2:4-dimethylpyrrolyldiphenylcarbinol, $\text{OH} \cdot \text{CPh}_2 \cdot \text{C}(\text{NHMe}_2) \cdot \text{CO}_2\text{Et}$, pure white, long, blunt needles, m. p. 156° , easily soluble in the usual organic solvents. It forms an orange *picrate*, $\text{C}_{22}\text{H}_{21}\text{O}_2\text{N} \cdot \text{C}_6\text{H}_3\text{O}_7\text{N}_3$, m. p. 181° (decomp.), which is apparently really the picrate of the *dye*, $\text{C}_{22}\text{H}_{21}\text{O}_2\text{N}$, fine, yellow needles, m. p. 178° , formed from the carbinol on boiling with acetic acid. This compound, however, which presumably has the formula $\text{CPh}_2 \cdot \text{C} \begin{smallmatrix} \text{C} \cdot \text{Me} \\ \diagup \diagdown \\ \text{N} : \text{CMe} \end{smallmatrix} \text{C} \cdot \text{CO}_2\text{Et}$, forms no picrate directly.

The carbinol can be reduced catalytically with hydrogen and platinum to form 3-carbethoxy-2:4-dimethylpyrrolyldiphenylmethane, m. p. 138° . The constitution of this compound is proved by the fact that it is obtained from diphenylcarbinol and ethyl 2:4-dimethylpyrrole-3-carboxylate on boiling in acetic acid. Ethyl 2:3:5-trimethylpyrrole-4-carboxylate does not react with magnesium phenyl bromide.

p-Anisyl-bis(3-carbethoxy-2:4-dimethylpyrrolyl)methane, formed from the condensation of anisaldehyde and ethyl 2:4-dimethylpyrrole-3-carboxylate, melts at 170° [cf. Feist, A., 1902, i, 491]. From terephthalaldehyde and ethyl 2:5-dimethyl-3-pyrrolylcarboxylate, *p*-bis(3-carbethoxy-2:5-dimethylpyrrolyl)-methylbenzaldehyde is obtained, m. p. 202.5° (hydrazone, $\text{C}_{32}\text{H}_{36}\text{O}_4\text{N}_4$). W. O. K.

2:2'-ββ-Naphthindigotin. HANS EDUARD FIERZ and RICHARD TOBLER (*Helv. Chim. Acta*, 1922, **5**, 557—560).—2:2'-ββ-Naphthindigotin was prepared by the usual series of reactions for comparison with other dyes of the naphthindigotin series. It was found that 3-hydroxy-β-naphthoic acid could be converted into 3-amino-β-naphthoic acid in good yield by heating with ammonium chloride and zinc chloride ammoniate in a current of ammonia at

180—190°. The presence of zinc oxychloride induces side reactions with formation of β -naphthylamine and dinaphthacridone. The aminonaphthoic acid is converted quantitatively into the corresponding glycine by condensing with chloroacetic acid. β -Naphthylglycine-3-carboxylic acid, $\text{CO}_2\text{H}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{C}_{10}\text{H}_6\cdot\text{CO}_2\text{H}$, crystallises from alcohol in groups of yellow needles, m. p. 240°. The hygroscopic sodium salt crystallises from concentrated solution in yellowish-



brown needles. Very poor yields of the naphthindigotin are obtained from the glycine by any of the usual methods;

2:2'- β -naphthindigotin (annexed formula) crystallises from nitrobenzene in nearly black tablets. When brominated, it takes up three atoms of bromine, but the resulting dye is not fast to chlorine [cf. *J. Soc. Chem. Ind.*, 1922, 41, 625A.].

E. H. R.

Attempts to Prepare *peri*-Naphthindigotin, and the Behaviour of Azo-dyes from Naphthylglycines. HANS EDUARD FIERZ and RICHARD SALLMANN (*Helv. Chim. Acta*, 1922, 5, 560—566).—Attempts to prepare a *peri*-naphthindigotin from α -naphthylglycine-8-carboxylic acid were unsuccessful, owing to the instability of the naphthylglycines, which is reflected in the ease with which azo-dyes prepared from them are decomposed. In the preparation of naphthastyril from naphthalimide by oxidation with sodium hypochlorite, the maximum yield obtained was 50%. By condensation of naphthastyril with chloroacetic acid, naphthastyrilacetic acid, m. p. 256°, was obtained, which by boiling with sodium ethoxide was converted into disodium α -naphthylglycine-8-carboxylate, a white powder. α -Naphthylglycine-8-sulphonic acid was prepared by condensing α -naphthylamine-8-sulphonic acid with chloroacetic acid, and forms colourless needles containing $1\text{H}_2\text{O}$. α -Naphthylglycine-4-sulphonic acid has a yellow colour, and crystallises with $1\text{H}_2\text{O}$; in alkaline solution, it shows a strong blue fluorescence. α -Naphthylglycine-5-sulphonic acid crystallises in anhydrous, colourless leaflets or needles, and shows a green fluorescence in alkaline solution. β -Naphthylglycine-1-sulphonic acid crystallises with $2\text{H}_2\text{O}$ in colourless, fan-shaped aggregates of needles. The azo-dyes from all these naphthylglycinesulphonic acids are decomposed by boiling water. The α -4-acid does not couple readily with diazo-compounds; with diazobenzene in alkaline solution it forms a crystalline additive compound. The decomposition of azo-dyes derived from β -naphthylglycine ethyl ester was studied particularly. Benzeneazo- β -naphthylglycine ethyl ester, $\text{C}_{20}\text{H}_{19}\text{O}_2\text{N}_3$, forms bright red needles, m. p. 135°. *p*-Nitrobenzeneazo- β -naphthylglycine ethyl ester, $\text{C}_{20}\text{H}_{18}\text{O}_4\text{N}_4$, forms brown or bronze needles, decomposing at 156°; in glacial acetic acid it gives a violet colour and in sulphuric acid cherry-red. From the decomposition products of the latter when boiled with acetic acid were isolated the following: ethyl 2-*p*-nitrophenyldihydro-1:2:4-isonaphthatriazine-3-carboxylate, $\text{C}_6\text{H}_4\text{—}\overset{\text{C}}{\underset{\text{CH}\cdot\text{CH}\cdot\text{C}\cdot\text{N}}{\text{N}}}\cdot\text{N}\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, m. p. 210°, naphthiminazole, and *p*-nitroaniline.

E. H. R.

glyoxalone. The formation of this compound is clear proof that the methyl group must be in the 2-position, whence the orientation of the original dihydroglyoxalone and of its parent oxide follows. On oxidation by alkaline permanganate at the ordinary temperature the above dihydroglyoxalone is converted into 4 : 4-diphenyl-4 : 5-dihydro-5-glyoxalone-2-carboxylic acid, which on heating begins to decompose at about 65—66°, giving 4 : 4-diphenyl-4 : 5-dihydro-5-glyoxalone (*loc. cit.*).

In the previous paper it was noted that a by-product, $C_{19}H_{18}O_4N_2$, m. p. 224—225°, was obtained when the diphenyl-dihydroglyoxalone was acetylated (*Annalen*, 1912, 391, 225). It is now evident that this substance is 3-formyl-1-acetyl-2-hydroxy-5 : 5-diphenyl-2-methyltetrahydro-4-glyoxalone, and that it is formed as a result of a preliminary ring-fission as with the oxides described in this paper. Confirmation is found in the fact that the substance yields 4 : 4-diphenyl-2-methyl-4 : 5-dihydro-5-glyoxalone on hydrolysis.

The action of formic acid on 5 : 5-diphenyltetrahydro-4-glyoxalone gives rise to 5 : 5-diphenyl-1-methyltetrahydro-4-glyoxalone 1' : 2-oxide, which forms glistening, hexagonal leaflets, m. p. 260°. The substance is hydrolysed by hydrobromic or hydriodic acid to the original tetrahydroglyoxalone, and is oxidised by alkaline permanganate to 5 : 5-diphenylhydantoin. Its 3-acetyl derivative, m. p. 127°, and 3-benzoyl derivative, m. p. 176°, are each hydrolysable to the original oxide, whilst the 3-methyl derivative, m. p. 146°, obtained with the aid of methyl sulphate, is oxidised by permanganate or chromic acid to 5 : 5-diphenyl-3-methylhydantoin, and is hydrolysed by hydrobromic acid to 5 : 5-diphenyl-3-methyltetrahydro-4-glyoxalone, which forms hexagonal prisms, m. p. 90°.

The action of formic acid on 5 : 5-diphenyl-2-methyltetrahydro-4-glyoxalone gives rise to 5 : 5-diphenyl-1-ethyltetrahydro-4-glyoxalone 1' : 2-oxide, small needles, m. p. 256°, which on oxidation by chromic oxide in acetic acid gives 5 : 5-diphenylhydantoin, and, on hydrolysis by means of hydrobromic acid, yields 5 : 5-diphenyl-2-methyltetrahydro-4-glyoxalone.

4 : 4-Diphenyl-1-methyl-4 : 5-dihydro-5-glyoxalone on oxidation with chromic acid gives 5 : 5-diphenyl-3-methylhydantoin, and on reduction yields 5 : 5-diphenyl-3-methyltetrahydro-4-glyoxalone, which, on oxidation, gives the same hydantoin. In view of these facts and others recorded above, the constitutions previously assigned (*loc. cit.*) to 4 : 4-diphenyl-4 : 5-dihydro-5-glyoxalone must be revised in the sense indicated by the name now employed. The substance was previously regarded as 5 : 5-diphenyl-4 : 5-dihydro-4-glyoxalone by reason of its fission by alkalis to "methylamino-diphenylacetic acid," but it is now held that the constitution of this substance is uncertain, since attempts to synthesise it have not yet been successful.

C. K. I.

Preparation of isoPropylallylbarbituric Acid. F. HOFFMANN-LA ROCHE & Co. (Brit. Pat. 181247).—isoPropylallylbarbituric acid is obtained in 80% yield by the action of allyl bromide

(130 parts) on a solution of isopropylbarbituric acid (170 parts) in 500 parts of water and 135 parts of 30% sodium hydroxide at 25° for twelve hours. The product is collected and crystallised from dilute alcohol. It is sparingly soluble in water, readily soluble in alcohol and ether, and melts at 137—138°. G. F. M.

The Methylalkylpyridazinonecarboxylic Esters. H. GAULT and T. SALOMON (*Compt. rend.*, 1922, 175, 274—277).—*Ethyl 3-methyl-6-pyridazinone-5-carboxylate* is obtained by the reaction in the cold of equimolecular proportions of hydrazine hydrate and ethyl acetonilmalonate in absolute alcoholic solution. It is a crystalline substance soluble in water, m. p. 76—77°. The *hydrazide* of the corresponding acid is obtained if 2 mols. of hydrazine are used in the above reaction. It is a white substance, m. p. 153°. The above ester readily gives a sodium derivative which condenses with alkyl iodides to give 3-methyl-5-alkylpyridazinonecarboxylic esters. *Ethyl 3-methyl-5-ethylpyridazinone-5-carboxylate* prepared in this way melts at 72°. On hydrolysis with 10% sodium hydroxide in the cold, it gives the corresponding *acid*, m. p. 130°, which on heating loses carbon dioxide, giving the methylalkylpyridazinone. *3-Methyl-6-pyridazinone* melts at 94°, and both it and its alkyl derivatives on treatment with dilute mineral acid are converted into α -alkyl-lævulic acids. G. F. M.

Spirans. X. Proof of the Peculiar Spiran Asymmetry by the Preparation of an Optically Active Spiran. HERMANN LEUCHS, EVA CONRAD, and HANS VON KATINSZKY (*Ber.*, 1922, 55, [B], 2131—2139).—Although bishydrocarbostyryl-3 : 3'-spiran, $C_6H_4 \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \cdot \text{CO} \end{smallmatrix} > C \begin{smallmatrix} \text{CH}_2 \\ \text{CO} \cdot \text{NH} \end{smallmatrix} > C_6H_4$ (this vol., i, 471), does not contain an asymmetric carbon atom, it does not possess a plane of symmetry, since the planes of the two rings are at right angles to one another and it should therefore exist in two enantiomorphous, optically active forms. The spiran itself is neutral in character and scarcely suitable for experimental resolution. The communication is devoted to a description of compounds prepared for the purpose of introducing basic or acidic substituents into the molecule and of the resolution of a disulphonic acid into its optically active forms.

Di-p-bromodihydrocarbostyryl-3 : 3'-spiran, colourless, hexagonal leaflets which do not melt below 300°, is prepared by the action of bromine on the parent spiran in boiling glacial acetic acid solution. *Di-op-dichlorodihydrocarbostyryl-3 : 3'-spiran* crystallises in colourless, hexagonal leaflets which are unchanged at 290°. *Di-p-nitrodihydrocarbostyryl-3 : 3'-spiran*, from the spiran and concentrated nitric acid at 70°, forms yellow leaflets which do not melt below 290°, whereas *di-op-dinitrodihydrocarbostyryl-3 : 3'-spiran*, from the spiran and nitric and sulphuric acids at 0°, crystallises in pale yellow needles which darken without melting above 280°. *Bis-dihydrocarbostyryl-3 : 3'-spiran-6 : 6'-disulphonic acid*, colourless, quadratic plates (+aq), m. p. 105—115° after softening at 80°,

*h h**

re-solidification at 140—150°, and decomp. about 260° after becoming yellow at 220°, is prepared by the action of cold concentrated sulphuric acid on the spiran; the corresponding *barium* salt, $C_{17}H_{12}O_8N_2S_2Ba \cdot 8H_2O$, is described. The acid is resolved by quinine in methyl alcoholic solution; from the product the quinine salt of the *l*-acid separates first. *l*-Bisdihydrocarbostyryl-3:3'-spiran-6:6'-disulphonic acid crystallises in needles ($+6H_2O$), m. p. 230—235° (decomp.) after softening at 200°; $[\alpha]_D^{25} -233.8^\circ$ in aqueous solution; the corresponding *barium* salt ($+6H_2O$) has $[\alpha]_D^{25} -189.6^\circ$ in water. *Barium d-bisdihydrocarbostyryl-3:3'-spiran-6:6'-disulphonate* has $[\alpha]_D^{25} +192.2^\circ (\pm 2.6^\circ)$ in aqueous solution.
H. W.

Brominated isoCyanines. KISHORI LAL MOUDGILL (T., 1922, 121, 1509—1511).

The Action of Hydroxylamine and of Hydrazine on the Aryl Monothioamides of Ethyl Acetylmalonate. DAVID E. WORRALL (*J. Amer. Chem. Soc.*, 1922, 44, 1551—1557).—The additive compounds of ethyl acetylmalonate and phenyl-, *p*-bromophenyl-, and *p*-tolyl-thiocarbimides react with hydroxylamine and hydrazine to form, respectively, *isooxazoles* and *pyrazoles*.

3-Anilino-5-ketoisooxazole, $O \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CO \cdot CH_2 \\ N=C \cdot NPh \end{smallmatrix}$, slender, cream-coloured needles, m. p. 186° (decomp.) when rapidly heated (it darkens above 165° and is changed completely to a black tar at 180° when heated), is prepared by the action of two equivalent proportions of hydroxylamine on ethyl acetylmalonatemonothioanilide in boiling alcoholic solution. It forms a *sodium* salt and a *hydrochloride*, m. p. 135° (gas evolution). It is converted by nitrous acid into 3-anilino-4-oximino-5-ketoisooxazole, slender, scarlet needles which deflagrate at 149°. With benzenediazonium chloride, it yields 4-benzeneazo-3-anilino-5-ketoisooxazole, yellow needles, m. p. 195—197° (decomp.). Benzaldehyde converts it into 4-benzylidene-3-anilino-5-ketoisooxazole, orange-coloured needles, m. p. 170—171°. The *isooxazole* is converted by acetic anhydride into the 2(or 5)-acetyl derivative, colourless plates or flattened needles, m. p. 145—146°, and by benzoyl chloride and sodium hydroxide into the benzoyl compound, colourless, lustrous needles, m. p. 157—158°.

Ethyl acetylmalonatemonothioanilide is transformed by two equivalent proportions of hydrazine into 3-anilino-5-ketopyrazole, $NH \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CO \cdot CH_2 \\ N=C \cdot NPh \end{smallmatrix}$, minute, colourless plates, decomp. 255—256°. Its *sodium* salt, *hydrochloride*, *benzoyl* derivative, and *acetyl* compound, needles, m. p. 101°, are described. The *oximino*-derivative crystallises in brilliant, red needles. With benzenediazonium chloride, it gives an *azo-compound*, maroon-coloured, irregular plates, decomp. 211—212°.

3-*p*-Toluidino-5-ketoisooxazole forms diamond-shaped, pale yellow

crystals which blacken and foam at 155—156° after darkening above 145°; the *sodium salt*, *hydrochloride*, *oximino-derivative*, orange-coloured needles, decomp. 142°, and *acetyl compound*, colourless, slender needles, m. p. 149—150°, are described.

3-p-Toluidino-5-ketopyrazole crystallises in small, glistening, square plates, decomp. 246—247°; the *hydrochloride*, lustrous plates, m. p. 72—73°, and *acetyl compound*, m. p. 178—179° after softening, are described.

3-p-Bromoanilino-5-ketoisooxazole forms slender, cream-coloured needles, decomp. 188—189° after softening at 150°. *3-p-Bromoanilino-5-ketopyrazole* crystallises in minute, colourless plates, m. p. 234—235° (decomp.).

Thioacetoacetyl-*o*-toluidide, $\text{COMe} \cdot \text{CH}_2 \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4\text{Me}$, is converted by hydroxylamine mainly into thioacetyl-*o*-toluidide, hydroxyl amine acetate being also formed.

Ethyl acetylmalonatemonothioanilide and phenylhydrazine give mainly acetylphenylhydrazide, m. p. 128°. H. W.

Constitution of the so-called Dithiourazole of Martin Freund. I. PRAPHULLA CHANDRA GUHA (*J. Amer. Chem. Soc.*, 1922, 44, 1502—1510).—Dithiourazole, $\text{C}_2\text{H}_2\text{N}_3\text{S}_2$, has been prepared by Freund and his co-workers (A., 1894, i, 97; 1895, i, 400; 1896, i, 415) by the action of hydrochloric acid on hydrazodithio-

dicarbonamide, and the constitution $\text{NH} \begin{smallmatrix} \text{CS} \cdot \text{NH} \\ \text{CS} \cdot \text{NH} \end{smallmatrix}$ has been assigned to it without experimental evidence being adduced. It is now shown, however, that Freund's dithiourazole contains only one atom of hydrogen replaceable by metals such as potassium, sodium, or silver, and that it loses only one atom of hydrogen from each molecule when treated with ferric chloride, hydrogen peroxide, or iodine with formation of a disulphide, $(\text{C}_2\text{H}_2\text{N}_3\text{S})_2\text{S}_2$, the molecular complexity of which is established by determination of the molecular weight of the allyl derivative. These observations are in harmony with the formula $\text{S} \begin{smallmatrix} \text{C}(\text{SH})=\text{N} \\ \text{C}(\text{NH}) \cdot \text{NH} \end{smallmatrix}$, or

$\text{S} \begin{smallmatrix} \text{C}(\text{SH})=\text{N} \\ \text{C}(\text{NH}_2) \cdot \text{N} \end{smallmatrix}$, for dithiourazole. The existence of a diacetyl compound from which one acetyl radicle is removed with great readiness, whereas the other is firmly retained, is thereby explained as well as the conversion of the monoacetyl derivative into a diacetyl disulphide and into monoacetylalkyl compounds. The reason of the failure of previous workers to obtain dialkyldithiourazoles analogous to the diacetyl derivatives is now rendered obvious.

5-Amino-2-thiol-1 : 3 : 4-thiodiazole is prepared conveniently by Freund's method, but the yields are greatly improved if the action of the acid is interrupted after ten minutes instead of after an hour. The following derivatives do not appear to have been described previously: the *sodium* and *silver* salts; the *compound*, $\text{C}_2\text{H}_2\text{N}_3\text{S} \cdot \text{SHg}(\text{NO}_2)$, from the parent substance and mercuric

nitrite (cf. Rây and Guha, T., 1919, **115**, 261, 541), and the derivative, $C_6H_{12}N_3I_3S_3Hg$, from the nitromercaptide and ethyl iodide (cf. Rây, T., 1916, **109**, 698).

5-Amino-2-thiol-1 : 3 : 4-thiodiazole is decomposed by concentrated hydrochloric acid at 190—200° into hydrazine dihydrochloride, ammonium chloride, carbon disulphide, and carbon dioxide. H. W.

Constitution of the so-called Dithiourazole of Martin Freund. II. New Methods of Synthesis, Isomerism, and Poly-derivatives. PRAPHULLA CHANDRA GUHA (*J. Amer. Chem. Soc.*, 1922, **44**, 1510—1517; cf. preceding abstract).—The only method available hitherto for the preparation of the so-called dithiourazoles consists in the elimination of ammonia from hydrazo-

dithiocarbonamides by the action of concentrated hydrochloric acid, when, simultaneously, iminothiourazole is formed by loss of hydrogen sulphide. It is now shown that dithiourazole (aminothiodiazolethiol) is produced readily from thiosemicarbazide, carbon disulphide, and alcoholic potassium hydroxide solution, potassium hydrazothiocarbonamidethiocarboxylate being immediately formed: $NH_2 \cdot CS \cdot NH \cdot NH_2 + KOH + CS_2 \rightarrow H_2O + NH_2 \cdot CS \cdot NH \cdot NH \cdot CS_2K \rightarrow S < \begin{smallmatrix} C(NH) \cdot NH \\ CS \end{smallmatrix} \cdot NH$ or $S < \begin{smallmatrix} C(NH) \cdot NH \\ C(SH) = N \end{smallmatrix}$.

The method has been found to apply to all substituted and unsubstituted thiosemicarbazides when used in a slightly modified form. Except in the case of thiosemicarbazide itself, the potassium salt of the dithiocarboxylic acid is rarely formed, but, on continued heating, all the thiosemicarbazides without exception yield the corresponding thiodiazole derivatives. Reaction probably occurs in accordance with the scheme: $R \cdot NH \cdot CS \cdot NH \cdot NHR' \xrightarrow{CS_2 + alkali} SH \cdot C(NR) \cdot NH \cdot NHR' \rightarrow S < \begin{smallmatrix} C(NR) \cdot NH \\ CS \end{smallmatrix} \cdot NH + H_2S$. In this connexion,

the synthesis of aminothiodiazolethiol from thiosemicarbazide by the direct action of carbon disulphide is of special significance, since 2 : 5-dithiotetrahydro-1 : 3 : 4-thiodiazole is also formed in small quantity by the action of the liberated hydrogen sulphide on the thiodiazole compound at a high temperature. The second method of synthesis is not of general application. It appears essential that the 1-position of the thiosemicarbazide should always be unsubstituted or substituted by positive groups such as methyl or ethyl; in other words, the basic character of the thiosemicarbazide should be kept unimpaired, so that carbon disulphide can combine with it directly.

The following substances have been prepared. 5-Imino-2-thio-4-phenyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, dull yellow needles, m. p. 183° (from 1-phenylthiosemicarbazide, carbon disulphide, and potassium hydroxide in absolute methyl alcoholic solution). 5-Phenylimino-2-thio-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 208°. 5-Phenylimino-2-thio-3-phenyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 202°. 5-Tolylimino-2-thio-

3-tolyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 205°. 5-Naphthylimino-2-thio-3-naphthyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 218°. 5-Tolylimino-2-thio-3-phenyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 188—189°. 5-Phenylimino-2-thio-3-tolyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 222°. 5-Naphthylimino-2-thio-3-phenyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 219°. 5-Phenylimino-2-thio-3-naphthyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 261°. 5-Naphthylimino-2-thio-3-tolyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 217°. 5-Tolylimino-2-thio-3-naphthyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 268°. 5-Allylimino-2-thio-3-phenyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 145°. 5-Allylimino-2-thio-3-tolyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, dull yellow needles, m. p. 125—126°. 5-Methylimino-2-thio-4-phenyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, dull yellow crystals, m. p. 142—143°. 5-Methylimino-2-thio-4-tolyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, dull yellow needles, m. p. 174—175°. 5-Methylimino-2-thio-3-naphthyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 183°. 5-Methylimino-2-thio-4-naphthyl-2 : 3 : 4 : 5-tetrahydro-1 : 3 : 4-thiodiazole, m. p. 175°.

Potassium thiosemicarbazidedithiocarboxylate is prepared by heating at 70—75° an alcoholic solution of equivalent amounts of thiosemicarbazide, carbon disulphide, and potassium hydroxide; it is converted by iodine into aminothiodiazolethiol disulphide.

Thiosemicarbazide and carbon disulphide at 150° form aminothiodiazolethiol and dithiotetrahydrothiodiazole, m. p. 167°.

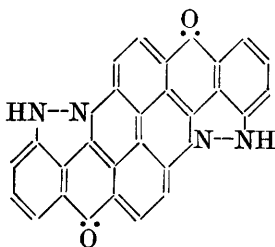
Freund's dithiourazole, m. p. 245°, had m. p. 232° after being preserved during about two months; either variety, when heated with hydrochloric acid at 150°, gave a *modification*, brownish-yellow, rectangular crystals, m. p. 224°.

Freund and Imgart obtained "phenyldithiourazole" in the form of colourless leaflets, m. p. 219°; de-acetylation of acetylphenyliminothiiodiazole gives a tautomeric *variety*, dull yellow needles, m. p. 207°.

Acetylphenyliminothiotetrahydrothiodiazole has m. p. 244° (Freund and Imgart give 252°) when freshly prepared; after being preserved during several weeks it has m. p. 236°. The latter *variety* is also formed when the corresponding diacetyl compound is heated at 175° during five minutes.

H. W.

The Constitution of Pyrazoleanthrone-yellow. FRITZ MAYER and RUDOLF HEIL (*Ber.*, 1922, 55, [B], 2155—2164).—Pyrazoleanthrone-yellow (cf. A., 1913, i, 533) is prepared by the mild action of potassium hydroxide on pyrazoleanthrone and was initially regarded as a derivative of indanthrene. Analyses of the dye, however, agree with the formula $C_{28}H_{12}O_2N_4$ or $C_{28}H_{14}O_2N_4$, according to which two molecules of pyrazoleanthrone are united with loss of two or four atoms of hydrogen. The formation of a potassium salt, of mono- or di-benzyl or substituted benzyl derivatives, and of a dibenzoyl compound proves that the replaceable hydrogen atoms of pyrazoleanthrone are retained in the new dye.



Further insight into its constitution is obtained from attempts to prepare derivatives of it from substituted pyrazole-anthrone. The presence of substituents in position 2 or 4 does not impede the formation of dyes, whereas a substituent in position 8 either inhibits the production of a dye or is removed during the process of formation. The tinctorial properties of the dye indicate that it is allied to flav-anthrene. Its constitution is most pro-

bably indicated by the annexed formula, in which, however, the distribution of valencies is somewhat unusual.

Pyrazoleanthrone-yellow is most conveniently prepared in the ash-free condition by the hydrolysis of its dibenzoyl derivative with sulphuric acid. It is not affected by prolonged treatment with chromic and glacial acetic acids. When distilled with zinc dust, it gives anthracene. The following derivatives are described: *monobenzylpyrazoleanthrone-yellow*, slender, red needles; *p-chlorobenzylpyrazoleanthrone-yellow*, red needles; *o-nitrobenzylpyrazoleanthrone-yellow*, yellowish-red needles; *dibenzoylpyrazoleanthrone-yellow*, pale yellow, transparent rhombs.

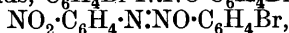
1-Chloro-2-methylantraquinone is converted by hydrazine hydrate and a trace of iodine in boiling pyridine solution into 2-methylpyrazoleanthrone, short, yellowish-red needles, m. p. 298—300°. The latter is transformed by potassium hydroxide and alcohol into 2:2'-dimethylpyrazoleanthrone-yellow, which was not completely purified; the corresponding *dibenzyl* derivative, dark red, slender needles, and *dibenzoyl* compound, a yellow, microcrystalline product, are described.

1-Chloro-4-methylantraquinone is transformed by hydrazine hydrate into 1-hydrazino-4-methylantraquinone, brownish-red needles, m. p. 185—186°, which is converted by aniline and aniline hydrochloride into 4-methylpyrazoleanthrone, slender, yellow needles, m. p. 288—290°. The latter substance yields 4:4'-dimethylpyrazoleanthrone-yellow, which is characterised as its *dibenzoyl* derivative, yellow prisms.

6-Chloro-o-2':5'-dimethylbenzoylbenzoic acid, colourless prisms, m. p. 215°, is prepared from *p*-xylene and 3-chlorophthalic anhydride in the presence of aluminium chloride and is converted by fuming sulphuric acid into 1-chloro-5:8-dimethylantraquinone, thin yellow needles, m. p. 186°. The latter is transformed into 5:8-dimethylpyrazoleanthrone, golden-yellow leaflets, m. p. 291—292°, which could not be converted into a dye by treatment with potassium hydroxide and alcohol. On the other hand, 8-chloropyrazoleanthrone is transformed into pyrazoleanthrone-yellow. H. W.

Azoxyphenols. A. ANGELI, DINO BIGIARI, and GINO CARRARA (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 439—446).—The difference in behaviour towards oxidising agents shown by isomeric azoxyphenols (A., 1921, i, 364) resembles that observed in the action

of halogens or nitric acid on their isomeric monosubstituted derivatives. Thus, of the two para-compounds, $\text{O:NPh:N}\cdot\text{C}_6\text{H}_4\text{Br}$ and $\text{NPh:NO}\cdot\text{C}_6\text{H}_4\text{Br}$, only the latter readily yields the further para-substituted compounds, $\text{C}_6\text{H}_4\text{Br:N:NO}\cdot\text{C}_6\text{H}_4\text{Br}$ and



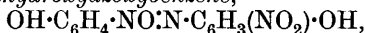
the former resisting the action of bromine or nitric acid. Hence the oxygen atom of the azoxy-group protects the aromatic nucleus united to the nitrogen atom carrying the oxygen from the action, not only of halogens or nitric acid, but also of permanganate.

Further, this protective action is exercised against nitrous acid in cold, dilute solution; in this case, one of the isomeric azoxyphenols remains unaltered, whereas the other, instead of being destroyed, is transformed into a nitro-derivative, usually easy to characterise, the structure of the original compound being thus rapidly established. Azobenzene, azoxybenzene, *p*- α -azoxyphenol ethyl ether, *p*- β -azoxyphenol, and *p*-nitrophenol are not changed when excess of sodium nitrite is gradually added to their glacial acetic acid solutions, whilst *p*-hydroxyazobenzene, *pp'*-dihydroxyazobenzene, *p*- α -azoxyphenol, and *pp'*-dihydroxyazoxybenzene, under the same conditions, readily yield nitro-derivatives in which the nitro-groups occupy ortho-positions with respect to the hydroxyl. For this reaction to occur, it is not sufficient for the aromatic ring to contain a hydroxyl group, it being necessary also that the hydroxylated nucleus be attached to a tervalent nitrogen atom. In the action of nitrous acid on *pp'*-dihydroxyazobenzene, the dinitro-derivative formed is accompanied by *p*-nitrophenol, the reagent acting partly as an oxidising agent; this oxidation is completely analogous to that of hyponitrous acid by permanganate when the latter acts first in an alkaline, and subsequently in an acid, solution.

3 : 3'-Dinitro-4 : 4'-dihydroxyazobenzene, obtained from *pp'*-dihydroxyazobenzene, forms lustrous, greenish-yellow needles, m. p. 236° (decomp.), and is probably identical with the compound, m. p. 240° , obtained by Robertson (T., 1913, 103, 1473) by treating *pp'*-dihydroxyazobenzene in acetic acid solution with concentrated nitric acid.

3-Nitro-4-hydroxyazoxyphenol, $\text{O:NPh:N}\cdot\text{C}_6\text{H}_3(\text{NO}_2)\cdot\text{OH}$, obtained from *p*- α -azoxyphenol, forms transparent, greenish-yellow, rhombohedral plates or green, straw-like crystals, m. p. 125° .

3-Nitro-4 : 4'-dihydroxyazoxybenzene,



prepared from *pp'*-dihydroxyazoxybenzene, forms lustrous, reddish-yellow needles or red, straw-like crystals, m. p. 193° (decomp.).
T. H. P.

The Mechanism of Coupling Reactions. II. 1 : 8-Naphthasultam and its *N*-Methyl Derivative as Azo-components. W. KÖNIG and K. KÖHLER (*Ber.*, 1922, 55, [B], 2139—2149).—In a previous communication (A., 1921, i, 459), the power of aromatic acylamines to couple with reactive diazo-compounds with the formation of normal azo-substances has been attributed to

their ability to react in the enolic form, $\text{Ar}-\text{N}:\text{C}(\text{OH})\cdot\text{R}$ and $\text{Ar}-\text{N}:\text{SR}(\text{:O})\cdot\text{OH}$. An examination of the coupling power of

1:8-naphthasultam, $\text{C}_{10}\text{H}_6\begin{smallmatrix} \text{NH} \\ | \\ \text{SO}_2 \end{smallmatrix}$, has shown this hypothesis to

be erroneous, since the methyl ether of this compound, $\text{C}_{10}\text{H}_6\begin{smallmatrix} \text{NMe} \\ | \\ \text{SO}_2 \end{smallmatrix}$,

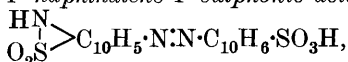
can yield normal azo-compounds in good yield. The absorption spectra of the sultam and its methyl ether prove these substances to be closely related constitutionally, and, in harmony with these observations, sodium naphthasultam is shown to stand in the same relationship to naphthasultam as does sodium α -naphthoxide

to α -naphthol, so that it must be formulated $\text{C}_{10}\text{H}_6\begin{smallmatrix} \text{SO}_2 \\ | \\ \text{NNa} \end{smallmatrix}$ instead

of $\text{C}_{10}\text{H}_6\begin{smallmatrix} \text{S}(\text{:O})\cdot\text{ONa} \\ | \\ \text{N} \end{smallmatrix}$.

The remarkable inability of *p*-toluenesulphonylmethyl- α -naphthylamide, $\text{C}_{10}\text{H}_7\cdot\text{NMe}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_4\text{Me}$, to couple with diazo-compounds is explained by the assumption that the *p*-toluenesulphonyl group hinders the primary additive reaction on which coupling ultimately depends. This influence is not observed with methyl-naphthasultam in which the position of the sulphonyl group is definitely fixed, so that the nitrogen atom can exert its subsidiary valencies.

The following individual substances are described. *N*-Methyl-1:8-naphthasultam, from sodium naphthasultam and methyl sulphate in 75% yield, pale yellow needles, m. p. 125°. 4-1:8-Naphthasultamazo-1'-naphthalene-4'-sulphonic acid,



small, orange-coloured needles, decomp. 320°. 4-*p*'-Nitrobenzene-azo-1:8-naphthasultam, tile-red needles, m. p. 288—289°. 4-*op*-Dinitrobenzeneazo-1:8-naphthasultam, small, red rhombohedra with a strong pale green lustre, which darkens at 305°, but does not melt below 355°. 4-*p*-Nitrobenzeneazo-*N*-methyl-1:8-naphthasultam,

$\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}:\text{N}\cdot\text{C}_{10}\text{H}_5\begin{smallmatrix} \text{SO}_2 \\ | \\ \text{NMe} \end{smallmatrix}$, lustrous, red leaflets, m. p.

236—237°. 4-*op*-Dinitrobenzeneazo-*N*-methyl-1:8-naphthasultam, m. p. 263°. 4-*op*-Dinitrobenzeneazo-1-methylaminonaphthalene-8-sulphonic acid, microscopic, red needles which have no distinct melting point.

H. W.

The Alkylhydrazones. OSCAR LISLE BRADY and GERALD PATRICK McHUGH (T., 1922, 121, 1648—1652).

isoPropyl-, Menthyl-, and Bornyl-semicarbazides. Reduction of Phenylhydrazones. DE WITT NEIGHBORS, A. L. FOSTER, S. M. CLARK, J. E. MILLER, and J. R. BAILEY (*J. Amer. Chem. Soc.*, 1922, 44, 1557—1564; cf. Noyes, Lochte, and Bailey, this vol., i, 329).—Certain semicarbazones and hydrazones can be

successfully reduced by catalytic hydrogenation, whereas the older chemical methods have given only negative results.

Acetonesemicarbazone is reduced by hydrogen in the presence of colloidal platinum to *isopropylsemicarbazide*, rhombic plates, m. p. 128° (*hydrochloride*, short, stout prisms, m. p. 186.5° , *oxalate*, $C_6H_{13}O_5N_3$, large prisms, m. p. 172°); the yield is about 70% of that theoretically possible. A small amount of the semicarbazide is reduced further to *isopropylamine*. *isoPropylsemicarbazide hydrochloride* is transformed by sodium nitrite into the corresponding *nitroso*-derivative, short, pale yellow prisms, decomp. 128° , and by sulphuric acid (80%) into *isopropylhydrazine*, which is identified as the dibenzoyl compound, m. p. 161.5° . *Benzoyl-isopropylsemicarbazide*, needles, m. p. 228° , is converted by sodium hydroxide solution (30%) at 80° into *3-hydroxy-5-phenyl-1-isopropyltriazole*, prisms, m. p. 185.5° . Oxidation of *isopropylsemicarbazide* with potassium permanganate in alkaline solution gives acetonesemicarbazone, whereas in acid solution, *carbamylazopropane*, $NPr^2 \cdot N \cdot CO \cdot NH_2$, dark yellow crystals, m. p. $65.5-66^{\circ}$, is produced (the substance is readily transformed by a trace of alkali hydroxide or by protracted exposure to the air into acetonesemicarbazone). It is probable that the azo-compound is formed intermediately during the oxidation of the semicarbazide in alkaline solution.

Acetaldehydephenylhydrazone is similarly reduced to phenylethylhydrazine, $NHPh \cdot NHEt$, the yield being about 95% of that theoretically possible. It is transformed by potassium cyanate into *phenylethylsemicarbazide*, $C_9H_{13}ON_3$, microscopic needles, m. p. 138° . Acetonephenylhydrazone can be reduced similarly and with equal ease.

Menthonesemicarbazone is catalytically hydrogenated to *menthylsemicarbazide*, colourless, acicular needles, m. p. $179-180^{\circ}$, $[\alpha]_D^{20} -43.8^{\circ}$ in methyl-alcoholic solution. Similarly, camphorsemicarbazone gives *bornylsemicarbazide*, prisms, m. p. 192.5° , which, however, could not be converted into bornylhydrazine by the action of sulphuric acid. H. W.

Ionising Influence of Salts with Tervalent and Quadrivalent Ions on Crystalline Egg-albumin at the Isoelectric Point. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 6, 759—768).—Additional evidence in favour of the formation of ionisable salts of protein with salts containing trivalent and quadrivalent ions is afforded by the observation that lanthanum chloride and sodium ferrocyanide inhibit the heat coagulation of egg-albumin at its isoelectric point; salts containing only univalent or bivalent ions do not have this effect. C. R. H.

Isoelectric Point of the Vegetable Albumin Leucosin. HEINRICH LÜERS and MAX LANDAUER (*Z. Elektrochem.*, 1922, 28, 341—347).—It is shown that the isoelectric point of proteins is one of the most important constants of these substances, and methods for the determination of this quantity are discussed. The isoelectric point of the vegetable albumin leucosin has been deter-

mined by five methods in an acetate buffer solution. The following values are recorded: (1) from the optimum of coagulation 2.6×10^{-5} ; (2) by cataphoresis experiments 2.8×10^{-5} ; (3) from measurements of the optimum of alcohol precipitation 2.7×10^{-5} ; (4) from measurements of the minimum of the internal friction 2.3×10^{-5} ; and (5) from the maximum of the surface tension 2.2×10^{-5} . The mean of the values gives $[H^+] = 2.5 \times 10^{-4}$, from which the relative acidity of leucosin, $k_a/k_b = 8.6 \times 10^4$. The isoelectric point of serum-, vegetable-, and yeast-albumins is thus practically the same; further, there is no noteworthy difference in the chemical composition and it is only in the biological properties that the three substances differ markedly. J. F. S.

The Physical Chemistry of the Proteins. I. The Solubility of certain Proteins at their Isoelectric Points. EDWIN JOSEPH COHN (*J. Gen. Physiol.*, 1922, 6, 697—722).—The proteins investigated were serum-globulin, tuberin, and casein. They were subjected to a rigorous process of purification, of which full details are given. After this treatment it was found that, at 25° , 1 litre of water dissolved 0.07 gram of serum-globulin, 0.1 gram of tuberin, and 0.11 gram of casein. These values were constant within wide limits of variation of the amount of protein exposed to the solvent, and are claimed to be fundamental physical characteristics which may be used in the identification of proteins.

The hydrogen-ion concentration imparted to water by the dissociated ions of the dissolved protein is also a characteristic of the protein employed. C. R. H.

The Combination of Gelatin with Hydrochloric Acid. DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1922, 6, 733—739).—The P_H was determined by hydrogen electrode measurements of 1%, 2.5%, and 5% solutions of gelatin with varying amounts of hydrochloric acid. The amounts of hydrochloric acid required to impart to pure water corresponding values of the P_H were similarly estimated. For the same P_H the difference between the total hydrochloric acid present in the first experiment and that determined by the second one represented the amount in combination with the gelatin. It was found that between P_H 1 and 2 the amount in combination is constant and amounts to 0.00092 mol. for 1 gram of gelatin. C. R. H.

The Mechanism by which Tervalent and Quadrivalent Ions Produce an Electrical Charge on Isoelectric Protein. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 6, 741—757).—Direct measurements of the potential difference between originally isoelectric gelatin and solutions of various salts at P_H 4.7, with which it has been brought into equilibrium, show that a positive charge is imparted to the gelatin by a salt with trivalent kation (lanthanum chloride) and a negative charge by one with a quadrivalent anion (sodium ferrocyanide); salts containing only univalent or bivalent ions produce no charge. The effects of these salts on the osmotic pressure of solutions of isoelectric gelatin are similar to those on

the potential difference. The behaviour of lanthanum chloride towards gelatin is similar to that of an acid, whilst sodium ferrocyanide behaves like a base, and it is assumed that the effects obtained with these salts are due to the formation of complex protein-ions. Thus with lanthanum chloride there is formation of positive protein-lanthanum-ions and negative chlorine-ions; with sodium ferrocyanide of negative protein-ferrocyanide-ions and positive sodium-ions.

At P_H 3.0, when the greater part of the gelatin is ionised, solutions of lanthanum chloride have a depressing effect on the potential difference and the osmotic pressure of the solution, which is identical with that of solutions of sodium chloride and calcium chloride containing equivalent concentrations of chlorine. C. R. H.

The Influence of Aggregates on the Membrane Potentials and Osmotic Pressure of Protein Solutions. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 6, 769—776).—The potential difference between a solution of gelatin chloride in a collodion bag and an outside aqueous solution is practically unaffected if, at the same P_H , part of the gelatin in solution is replaced by powdered gelatin; moreover, the membrane potential can be calculated from the differences in P_H inside and outside the bag, which shows that the gelatin particles take part in the establishment of the membrane equilibrium. On the other hand, the osmotic pressure of a gelatin chloride solution is progressively lowered as the gelatin in solution is replaced by powdered gelatin, showing that the particles of gelatin do not participate in the production of the osmotic pressure of the solution. This is explained by the fact that, since each particle is subject to the conditions of the Donnan equilibrium, a special osmotic pressure is set up in each particle which is balanced by an increase in the cohesion pressure of the particles, and does not therefore manifest itself in the hydrostatic pressure by which the osmotic pressure of the solution is measured; it is due to the gelatin in true solution alone. C. R. H.

The Hydroxyproteic Acids. S. EDLBACHER (*Z. physiol. Chem.*, 1922, 121, 164; cf. this vol., i, 692).—The compound $C_{16}H_{18}O_2N_4$ described by the author (*loc. cit.*) is apparently acetylphenylhydrazine. W. O. K.

The Absorption Spectra of Methæmoglobin, and the Alleged Transformation of Methæmoglobin into Oxyhæmoglobin by the Action of Alkali. G. QUAGLIARIELLO (*Arch. Sci. biol.*, 1922, 3, 65—86; from *Physiol. Abstr.*, 1922, 7, 215).—Neutral methæmoglobin has four absorption bands, at λ 631 $\mu\mu$, λ 576 $\mu\mu$, λ 540 $\mu\mu$, and λ 500 $\mu\mu$. Alkaline methæmoglobin has three absorption bands; the first at λ 600 $\mu\mu$; the other two are in the same place as the second and third of neutral methæmoglobin. The absorption bands in the yellow and green are proper to methæmoglobin, and not due to the presence of oxyhæmoglobin. A transformation of methæmoglobin into oxyhæmoglobin through the action of hydroxyl ions is excluded. W. O. K.

The Prosthetic Group of the Blood Pigments. Hæmatin.

WILLIAM KÜSTER (*Z. physiol. Chem.*, 1922, **121**, 121—134).—*Bromodimethylhæmin*, $C_{36}H_{36}O_4N_4BrFe$, small needles, is prepared from the part of a crude β -hæmin insoluble in chloroform, by boiling with methyl alcohol containing sulphuric acid, and precipitating with 66% hydrobromic acid. Although chlorine cannot be quantitatively eliminated from chlorodimethylhæmin by methyl-alcoholic potash without causing hydrolysis, the bromo-compound can be dehalogenated completely, to form a *dimethylhæmatin*, $C_{36}H_{36}O_4N_4Fe \cdot OH, H_2O$, a dark-coloured compound with a metallic lustre. If this be treated with sodium hydroxide solution at the room temperature, not only does hydrolysis take place, but water is also eliminated. This bears out the view that in the formation of hæmatin from hæmin the bond between the iron and a nitrogen atom is hydrolysed, and that the iron then forms an internal salt with a carboxyl group, eliminating water. If, as in this instance, the carboxyl group is first methylated, the internal salt cannot be formed until the ester is hydrolysed.

Treatment of bromodimethylhæmin with pyridine leads to simple replacement of bromine by hydroxyl, forming *hydroxydimethylhæmin*, $C_{36}H_{36}O_4N_4Fe \cdot OH$, from which a bromodimethylhæmin can be regenerated by treating it in acetone solution with hydrogen bromide solution, although the absolute identity of the compound formed with the initial bromodimethylhæmin is not yet certain.

A particular preparation of hæmatin, obtained from hæmin and de(hydrohalogen)hæmin, was found to be readily methylated by methyl sulphate and alkali to yield a *dimethylhæmatin*, $C_{36}H_{37}O_5N_4Fe$, as an amorphous, dark blue, metallic compound, which with alkali loses a methyl group to form a *monomethyl* derivative, $C_{35}H_{35}O_5N_4Fe$. This dimethylhæmatin was further methylated by boiling with methyl alcohol containing sulphuric acid, and then treating with 66% hydrobromic acid, when a *bromodimethylhæminium trimethobromide*, with the formula $C_{34}H_{30}O_2N(NMeBr)_3(OMe)_2FeBr$, is precipitated, indicating the presence of three basic nitrogen atoms in hæmatin. This new compound is more completely demethylated with alkali than dimethylhæmatin itself, pointing to the opening of the bond between nitrogen and iron on boiling in acid solution. Preparations of hæmatin from formylhydroxylhæmin or from chlorodimethylhæmin were not methylated in a similar manner. In the first case, the compound finally obtained had the formula $C_{39}H_{48}O_7N_4BrFe$. W. O. K.

Hæmocyanin. VI and VII. C. DHÉRE and A. SCHNEIDER (*J. Physiol. Pathol. gén.*, 1922, **20**, 1—13, 34—40; from *Physiol. Abstr.*, 1922, **7**, 218).—Oxyhæmocyanin of *Helix*, *Octopus*, *Homarus*, etc., is easily and rapidly reduced by the passage of inert gas at 15° to 20°, or by exposure to a vacuum at 40°. The solutions were made of pure crystallised preparations, and usually in presence of an antiseptic. The gas must be absolutely deprived of oxygen. The hæmocyanin of *Limulus* may be different. That of the above

animals forms a less dissociable compound with nitrous oxide, but not with methane, ethylene, or acetylene. It does not combine with carbon monoxide, or if it does the compound is very easily dissociable.

W. O. K.

Bile Pigments. XI. The Preparation and Purification of Bilirubin from Ox Gallstones. WILLIAM KÜSTER (*Z. physiol. Chem.*, 1922, **121**, 80—93).—Experiments are described on the preparation and purification of bilirubin from ox gallstones. It is found convenient to isolate the bilirubin in the form of its crystalline compound with ammonia, $C_{33}H_{36}O_6N_4.NH_3$.

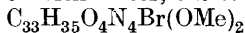
The statement of Reihling (*A.*, 1915, i, 831) that choleprasin yields hæmatic acid on oxidation is apparently to be explained by the presence of some bilirubin in the choleprasin. W. O. K.

Bile Pigments. XII. The Action of Diazomethane on Bilirubin and Biliverdin, the Oxidation of Bilirubin in Alkaline Solution, and the Action of Hydrogen Bromide—Acetic Acid on Bilirubin. WILLIAM KÜSTER (*Z. physiol. Chem.*, 1922, **121**, 94—109).—By treating crude bilirubin, $C_{33}H_{36}O_6N_4$, with diazomethane in ethereal solution, two methyl groups enter the molecule and in addition a molecule of diazomethane is combined, forming a compound, $C_{36}H_{42}O_6N_6$, which on heating loses nitrogen to form the compound $C_{36}H_{42}O_6N_4$. Using bilirubin-ammonia in the methylation, the ammonia group is retained, and a compound, $C_{36}H_{45}O_6N_7$, formed, a dark brown, resinous material, which also loses nitrogen when heated, forming the compound $C_{36}H_{45}O_6N_5$.

Biliverdin, $C_{33}H_{36}O_8N_4$, obtained by the atmospheric oxidation of bilirubin in alkaline solution, forms with alcoholic hydrogen chloride a dimethyl ester, $C_{35}H_{40}O_8N_4$, a dark, lustrous material, and with diazomethane a dimethyl ester of similar composition, although it is not certain whether the preparations are identical.

Bilirubin-ammonia, on long-continued action of alkali hydroxide, and exposure to the air with stirring, yields hæmatic acid and an acid, $C_7H_{10}O_5$ (barium salt, $C_7H_5O_5Ba$; silver salt, $C_7H_8O_5Ag_2$), which may be a methylhydroxyethylmaleic acid.

Treatment with hydrogen bromide—acetic acid and then with water converts bilirubin-ammonia into the compound $C_{33}H_{41}O_8N_4Br$, which on treatment with 10% sodium hydroxide solution loses bromine to form the compound $C_{33}H_{42}O_9N_4$. If the material from the treatment with hydrogen bromide—acetic acid be treated with methyl alcohol instead of with water, the compound



is obtained, which also loses bromine on treatment with sodium hydroxide solution.

Sometimes the reaction with hydrogen bromide—acetic acid, followed by treatment with water proceeds differently, and a compound, $C_{29}H_{39}O_9N_4Br$, is formed which on oxidation forms hæmatic acid, and on reduction hæmatic acid and the imide of methyl-ethylmaleic acid.

W. O. K.

Bile Pigments. XIII. Hexachlororubilic Acid. WILLIAM KÜSTER and WALTER HERRMANN (*Z. physiol. Chem.*, 1922, **121**, 110—120).—By treatment of bilirubin with a mixture of Merck's perhydrol and concentrated hydrochloric acid, *hexachlororubilic acid* is formed, a light yellow powder which, after thorough desiccation, decomposes at about 80°, and has the formula $C_{18}H_{20}O_6N_2Cl_6$. It is a dibasic acid forming a *monomethyl ester*, $C_{19}H_{22}O_6N_2Cl_6$, a citron-yellow powder, on dissolving in methyl alcohol, saturating with hydrogen chloride, and keeping cooled with ice, whilst if the methyl alcohol solution is boiled after saturating with hydrogen chloride, the *dimethyl ester* is formed, which on treatment with sodium hydroxide solution yields the *dimethyl ester* of pentachlorohydroxyrubilic acid, $C_{20}H_{25}O_7N_2Cl_5$. Sodium hydroxide solution removes one of the chlorine atoms from hexachlororubilic acid, forming *pentachlorohydroxyrubilic acid*, $C_{18}H_{21}O_7N_2Cl_5$. Hexachlororubilic acid loses hydrogen chloride slowly on keeping, more quickly on heating in a vacuum, to form a *compound*, $C_{18}H_{19}O_6N_2Cl_5$. With sulphuric acid, it reacts to yield a *compound*, $C_{18}H_{18}O_5N_2Cl_6$, by elimination of water, and with gaseous ammonia it forms the *compound* $C_{18}H_{23}O_6N_3Cl_6$. W. O. K.

Degree of Dispersion of Saccharase. H. VON EULER and GÖETA ERICSON (*Kolloid Z.*, 1922, **31**, 3—7).—A number of diffusion experiments with highly purified yeast saccharase solutions are described from which calculations of the molecular weight of the saccharase particle have been made by means of the formula $D\sqrt{M}=\text{const.}$ The saccharase solutions were purified by a combination of the methods previously used by Willstätter and Racke (A., 1921, i, 823; this vol., i, 598) and the older precipitation methods. In this way, the albuminous substances and yeast gums have been removed and the purity of the saccharase solution increased in the proportion 1:20. The purest material gives an average molecular weight of 20,000 as compared with the values 27,000 and 22,000 found by Euler and Kullberg (A., 1911, i, 825) and Euler, Hedelius, and Svanberg (A., 1921, ii, 170; 1920, ii, 595), respectively. J. F. S.

Influence of Various Antiseptics on the Activity of Lipase. LEROY S. PALMER (*J. Amer. Chem. Soc.*, 1922, **44**, 1527—1538).—Data are presented on the influence of various concentrations of several antiseptics on the hydrolysis of emulsions of milk fat in gum acacia solutions, using commercial steapsin as the source of lipase.

Formaldehyde in concentrations up to one part in two hundred and fifty parts had no detrimental effect on the activity of the lipase, 1% solutions being required to produce a retardation of the enzyme. Chloroform in concentrations from 1.5 to 2.5% retarded the lipase activity from 20 to 60%. Acetone in concentrations of 6% and 12% retarded the lipolysis 12% to 25%. A freshly prepared 3% solution of iodoform in acetone added so as to give a concentration of 0.3% of iodoform retards the lipase action 25% to 40%. When using a similar solution of iodoform,

which had stood for some time, practically complete inhibition was obtained with this and even smaller concentrations of iodoform. In the experimental examination of these results, it was found that iodoform alone retarded lipolysis in direct proportion to the concentration of the iodoform present. This varied from a 15% retardation with 0.03% concentration of iodoform to a 55% retardation with 0.5% concentration of the antiseptic. It was found, also, that old solutions of iodoform in acetone contain free iodine, which has a marked effect on lipase activity. Iodine, in concentrations of 0.045% or more, inhibited lipolysis entirely. Results similar to those with iodine were obtained by the use of bromine water. Higher concentrations of bromine were found necessary to inhibit the lipase, however, concentrations of 0.25% retarding the enzyme activity only 93% to 94%. Mercuric chloride inhibited lipase activity completely in 0.1, 0.2, and 0.3% concentrations. Chloral hydrate not only retarded the lipase, but also failed as a germicide when cow's milk was used as substrate.

The results obtained with the halogens appear to indicate that lipase has an unsaturated structure which is probably aliphatic rather than cyclic. This suggestion is supported by the results on the failure of formaldehyde to retard lipase even in fairly high concentrations.

H. W.

Periodicity of Enzymes. The Lipase of the Stomach.

E. SLUITER (*Nederland Tijdschr. Geneeskunde*, 1922, **66**, 572).—The activity of a solution of lipase, prepared from mucous membranes, and kept in an ice-chest, was determined daily by shaking with an equal volume of milk for twenty-four hours at 39° and titrating the free fatty acid with 0.1*N*-alkali solution. Whether or not the preparation is kept slightly acid, the activity is found to change irregularly in periods of several days. It is not considered that such variations play any part in vivo.

CHEMICAL ABSTRACTS.

Action of Quinine and Atoxyl on Liver Lipase. P. RONA and R. PAVLOVIĆ (*Biochem. Z.*, 1922, **130**, 225—238).—Although liver lipase and serum lipase act identically on tributyrin, liver lipase is not influenced detrimentally by quinine in concentrations which far exceed those which completely inhibit the action of serum lipase. Liver lipase is, however, more sensitive to atoxyl than serum lipase. In the case of both lipases, the velocity constants for the hydrolysis of tributyrin fall off in arithmetical progression as the concentrations of toxic substances are raised in geometrical progression.

H. K.

Isolation of Vitamin. A. SEIDELL (*Abstr. of Bacteriol.*, 1922, **6**, Proc., 101; from *Physiol. Abstr.*, 1922, **7**, 245—246).—An aqueous solution of vitamin is prepared from brewer's yeast by suspending in water and heating at about 90° for several minutes. The coagulated protein is removed and fuller's earth added to the clear solution. The fuller's earth, which selectively adsorbs the vitamin, is filtered, washed, and dried, and designated "activated

solid." The vitamin is most conveniently recovered from the activated solid by rapidly extracting with saturated barium hydroxide solution and acidifying the clear extract with sulphuric acid. Addition of solid barium carbonate removes the excess of acid. The filtered neutral solution is then evaporated and yields a crude extract which will protect pigeons when fed exclusively on polished rice in doses of about 10 mg. every other day. The vitamin extract was subjected to fractionation by silver precipitation, and it was found that a small amount of adenine was present and a larger amount of histidine. The characteristic vitamin action always accompanied the histidine fraction, and it appears possible that either vitamin is a derivative of histidine, or it is a compound of similar chemical properties which accompanies the histidine as an impurity. It was found that when the silver was removed from the histidine-silver precipitate by suspension in dilute hydrochloric acid, the clear solution could be evaporated to dryness on the steam-bath without appreciable impairment of its vitamin activity. The residue so obtained was found to protect pigeons on a diet of polished rice in doses of less than 1 mg. every other day.

W. O. K.

Arsenical Acridine Compound. L. BENDA (U.S. Pat. 1408974). The diazo-compound of 3:6-diamino-10-methylacridinium chloride is treated with sodium arsenite, producing a reddish-brown *powder* which combines with R salt to produce a red *compound* and with resorcinol to produce an orange-yellow *product*. The compound is of low toxicity and its use medicinally is proposed.

CHEMICAL ABSTRACTS.

Organic Mercury Compounds prepared from o-Chloromercuri-p-nitrobenzoyl Chloride. FRANK C. WHITMORE and EDMUND BURRUS MIDDLETON (*J. Amer. Chem. Soc.*, 1922, **44**, 1546—1551).—Phosphorus pentachloride can be used as well as thionyl chloride in the preparation of acid chlorides of mercurated aromatic acid. o-Chloromercuri-p-nitrobenzoyl chloride has been obtained in this manner and converted into a number of its esters. The latter compounds react with inorganic iodides to form the corresponding compounds of the type R_2Hg ; these substances can be hydrolysed without breaking the C-Hg linking.

o-Hydroxymercuri-p-nitrobenzoic acid, prepared by heating mercuric p-nitrobenzoate at 200—220°, is converted by phosphorus pentachloride in the presence of chloroform into o-chloromercuri-p-nitrobenzoyl chloride, which could only be obtained with difficulty in the analytically pure condition. It is transformed by the requisite alcohol into the n-butyl ester, m. p. 125—126°; n-propyl ester, m. p. 145—150°; isopropyl ester, m. p. 179—180°; ethyl ester, m. p. 220—222°; methyl ester, m. p. 240—245°, and chloroethyl ester, m. p. 163—164°. The acid chloride reacts readily with ethylene bromohydrin and diethylaminoethyl alcohol, but a homogeneous product could not be isolated. The position of the mercury complex in the esters is established by the observation that they are converted by cold bromine water and subsequent hydrolysis

into *o*-bromo-*p*-nitrobenzoic acid. *o*-Chloromercuri-*p*-nitrobenzanilide is described.

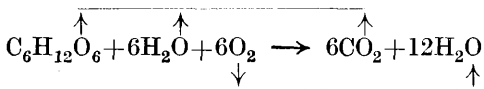
Butyl *o*-chloromercuri-*p*-nitrobenzoate is converted by potassium iodide in boiling ethyl alcoholic solution into *n*-butyl *o*-mercuribis-*p*-nitrobenzoate, $\text{Hg}(\text{C}_6\text{H}_3[\text{NO}_2]\cdot\text{CO}_2\text{C}_4\text{H}_9)_2$, colourless crystals, m. p. 158° ; the compound is converted by a boiling ethyl alcoholic solution of mercuric chloride into butyl *o*-chloromercuri-*p*-nitrobenzoate, m. p. 125° , and by ethyl alcoholic sodium hydroxide solution into *o*-mercuribis-*p*-nitrobenzoic acid. The corresponding *n*-propyl ester, m. p. 189° , and ethyl ester, m. p. $227\text{--}232^\circ$, are described.

n-Butyl *o*-chloromercuribenzoate, m. p. 115° , is prepared by the successive action of phosphorus pentachloride (or thionyl chloride) and *n*-butyl alcohol on *o*-hydroxymercuribenzoic anhydride.

H. W.

Physiological Chemistry.

Is there a Genetic Relation between the Oxygen Inhaled and the Oxygen of the Exhaled Carbon Dioxide? TORSTEN THUNBERG (*Naturwiss.*, 1922, **10**, 417—420).—Hydrogen is regarded as the basic, elementary combustible of living cells; it is supposed to be directly oxidisable by oxygen at low temperatures, in consequence of activation by catalysts. Decomposition of complex compounds occurs by enzyme action through a series of progressive dehydrogenations, the hydrogen eliminated being directly oxidised to water; at the same time, there is addition of water and elimination of carbon dioxide. It is contended that there is no relation between inhaled oxygen and exhaled carbon dioxide; this is represented, for example, by the scheme:



(cf. Dixon, T., 1886, **49**, 94; Wartenberg and Sieg, A., 1921, ii, 107). CHEMICAL ABSTRACTS.

Anæsthetics and Carbon Dioxide Output. I. The Effect of Anæsthetics and Other Substances on the Production of Carbon Dioxide by certain Orthoptera. J. H. BODINE (*J. Expt. Zool.*, 1922, **35**, 323—334).—Ethyl ether (in large doses), acetone, xylene, and formaldehyde produce an increase in carbon dioxide output, followed by a decrease which is irreversible. Chloroform causes a decrease followed by an increase and later by a decrease, the change being irreversible. With small doses of acetone, the increase extends over a long period of time; with large doses it is short-lived; the decrease is to a rate of carbon dioxide output still above normal. With formaldehyde, the

decrease is to the normal rate, but with large doses it is below normal. Ethyl ether, chloroform, acetone, and xylene inhibit respiratory movements in ten to fifteen minutes; formaldehyde in relatively large doses does not inhibit these movements in two hours. These results show that narcosis is not due to asphyxia. Anæsthetics have an action other than that on respiration. Grasshoppers of several species were used in these experiments.

CHEMICAL ABSTRACTS.

Respiratory Metabolism in Alimentary Glycæmia. I. A. BORNSTEIN and KURT HOLM (*Biochem. Z.*, 1922, **130**, 209—224).—In a fasting man oral administration of 100 grams of dextrose causes the blood-sugar content to rise progressively after a few minutes, but respiratory experiments show that the combustion of the dextrose only sets in about half an hour later, often after the blood-sugar has reached or passed its maximum value. When, however, 100 grams of lævulose are administered, the blood-sugar scarcely rises at all, owing to immediate combustion of sugar. Phosphate administration has no influence, but it is thought that the dextrose must first pass into lævulose or a closely related substance before combustion.

H. K.

Direct Measurement of the Partial Pressure of Oxygen in Human Blood. J. BARCROFT and M. NAGAHASHI (*J. Physiol.*, 1921, **55**, 339—345).—The principle of the method is as follows: Blood is withdrawn from a vessel, artery, or vein, by direct puncture; to this blood is exposed a small bubble of alveolar air at 37° until an equilibrium is reached between the blood and the bubble. The bubble is then analysed in a suitable apparatus. The original must be consulted for details. Oxygen pressure in blood can be measured to within 2 mm. on the average. The calculated dissociation curves for venous blood were experimentally confirmed. The observation of Meakins and Davies (*J. Path. Bact.*, 1920, **23**, 451) on the great range of unsaturation of blood from the basilar vein when the arm is exposed to widely differing temperatures was confirmed.

CHEMICAL ABSTRACTS.

Acid Production in Shed Blood. C. L. EVANS (*J. Physiol.*, 1922, **56**, 146—156; from *Physiol. Abstr.*, 1922, **7**, 233—234).—The carbon dioxide capacity of blood is at its highest level in freshly-drawn blood, and usually suffers considerable reduction when the blood is kept. The change is due to conversion of dextrose into lactic acid as a result of glycolysis; it is greatly accelerated by a lowering of the carbon dioxide pressure of the blood, because this gives a P_H favourable to the glycolytic process. These facts are of importance in the plotting of carbon dioxide dissociation curves. When blood-gas phase equilibration is to be carried out at body temperature, the glycolytic change, with its accompaniment of reduction of carbon dioxide capacity, can be inhibited by the addition of 0.05 to 0.1% of sodium fluoride to the blood.

W. O. K.

The Hydrogen-ion Concentration and some Related Properties of Normal Human Blood. J. BARCROFT, A. V. BOCK, A. V. HILL, T. R. PARSONS, W. PARSONS, and R. SHOJI (*J. Physiol.*, 1922, **56**, 157—178; from *Physiol. Abstr.*, 1922, **7**, 233).—Between 20 and 40 mm. pressure of carbon dioxide, the relation between the P_H in the plasma and the pressure of carbon dioxide (pCO_2) is nearly linear. So also is that for the relation between pCO_2 and vCO_2 (volume of carbon dioxide absorbed), the empirical expression being $P_H = 4.7pCO_2/vCO_2$. Hence the relation between P_H and vCO_2 is also linear, and is expressed by the formula $vCO_2 = b(10^3 P_H) + c$, where $b = 8.4 \pm 2$ and $c = 16.6 \pm 10$. The quantity b is a measure of the buffering power of the blood; that is, it expresses the slope of the $vCO_2 - P_H$ curve. The relation between $1/K$ and pCO_2 is not quite linear but slightly S-shaped (K is the constant of Hill's oxygen dissociation equation), although the relation between $\log 1/K$ and $\log P_H$ is linear. W. O. K.

The Comparative Blood-pressure raising Power of Racemic and Lævo-Adrenaline. A. RICHAUD (*J. Pharm. Chim.*, 1922, [vii], **26**, 81—86).—*r*-Adrenaline employed in very small doses of the order of 0.01 mg. increases the blood pressure to a somewhat lesser degree than *l*-adrenaline, but the difference in activity is not by any means so great as has been supposed. It is not constant, but varies from 10—15% in general, although it may be as much as 25—30%. As the dose is increased to 0.04—0.05 mg. the difference in activity disappears entirely, and as the usual therapeutic dose is 0.04—0.1 mg. there is no disadvantage attendant on the use of the racemic compound, and the resolution of the synthetic substance into its optical isomerides is therefore quite unnecessary. G. F. M.

Condition of Electrolytes in the Blood. BENJAMIN S. NEUHAUSEN (*Nature*, 1922, **110**, 8—9).—*E.M.F.* measurements of serum and plasma were made, using 0.2% sodium amalgam as a sodium electrode. Calculation of the total concentrations of sodium on the basis that the degree of ionisation of the sodium salts was the same as in an aqueous solution, gave results which were in very good agreement with those found by analysis. Thus the conclusions of other investigators that sodium is not bound in the serum have been confirmed. Chlorine likewise is apparently as free as in an aqueous solution. A silver|silver chloride electrode was used for these experiments. It is proposed to use a calcium electrode to determine the state of calcium in the blood.

A. A. E.

The Calcium in the Blood in Different Species. P. MAZZOCCO (*Compt. rend. Soc. Biol.*, 1921, **85**, 690—691; from *Chem. Zentr.*, 1922, i, 209; cf. A., i, 788).—The calcium content of the total blood and of individual blood constituents for a number of different animal species is given. The calcium content of blood corpuscles was found to be the same in citrated blood and in blood treated with hirudin. G. W. R.

Influence of Water Supply on the Content of Reducing Substances in the Blood and Urine. A. NORGAARD (*Biochem. Z.*, 1922, **130**, 304—311).—Administration of a litre of water to fasting persons has little effect on the amount of reducing substances in the blood. In the urine, the reducing substances fall off considerably during the increased diuresis, but the actual quantity of reducing substances excreted is not affected. H. K.

The Action of Heterogeneous Proteins in the Organism. A. LÜTTICHAU (*Arch. int. physiol.*, 1922, **19**, 1—16).—The effect on the blood-sugar was investigated of intravenous injection into dogs of solutions or suspensions of egg-albumin, egg-globulin, human saliva, casein, horse-serum, gelatin, ascitic fluid, and Witte's peptone. The ova-proteins, salivary proteins, and casein produced hyperglycæmia, but not glycosuria; the effect of egg-white is due to its globulin content. None of the substances used, except saliva, had any diastatic action on glycogen in vitro. The phenomenon is considered as probably a glucose mobilisation.

CHEMICAL ABSTRACTS.

The Inhibition of Blood Coagulation by Barium, Strontium, and Calcium Chlorides. JÖRGEN LEHMANN (*Skand. Arch. Physiol.*, 1922, **42**, 35—42; from *Chem. Zentr.*, 1922, i, 597).—When blood is mixed with half its volume of barium chloride solution so that the concentration in the mixture is 0.07%, coagulation is inhibited. Calcium has a weaker, and strontium a still weaker effect. G. W. R.

The Reaction of Blood. RUTH E. CONWAY and FLORENCE V. STEPHEN (*J. Physiol.*, 1922, **56**, Proc., xxv—xxvii; from *Physiol. Abstr.*, 1922, **7**, 233).—The inside of the blood-corpuscle is about 35% more acid than the outside. The basic ion concentration is considerably greater in the serum than in the corpuscle. The buffering of laked blood is less efficient than that of unlaked. Cases of pernicious or severe secondary anæmia show an alteration in buffering in direct relation to the percentage of hæmoglobin present. W. O. K.

Calcium Content of Blood Serum in Pregnancy and Childbirth. P. MAZZOCCO and R. BUSTOS MORON (*Compt. rend. Soc. Biol.*, 1921, **85**, 692; from *Chem. Zentr.*, 1922, i, 209—210).—The calcium content of the blood-serum in pregnancy and childbirth is only slightly below normal, namely, 8.77—8.79 mg. per 100 c.c. as against 9.19 mg. per 100 c.c. in normal sera. The calcium content of the serum is thus of no diagnostic value for pregnancy. No correlation can be shown between the fall in serum calcium and the development of pregnancy and its related maladies.

G. W. R.

Eosin Hæmolysis. CARL L. A. SCHMIDT and G. F. NORMAN (*J. Gen. Physiol.*, 1922, **6**, 681—687).—The hæmolysis of red blood cells which takes place on exposure to sunlight in the presence of eosin is inhibited by inorganic reducing agents and certain easily

oxidisable substances such as tyrosine, tryptophan, and other substances which react with the phosphotungstic reagent of Folin and Denis. It is assumed that the hæmolytic action of eosin involves the oxidation of the tyrosine and tryptophan which are contained in the stroma of the cells.

C. R. H.

The Digestibility of Proteins in Vitro. III. The Chemical Nature of the Nutritional Deficiencies of Arachin. D. BREESE JONES and HENRY C. WATERMAN (*J. Biol. Chem.*, 1922, **52**, 357—366).—Arachin is less readily digested in vitro by pepsin and trypsin than, for example, casein. Hydrolysis by hot, dilute sodium hydroxide yields a partial cleavage product which represents about one-third of the original arachin. This product is difficultly digestible in vitro and contains about two-thirds of the histidine, one-third of the arginine and of the cystine, and two-fifths of the lysine present in the arachin from which it was prepared. Further work is necessary to determine if the nutritional inadequacy of the protein is due to this factor.

E. S.

Carbohydrate Metabolism and Diabetes. IV. Dextrose-Nitrogen Ratios in Partially Depancreatized Dogs. F. M. ALLEN and MARY B. WISHART (*J. Metabolic Res.*, 1922, **1**, 97—107; cf. *J. Biol. Chem.*, 1920, **42**, 415; 1920, **44**, 563).—Total pancreatectomy does not invariably give rise to a permanent "total" dextrose:nitrogen ratio of 2.8:1, whilst incompletely depancreatized animals sometimes show this, and sometimes a lower ratio. The total basal metabolism, and the loss of both sugar and nitrogen are higher in the case of totally depancreatized animals, the former partly in consequence of greater protein breakdown.

CHEMICAL ABSTRACTS.

The Threshold of Ketogenesis. RUSSELL M. WILDER and MALCOLM D. WINTER (*J. Biol. Chem.*, 1922, **52**, 393—401).—From calculations, based on a number of assumptions, of the composition of the food being metabolised in certain cases, it is concluded that the molecular ratio of ketogenic substance to dextrose at which significant ketosis first appears is 2:1. This ratio, which is termed the ketogenic threshold, is lowered by infection and possibly also by other factors (cf. Shaffer, A., 1921, i, 754; Hubbard and Wright, this vol., i, 496).

E. S.

The Importance of Zinc in the Feeding of Animals. Experiments on Mice. GABRIEL BERTRAND and B. BENZON (*Compt. rend.*, 1922, **175**, 289—292).—The lives of mice fed on a specially prepared food containing an amount of zinc sulphate equivalent to 0.002% Zn were prolonged from 25—50% beyond those of animals from the same litter fed on the same food prepared absolutely free from zinc.

G. F. M.

The Measurement of Buffer Values and the Relationship of Buffer Value to the Dissociation Constant of the Buffer and the Concentration and Reaction of the Buffer Solution. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1922, **52**, 525—570).—A theoretical paper, the object of which is to give quantitative

expression to buffer effects. For this purpose, the buffer value, β , of a solution is defined as the number of gram equivalents of strong alkali or acid which must be added (strictly without change of volume) to one litre to produce unit change in P_H . Formulated mathematically, $\beta = dB/dP_H$ (cf. Koppel and Spiro, A., 1914, i, 1105, who have given a somewhat similar definition). An increment of strong acid is regarded as a negative increment of strong base; hence the value of β is always positive. Starting from the laws of ionic mass reaction, the following general equation for buffer value has been deduced: $\beta = 2.3(K'[H']C)/(K' + [H'])^2 + [H'] + [OH']$, in which K' represents either K_a/γ_s , or $K_w\gamma_s/K_b$, according as the buffer is a weak acid or a weak base, and C = the molecular concentration of buffer acid (or base). When the P_H is between 3 and 11 and C is not much less than 0.1N, $[H']$ and $[OH']$ may be neglected and the equation simplifies to $\beta = 2.3K'[H']C/(K' + [H'])^2$, an expression which has also been deduced directly from Henderson's equation: $K_a = [H']_{\gamma_s}[Ba]/[Ha]$. Under these conditions, $\beta/C (= \beta_M) = 2.3K'[H']/(K' + [H'])^2$, β_M being termed the molecular buffer value of the buffer acid or base. By differentiation of the last equation, it is shown that the maximum value of β_M occurs when $[H'] = K'$, and it follows that at this point $\beta_M = 2.3/4 = 0.575$ for all buffers. Further, when $K' = [H']$, $[Ha] = [Ba]$; hence at the maximum molecular buffer value half the buffer acid (or base) is present in the free state and half in the form of salt. The above methods have been extended to the calculation of β for solutions of multivalent, amphoteric, and mixed buffers. E. S.

The Relationship of Odour to Molecular Structure. RAYMOND DELANGE (*Bull. Soc. chim.*, 1922, [iv], **33**, 589—630).—Report of a lecture. An extensive bibliography is appended. H. J. E.

Odour Value Analysis. W. G. UNGERER and R. B. STODDARD (*Ungerer's Bull.*, 1922, **3**, 7—10).—It is suggested that odour is the response of the olfactory nerves to intermolecular vibrations, of a magnitude such that they can scarcely be detected. Every pure substance is assumed to have a specific rate of vibration, which may or may not be within those limits which produce the sensation of odour. Support is claimed for this theory from the fact that practically all substances having a perceptible odour are chemically unsaturated. The conception also explains the effect of impurities of characteristic but not powerful odour in modifying to a profound degree the odour of other substances which, in a pure state, may become almost odourless. CHEMICAL ABSTRACTS.

Chemical Composition of Amniotic Fluid. A. LABAT and M. FAVREAU (*J. méd. Bordeaux*, 1921, **92**, 341—342; from *Chem. Zentr.*, 1922, i, 210; cf. Uyeno, A., 1920, i, 201—202).—The authors give the following data for the composition of amniotic fluid: dry matter, 13.30%; organic matter, 6.56%; ash, 6.81%; sodium chloride, 5.25%; protein, 2.40%; urea, 0.28%. Dextrose was found occasionally in small quantities. An increase in dry matter, salts, and protein is found during pregnancy. G. W. R.

Quantity of Combined Carbonic Acid in Cerebrospinal Fluid. E. TOKUOKA and K. OGASAWARA (*Japan Med. World*, 1921, 1, 6; *J. Amer. Med. Assoc.*, 78, 387).—In the spinal fluid of healthy women the combined carbon dioxide averaged 63 vol. %. In the venous blood the carbon dioxide averaged 54.4 vol. %, and is decreased after starvation. In cancerous women, the carbon dioxide was about 3 vol. % in the spinal fluid and 4.7 vol. % less in the blood than in normal women.

CHEMICAL ABSTRACTS.

The Influence of the Concentration of Sugar on the Synthesis of Glycogen. STEFAN ÉDERER (*Biochem. Z.*, 1922, 130, 294—298).—Experiments, in vitro, with dog's liver pulp, on the change of glycogen content with time in presence of various concentrations of dextrose show that glycogen disappears. The fall of glycogen content is inhibited to a large extent by addition of sodium oleate. The glycogen-dextrose balance in the blood is therefore not governed by the law of mass action. H. K.

Unsaponifiable Constituents (Higher Alcohols) of Shark and Rayfish Liver Oils. II. YOSHIYUKI TOYAMA (*Chem. Umschau*, 1922, 29, 237—240, 245—247; cf. Tsujimoto and Toyama, this vol., i, 297).—The liver oil of *Chlamydoselachus anguineus* gave the following constants: d_4^{15} 0.8747—0.8885; acid number, 0.23—0.66; saponification number, 93.4—116.5; iodine number (Wijs), 112.1—136.3; n_D^{20} 1.4703—1.4725; unsaponifiable substances, 37.06—51.65%; acid number of the fatty acids, 182.8—189.8; iodine number of the fatty acids, 77.6—99.7; polybromide number of the fatty acids, 4.80—5.58. The principal constituent of the unsaponifiable substances is oleic alcohol. Squalene is also present together with small amounts of cetyl alcohol and cholesterol.

The oil from the liver of *Scymnorhinus licha* has d_4^{15} 0.8890; acid number, 0.20; saponification number, 98.1; iodine number, 191.5; n_D^{20} 1.4791; unsaponifiable substances, 48.51%. It contains 30% of squalene and selachyl and batyl alcohols.

Oil from the liver of *Centroscyllium Ritteri* has d_4^{15} 0.8917; acid number, 5.10; saponification number, 92.1; iodine number, 213.7; n_D^{20} 1.4812; unsaponifiable substances, 53.06%. The unsaponifiable substances contain squalene, selachyl, and batyl alcohols.

Oil from the liver of *Galeocerdo tigrinus* has d_4^{15} 0.9108; acid number, 0.26; saponification number, 174.0; iodine number, 75.2; n_D^{20} 1.4680; unsaponifiable substances, 11.48%, consisting almost entirely of selachyl and batyl alcohols.

Oil from the liver of *Heptranchias deani* has d_4^{15} 0.9162; acid number, 0.36; saponification number, 174.9; iodine number, 118.5; n_D^{20} 1.4734; unsaponifiable substances, 12.68%, consisting principally of selachyl and batyl alcohols.

Oil from the liver of *Centrophorus sp.* contains 49.7% of squalene and has d_4^{15} 0.8767; acid number, 0.22; saponification number, 54.0; iodine number, 259.8; n_D^{20} 1.4860; unsaponifiable substances, 71.38% containing, besides squalene, selachyl, and batyl alcohols.

Oil from *Zameus squamulosus* and *Centroscyllnus owstonii* contains

42.9% of squalene and has d_4^{15} 0.8816; acid number, 0.88; saponification number, 70.9; iodine number, 225.0; n_D^{20} 1.4825; unsaponifiable substances, 57.17% including squalene, selachyl, and batyl alcohols.

G. W. R.

Autolysis. VIII. The Nature of the Autolytic Enzymes.

H. C. BRADLEY (*J. Biol. Chem.*, 1922, **52**, 467—484).—Dernby (A., 1917, i, 500; 1918, i, 464) has described the autolytic enzymes as closely related to pepsin, trypsin, and erepsin, and has suggested that a mixture of these three enzymes is responsible for the autolysis of tissue. In the present paper, objection is taken to the application of these terms, which connote definite properties, to other proteases, unless these can be shown to have closely similar properties. The presence of erepsin (or the ereptases) in tissue is conceded; evidence, however, is advanced to prove the absence of both pepsin and trypsin. Thus, autolysis of liver or kidney occurs most rapidly in acid mixtures, the optimum P_H being 4.0 to 4.5, and is practically inhibited at P_H 8. Yet in the presence of trypsin the digestion of these organs resembles autolysis of the pancreas and proceeds most favourably at the last-named P_H value. It is evident that trypsin is absent from both liver and kidney. The absence of pepsin is more difficult to prove, since the action of this enzyme, like autolysis, is favoured by acidity. Addition of pepsin, however, to fresh tissue mixture (kidney or liver) at acidities from P_H 6.30 to 1.18 increases autolysis in every case, but the increase is smallest at the optimum for autolysis alone. Moreover, by estimating the amount of primary cleavage by the tyrosine reaction of Folin and Denis (A., 1912, ii, 1012), it is found that, whilst the action of the liver protease is inhibited at P_H 2.6+, that of pepsin not only continues at this acidity but also proceeds most rapidly at P_H 1.2+.

The hypothesis of the autolytic mechanism previously advanced (A., 1916, i, 582) is now extended. At an average P_H of 7.4, the tissue proteins are present as salts of sodium, potassium, and calcium, and in this form are not digested by the autolytic enzymes. With the development of acidity, however, free proteins or acid-protein salts are formed which then undergo cleavage, under the influence of an enzyme which is designated primary protease, into proteoses and peptones. The latter are then rapidly converted into amino-acids by the ereptase present in tissue. The last stage may take place in acid, neutral, or alkaline media, but acidity is essential for the conversion of the native proteins into peptones (cf. Dernby, *loc. cit.*).

E. S.

The Distribution of Quinine Alkaloids in the Animal Organism. EDUARD BOECKER (*Biochem. Z.*, 1922, **130**, 312—320).—Quinine and optochin solutions were injected into guinea-pigs and the quinine and optochin content of the liver and lungs determined approximately by the turbidities produced in aqueous solutions of the extracted alkaloids by potassium mercuric iodide. There is preferential fixation of the alkaloids by the lungs.

H. K.

Cell Penetration by Acids. V. The Estimation of Permeability Changes. W. J. CROZIER (*J. Gen. Physiol.*, 1922, 6, 723—731).—The behaviour was observed of strips of the pigmented mantle tissue of a nudibranch (*Chromodoris zebra*) on immersion in solutions of acids (for the most part dichloroacetic acid). It was found that the rates of penetration by acid and of outward diffusion of pigment bore no relation to one another. Both were facilitated on exposure of the tissue to tension, whereas the rate of acid penetration was accelerated by faradic stimulation and retarded by previous exposure to narcotics such as alcohol and chloroform. C. R. H.

Energy Exchanges in Muscle. OTTO MEYERHOF (*Pflüger's Archiv*, 1921, 191, 128—183; from *Chem. Zentr.*, 1922, i, 153—154; cf. this vol., i, 86, 87).—The "fatigue maximum" with frog muscle in a hydrogen atmosphere or in Ringer's solution corresponds with about 0.35% of lactic acid (calculated on muscle weight). With large additions of carbonate-hydrogen carbonate mixture, the lactic acid is increased to 0.5% and the production of work is also increased. The isometric coefficient, K_m , that is, the tension per centimetre of muscle length per mg. of lactic acid, falls slightly. The "fatigue maximum" is conditioned by the concentration of lactic acid within the muscle. K_m falls during anærobic stimulation and during narcosis. The ratio of the product of isometric tension and muscle length to work produced decreases with length of stimulus. The "work coefficient," K_a , that is, work produced per mg. of lactic acid, falls with increase of temperature and is smaller under ærobic than under anærobic conditions. The maximum potential energy developed in one stimulus is probably never more than 75% of the total energy. The relation between chemical and mechanical processes in the muscle of mammals is probably the same as in muscle of cold-blooded animals.

G. W. R.

The Relation between the Endogenous Katabolism and the Non-protein Constituents of the Tissues. H. H. MITCHELL, W. B. NEVENS, and F. E. KENDALL (*J. Biol. Chem.*, 1922, 52, 417—437).—Analyses were made of the tissue of rats maintained both on normal and nitrogen- and sulphur-free diets. The concentration of amino-nitrogen and of total non-protein nitrogen and sulphur was found to be approximately constant, whilst the value for creatine was slightly higher in the animals on the normal diet. Based on these observations, the view is advanced that the non-protein nitrogenous and sulphur-containing constituents of the tissues serve some special function in the organism other than that of intermediaries in protein metabolism. The endogenous katabolism represents the breaking down, not of tissue protein, but of these substances, which are replaced, normally, from exogenous sources. Only when the latter fail is replacement made by disintegration of body proteins. The conception that protein disintegration is an essential part of cell activity is thus dispensed with.

Creatine, present in the tissues, is an end-product both of endogenous and exogenous metabolism; hence its slightly higher value in the case of the rats on a protein diet. These views are discussed in relation to the literature of the subject. E. S.

Barium in the Viscera. K. BAUMANN (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 383).—A pudding which caused the death of a man through barium poisoning was found to contain 2.34% of barium carbonate. The following quantities of barium sulphate were found in the organs: stomach, liver, and kidneys, 40.0 mg.; urine, 29.0 mg.; intestines, 65.0 mg.; heart, lungs, and spleen, 11.5 mg.; total, 145.5 mg. No barium could be detected in the blood. Three other persons who had eaten of the same pudding suffered from vomiting and diarrhoea, but recovered on the following day. H. C. R.

Constituents of the Japanese Common Earthworm. II. YOSHIHARU MURAYAMA and SHINJIRÔ AOYAMA (*J. Pharm. Soc. Japan*, 1922, 482—492; cf. A., 1921, i, 477).—From the hot water extract of the dried earthworm (*Perichaeta communis* sinca, *Lumbricus Spenceri*) the following substances were isolated: xanthine 0.100%, epiguanine 0.163%, adenine 0.078%, guanidine 0.023%, lysine 0.250%, choline 0.004%, alanine 0.031%, valine 0.237%, leucine 0.464%, and phenylalanine 0.025%. Histidine and arginine were not definitely proved to be present. K. K.

The Presence of Amino-acids in Milk. G. VIALE (*Biochim. terapia sper.*, 1921, **8**, 321—324).—Fresh cow's milk which did not contain nitrogen as ammonia had an average content of 8.6 mg. of amino-nitrogen per 100 c.c. The amino-acids of milk (tryptophan, cystine) do not depend on the presence of a tryptic enzyme, but are secreted by the mammary glands. CHEMICAL ABSTRACTS.

Elimination of Iron in Urine. FRANZ KISCH (*Wiener Arch. inn. Med.*, 1922, **3**, 283—296).—The amount of iron eliminated in the urine is not an index of the amount of destruction of the erythrocytes in the body, as the urinary iron may be increased to a marked degree in pathological conditions in which there is either no, or only a slight, increased destruction of erythrocytes, as in chronic nephritis, catarrhal icterus, myeloid leucæmia, and amyloidosis, and, on the other hand, in conditions in which there is a marked increased destruction of erythrocytes as in pernicious anæmia, the urinary excretion of iron may be smaller than in diseases with no increased destruction of erythrocytes. The urinary elimination of iron is markedly increased in all pathological conditions in which a functional injury to the reticuloendothelial system is present or at least probable. The urinary elimination of iron in general shows no change after the intravenous injection of iron. In one case, however, after splenectomy, an intravenous injection of iron was followed by an increased excretion of iron, indicating that the spleen plays a rôle in intermediary iron metabolism. CHEMICAL ABSTRACTS.

The Presence and Detection of Tyrosine in Urine. O. SCHUMM and A. PAPENDIECK (*Z. physiol. Chem.*, 1922, **121**, 1—17).—Tyrosine can be detected by the Frerichs-Städeler method in normal or pathological urines in quantities of 0.2 gram in 400 c.c. of urine, and by Lippich's method in quantities of 0.01—0.02 gram in 100 c.c. of urine. In a number of cases of icterus, no tyrosine was present. Tyrosine was sometimes although not always present in cases of acute yellow atrophy. Sometimes in the absence of tyrosine, crystals resembling tyrosine were obtained. Being, however, easily soluble in water, and giving a blue colour with phosphotungstic acid and sodium carbonate solution, and showing no Millon's reaction, they were identified as disodium urate.

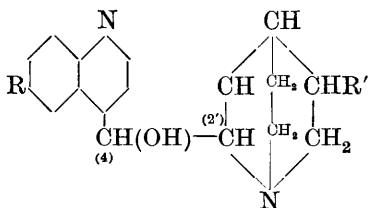
W. O. K.

Hydrogen-ion Concentration of Human Fæces. C. S. ROBINSON (*J. Biol. Chem.*, 1922, **52**, 445—466).—The reaction of human fæces is neutral (P_H 7.0 to 7.5) in normal subjects, but usually becomes acid under the influence of laxatives. The acidity is apparently regulated in the intestine, variations in the reaction being due to a physiological factor rather than to bacterial action. E. S.

Sensory Stimulation by Alcohols and Chlorohydrins. MARIAN IRWIN (*Amer. J. Physiol.*, 1922, **59**, 151—154; 1922, **60**, 270—273).—The effect of saturated monohydric alcohols on the sensory mechanism of the worm *Allolobophora foetida*, and their anæsthetic power are in the following order: methyl < ethyl < tert.-amyl < n-butyl < isoamyl < n-amyl. Experiments with allyl alcohol, ethylene chlorohydrin, glycerol monochlorohydrin, ethylene glycol, and glycerol show that increase in the number of hydroxyl groups results in a diminution of stimulating efficiency, whilst a great increase in efficiency results when a hydroxyl group is replaced by a chlorine atom, an effect which is independent of hydrogen-ion concentration.

CHEMICAL ABSTRACTS.

[Pharmacological Action of] Cinchona Alkaloids. HUGH W. ACTON (*Lancet*, 1922, **202**, 124—128).—The pharmacological action of the cinchona alkaloids is dependent on three factors in the complex alkaloidal molecule (annexed formula): (1) The



grouping of the quinuclidine system around the asymmetric carbon atom at position 2', as shown by their optical rotation. The dextrorotatory alkaloids (named the "cinchonine series") are more powerful in their effects in toxicity on mice and paramœcium, on inhibiting the action of enzymes, on blood pressure

and uterine muscle than the lævorotatory alkaloids (named the "cinchonidine series"), which are more powerful in their local anæsthetic effects. (2) The vinyl group (R') in the quinuclidine system. The natural alkaloids are slightly more toxic to paramœcium than the hydroalkaloids. The hydrogenation of the vinyl group to the ethyl group in the hydro-alkaloids renders these alkaloids more difficult

to oxidise, and they are accordingly not so easily broken down by the body-tissues. They are more toxic to mice, inhibit enzyme action, and cause a greater fall of blood pressure and uterine contraction than the natural alkaloids. (3) The group, R, occupying position 6 in the quinoline ring. The higher members of both series of the hydro-alkaloids are more toxic to mice, paramœcium, bacteria, and leucocytes, and are more powerful as local anæsthetics. This action is not maintained on blood pressure, uterine muscle, and inhibition of enzyme action.

A. A. E.

A New Hypnotic of the Barbituric Acid Series: Ethylbutylbarbituric Acid. PAUL CARNOT and MARC TIFFENEAU (*Compt. rend.*, 1922, **175**, 241—244).—A pharmacodynamical and clinical study was made of a new series of unsymmetrically disubstituted barbituric acids. The hypnotic powers referred to that of diethylbarbituric acid (veronal) as 10, were as follows: methyl-ethylbarbituric acid 5, ethylpropylbarbituric acid 20, ethylbutylbarbituric acid 30, ethylisobutylbarbituric acid 30, ethylisoamylbarbituric acid 30, ethylheptylbarbituric acid 25. As in the symmetrically disubstituted series, the members containing 10 and 11 carbon atoms are the most active, and the ethylbutyl derivative appears particularly suitable for therapeutic use on account of its greater solubility in water, which renders it rapid in action and quickly eliminated. The toxicity of this derivative is proportional to its hypnotic activity, 0.18 gram per kilo. weight of animal being a lethal dose for a mouse, compared with 0.54 gram of veronal. The normal human dose is 0.05—0.1 gram subcutaneously, and 0.1—0.2 gram per os.

G. F. M.

Arsenical Poisoning and the Distribution of Arsenic over the Human Body. H. SCHELLBACH (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 351).—The distribution of arsenic over the body, assuming the weights of the various organs to be normal, in a case of death from arsenical poisoning is calculated as follows: lungs, 6.1 mg.; kidneys, 10.5 mg.; liver, 51.6 mg.; brain, 3.1 mg. expressed as As_2O_3 . The total arsenic taken is estimated as 1 gram of As_2O_3 . The greater part of this was removed from the body again by vomiting and diarrhœa.

H. C. R.

Strychnine. SOMA WEISS and ROBERT A. HATCHER (*J. Pharm. Expt. Ther.*, 1922, **19**, 419—482).—A minimal dose of 0.15 mg. per kilo. body weight of strychnine sulphate produces marked physiological effects on frogs. A method of extraction of strychnine from tissues is described by which, in conjunction with a physiological test on frogs, it is claimed that as little as 0.5 mg. of strychnine in the blood of an adult human being can be detected. Strychnine when added to blood is partly adsorbed by the blood corpuscles (or their stroma after hæmolysis), the proportion adsorbed increasing with increasing concentrations of strychnine.

Strychnine is primarily destroyed by the liver, the kidney only excreting traces which have escaped such destruction.

C. R. H.

Chemistry of Vegetable Physiology and Agriculture.

Increased Velocity and Intensity of Action of Groups of Poisons or Active Drugs on Bacteria and Tadpoles produced by Variation of the Degree of Acidity or Alkalinity. RICHARD LABES (*Biochem. Z.*, 1922, **130**, 14—24).—The toxicity of alkaloidal salts to staphylococci and to tadpoles is the more pronounced the greater the alkalinity of the solution, but the toxicity of sodium salts of active acids, for example, benzoic and salicylic, increases with increased acidity, whilst neutral substances, for example, acetanilide and urethane, act independently of the degree of acidity.

H. K.

Formation of Indole, and Indole Reactions. Behaviour of Indole-negative Bacteria. WALTHER FRIEBER (*Zentr. Bakt. Parasitenkunde*, 1921, **87**, 254—277; from *Chem. Zentr.*, 1922, i, 420).—In an investigation of the formation or non-formation of indole by bacteria, the principal reactions for indole were examined, using indole, indole derivatives substituted in the 2-position (2-methylindole, indole-2-carboxylic acid), indole derivatives substituted in the 3-position (scatole, *p*-indole aldehyde, indole-3-acetic acid, indole-3-pyruvic acid, indole-3-ethylamine, indole-3-alanine, indole-3-glycylalanine), and indole derivatives substituted in the 2- and 3-positions (indole-2:3-dicarboxylic acid, 2-methylindole-3-alanine, indoxylcarboxylic acid, isatin). The sodium nitroprusside reaction is the most specific, being given only with the free indole nucleus. The Ehrlich reaction (*p*-dimethylaminobenzaldehyde), the vanillin, and the naphthaquinone reactions only require the 3-carbon atom to be free, whilst the Salkowski reaction only requires the 2-carbon atom to be free.

All indole-negative bacteria give the positive Salkowski reaction, probably on account of the formation of indole-acetic acid. The decomposition of tryptophan by indole-positive bacteria is probably accomplished in two stages with indoleacetic acid as an intermediate product. In the presence of easily assimilable carbon compounds, indole-positive bacteria may only perform the first stage of tryptophan decomposition. It is unnecessary to assume an inhibition of proteolysis by carbohydrates. No inhibition of the formation of indoleacetic acid by indole-negative bacteria is shown by carbohydrates. Of the bacteria hitherto described as indole-forming, a large number form indoleacetic acid only.

G. W. R.

Bacteria Fermenting Lactose, and their Significance in Water Analysis. M. LEVINE (*Iowa State Coll. Agric.*, **20**, [31], *Bull.* 62).—A critical review of the methods of detection and classification of the colon group of organisms is given. Recent pollution of water is indicated much more certainly by the presence of organisms typified by *Bacillus coli* than by *B. aerogenes* or

Clostridium enteritidis sporogenes. The latter are not considered as characteristic of the intestinal tract and, moreover, persist in water for considerable periods. A. G. P.

The Beneficial Action of Charcoal Suspensions and other Substances with large Surface Development, such as Colloidal Silica, Ferric Phosphate, and Agar-Agar, on the Formation of Fermentation Gases by *Bacillus coli* in Protein-free Nutrient Media. RICHARD LABES (*Biochem. Z.*, 1922, **130**, 1—13).—Finely divided substances of the type named exert a marked beneficial influence in weakly alkaline or acid protein-free nutrient media on the growth of *Bacillus coli* by preventing the detrimental supersaturation of the solution with gaseous products of fermentation. H. K.

Formation of Phenol by Bacteria. FRITZ SIEKE (*Z. Hyg.*, 1921, **94**, 214—223; from *Chem. Zentr.*, 1922, i, 472).—Phenol is formed from the degradation of tyrosine with the removal of the alanine side-chain by bacterial action. Experimental conditions for the culture of phenol-forming bacteria and the morphological, cultural, and serological behaviour of *Bacillus coli phenologenes*, and *B. paracoli phenologenes* are described. Varieties of *B. coli* capable of forming phenol are widely distributed. Indole formation appears to be associated with phenol formation. G. W. R.

Formation of Bacterial Toxins. II. Diphtheria Toxin. L. E. WALBUM (*Biochem. Z.*, 1922, **130**, 25—67).—The optimum temperature for the growth of diphtheria bacilli is 34° and the optimum P_H 7.0. The temperature limits of growth are 20° and 42° and the limits of P_H 5.2 to 8.9. Diphtheria toxin is completely destroyed after six days at 37° if the solution is more acid than P_H 5.5 or more alkaline than P_H 9.3. The optimum P_H for obtaining the toxin is between 7.2 and 7.6. The optimum temperature for toxin formation is 36°. The most suitable medium for preparation of toxin is calf's flesh broth with peptone. The addition of small amounts of manganous chloride has a marked beneficial action on toxin formation in many cases. H. K.

The Utilisation of Dextrose by the Tubercle Bacillus. C. J. GAMBLE and MARGARET C. HERRICK (*Amer. Rev. Tuberculosis*, 1922, **6**, 44—50).—Five strains of *Bacillus tuberculosis*, two human, two bovine, and one avian, consumed dextrose from a liquid medium of 2% dextrose and 0.8% dehydrated broth to the extent of from 12% to 80% (130 to 900 mg.) of the amount originally present (50 c.c.) when estimated by Folin's colorimetric method for blood-sugar (A., 1919, ii, 308; 1920, ii, 337) slightly modified. The amount consumed runs closely parallel to the amount of growth recorded. No differences in the rate of consumption of dextrose by the different strains were detected.

CHEMICAL ABSTRACTS.

Peptase, Lipase, and Invertase of Hæmolytic Streptococcus.

F. A. STEVENS and RANDOLPH WEST (*J. Exptl. Med.*, 1922, **35**, 823—846; cf. *Proc. Soc. Exptl. Biol. Med.*, 1921, **18**, 234).—A method is outlined by which the enzymes of hæmolytic streptococcus can be extracted with comparative ease. The peptolytic enzyme is active between p_H 4.4 and 8.7 with an optimum action at p_H 7.2. It is destroyed in neutral phosphate solution at a temperature of 57° continued for ten minutes and at p_H 5.0 deteriorates slowly at 37° . Concentration experiments with solutions of the enzyme have shown that it resembles other enzymes. It is exceedingly susceptible to chloroform and its action is inhibited by gentian-violet. Casein is attacked, but serum-albumin is not digested after three days at 37° . The invertase is active between approximately p_H 5.0 and 8.0 with an optimum at p_H 7.0. It is destroyed by a temperature of 52° continued for ten minutes at p_H 7.0 or after six hours at 37° at p_H 5.0. At this acidity it is more susceptible to heat than the peptase. The lipase is active above p_H 5.6. The greatest activity was observed at p_H 7.9. It is completely destroyed after heating above 55° for ten minutes and resembles the invertase in its susceptibility to acid.

CHEMICAL ABSTRACTS.

Is the Undecomposed Hydrogen Peroxide or the Oxygen Split from it the Carrier of Disinfecting Action?

A. MÜLLER (*Z. Hyg.*, 1921, **93**, 348—371).—Experiments with *Bacillus coli* in the presence of varying amounts of catalase show that the bactericidal action of hydrogen peroxide is a property of the hydrogen peroxide itself, and not of the oxygen liberated from it.

CHEMICAL ABSTRACTS.

Antiseptic Action of Acraldehyde.

ALBERT BERTHELOT (*Rev. hyg.*, 1922, **44**, 16—19).—Experiments on *Bacillus coli*, *B. mesentericus vulgatus*, *B. subtilis*, and *Staphylococcus aureus* showed that acraldehyde (stabilised by the addition of 0.2% of catechol) both in aqueous solution and as a vapour, is inferior to formaldehyde in its germicidal and inhibitory powers.

CHEMICAL ABSTRACTS.

The Action of Sublimite, Phenol, and Quinine on Yeast.

GEORG JOACHIMOGLU (*Biochem. Z.*, 1922, **130**, 239—248).—From measurements of the loss of weight due to carbon dioxide it is found that the growth of yeast is inhibited by mercuric chloride over the dilutions examined between 1 in 66,000 and 1 in 1,200,000; by quinine hydrochloride at dilutions between 1 in 360 and 1 in 675, but not at higher dilutions; by phenol at 1 in 1000, but not at 1 in 10,000. The so-called Arndt-Schulz law, that small quantities of a poison act in an opposite sense to large quantities, fails.

H. K.

The Occurrence of Emulsin in *Saccharomycetes* and the Existence of a Specific Enzyme Cellobiase.

J. GROENEWEGE (*Mededeel. Algemeen Proefstation voor den Landbouw.*, 1921, No. 9, 1—12).—A new species of yeast, *Willia javanica*, isolated from the

flora developing on moist caoutchouc and capable of splitting amygdalin into glucose, benzaldehyde, and hydrogen cyanide, is described. Pure cultures are easily propagated on usual yeast media; it ferments glucose, lævulose, mannose, sucrose, and raffinose, but not galactose, maltose, lactose, or cellobiose. Culture mediums containing 1% of the glucosides to be investigated were inoculated with the organism and incubated at 33°. After one to two days active splitting was demonstrated in the case of amygdalin, arbutin, æsculin, and salicin by the end-products formed. Fermentation of the glucose liberated occurred in the case of amygdalin and æsculin, but was soon inhibited in the case of the former by the toxicity of the benzaldehyde and hydrogen cyanide formed. By filtering cultures of the organism, drying over calcium chloride, and grinding to a fine powder, a powerful emulsin preparation is obtained which, in respect to purity, activity, and cost, is superior to present commercial preparations. Since *W. javanica* does not ferment cellobiose, the conclusion is that this disaccharide is not hydrolysed by emulsin as its component glucose would be fermented. The power of hydrolysing cellobiose, previously attributed to emulsin, must therefore be ascribed to a specific *cellobiase* occurring as an impurity in ordinary emulsin preparations. It is probable that traces of emulsin reported in brewer's yeast are due to the presence of species of *Willia*.

CHEMICAL ABSTRACTS.

The Fermentation of Glycerol in Presence of Sulphur.

HANS MÜLLER and LEO MÜLLER (*Helv. Chim. Acta*, 1922, 5, 628—629).—In the fermentation of dextrose, the presence of sulphur has the effect of oxidising or dehydrogenating the glycerol, probably according to the equation $C_3H_8O_3 + S = C_3H_6O_3 + H_2S$. In presence of sulphur, glycerol is readily attacked by yeast with evolution of carbon dioxide and hydrogen sulphide. The results are of interest in connexion with Neuberg's investigations of fermentation accelerators (A., 1921, i, 81).

E. H. R.

The Chemistry of the Higher Fungi. XV. Chemical Relations between the Higher Fungi and their Substrate.

II. RUDOLF HASENÖHRL and JULIUS ZELLNER (*Monatsh.*, 1922, 43, 21—41; cf. A., 1910, i, 886; 1921, i, 212).—In previous papers (A., 1914, i, 913; 1920, i, 131), the physico-chemical characteristics of heterotropic phanerogams were to a certain extent elucidated, and an attempt is now made to apply these results to the higher fungi, making use of old and new experimental data. The water content of a fungus is generally higher than that of its substrate or host. The composition of the mineral matter in fleshy fungi is very similar to that in phanerogams, potassium and phosphate being the principal constituents, calcium low, often less than the magnesium, sodium very low, except perhaps in some manure fungi, and iron always present, although sometimes in very small quantities. Precisely what elements are necessary to fungus growth, it is difficult to say; certainly potassium and phosphorus, but calcium is doubtful. The constitution of the substrate appears

not to influence the composition of the ash in fleshy fungi. Data concerning the ash constituents of woody and leathery forms are scanty, and new ash analyses are given of the following: *Polystictus microloma* (Léviér), *Polyporus fomentarius*, L., *P. borealis*, and *Auricularia mesenterica*, Fr. These differ in some respects from the fleshy forms in that potassium is lower and calcium higher. In *Trametes suaveolens*, *Polyporus ignarius*, and *P. fomentarius* calcium sulphate is specially high, and *Polystictus microloma* is extraordinarily rich in sodium chloride. In general, the fungi contain a high proportion of soluble salts, which are necessary to maintain the high osmotic pressure required in the sap of plants containing a high percentage of water. A number of experiments were made to compare the osmotic pressures in different fungi and their hosts, the osmotic pressure being calculated from the analytical figures, assuming the soluble substances present to be dissolved in the total water content. In almost every case, the osmotic pressure of each soluble constituent was higher in the fungus than in the host. In a number of cases, the osmotic pressure was determined from the freezing-point depression of the pressed sap or of an aqueous extract of the fungus reduced to the same concentration as the sap. When the results were compared with isotonic solutions of mannitol and potassium nitrate, it appeared that the mineral constituents found in the ash were far from sufficient to account for the high osmotic pressure of the sap. The discrepancy may be accounted for if a large proportion of the water in the sap, up to 80%, is combined with colloids as water of hydration. It is concluded that the physical and chemical characteristics of the phanerogams are common to the higher fungi.

In connexion with the problem of the manner in which the material of the host is made available for the nourishment of the fungus, experiments were made with the object of detecting cellulose- or lignin-splitting enzymes in a number of fungi, including *Polyporus ignarius*, *P. hirsutus*, *Trametes suaveolens*, *Leuzites sepiaria*, and *Armillaria mellea*, but without success. Analyses were made of a specimen of oak on which *P. ignarius* had been parasitic. The oak had lost 74% of its weight, as shown by its specific gravity, yet although it had lost the whole of its starch, sugar, and tannin, its composition was otherwise not different from that of healthy oak, showing that the material of the oak was taken up equally by the fungus.

E. H. R.

The Arsenic Content of some of the Marine Algæ. A. J. JONES (*Pharm. J.*, 1922, 109, 86—87).—Algæ generally appear to contain a certain proportion of arsenic, varying from about 0.01% in the coarser varieties such as *Laminaria* and *Fucus* sp. to as little as 0.0005% in the so-called edible seaweeds such as "Irish moss" (*Chondrus crispus*), the above percentages being calculated on the air-dried weed.

G. F. M.

Influence of Calcium on the Utilisation of the Reserve Material during the Germination of Seeds. L. MAQUENNE and E. DEMOUSSY (*Compt. rend.*, 1922, 175, 249—252).—In order

to determine whether the favourable influence of calcium salts on germination was due to an activation of the hydrolytic enzymes, or of the enzymes concerned in what may be described as the synthetic phase of germination, the juice of the germinating seeds of maize, wheat, radish, etc., was examined refractometrically for their soluble contents. It was found that calcium salts were practically without influence on the dissolubility of the reserve food material. An analysis of the juice of germinating maize, with and without calcium salts, indicated a smaller total amount of dissolved solids in the former case, although the ratio of the amount of sugars present was slightly higher than the ratio of the other constituents, which might indicate a slight activating effect on maltase. The general conclusion is drawn that the favourable influence of calcium salts is specially directed to accelerating the action of the still unknown enzymes concerned in the synthetic phase, that is, the building-up of celluloses, etc., from the soluble food material of the juice. G. F. M.

The Rôle of Manganese in Plants. J. S. MCHARGUE (*J. Amer. Chem. Soc.*, 1922, **44**, 1592—1598).—Radish, Alaska garden pea, Canada field pea, cowpeas, lettuce, tomatoes, spinach, carrots, onions, garden beans, cabbage, wheat, oats, clover, and velvet beans, when grown in a medium which did not contain manganese, made a normal growth for six or eight weeks, but thereafter developed a chlorotic condition and failed to make further growth of any consequence. The normal condition of the plants during the first few weeks of growth is accounted for by assuming that the manganese which the seed contained was sufficient to maintain a normal metabolic process during this part of the plant's growth, and that the chlorotic condition was a result of the lack of a further supply of available manganese. The first effect to be noted in the growth of plants from which manganese has been withheld is a lack in the development of chlorophyll in the newly formed tissues or the growing parts of the plant. This condition increases with time and finally results in the tips of the branches dying back and a cessation of further growth of any consequence in the plant. Leguminous plants appear to be more sensitive than non-legumes to lack of manganese, thus suggesting that manganese is concerned in nitrogen assimilation and the synthesis of proteins.

Apparently manganese plays the rôle of a necessary catalyst in plant metabolism, and together with iron functions in the synthesis of chlorophyll. H. W.

The Relative Distribution of Carbohydrates in Foliage in its Dependence on Water Content. H. SCHROEDER and TRUDE HORN (*Biochem. Z.*, 1922, **130**, 165—198).—If detached leaves of plants be allowed to wither the starch content falls off much more rapidly than if the leaves be kept turgid by water. In the case of detached leaves of *Tropaeolum majus* kept in the dark, if starch be present the sucrose content increases with diminution of the water content and decreases as the water content increases.

The sucrose content is independent of the content of hexoses if these be expressed in the form lævulose+dextrose. It is probable that the same happens in undetached leaves of plants. H. K.

Antagonistic Ion Effects. WIDAR BRENNER (*Hyllningsskrift tillägnad Ossian Aschan*, 1920, 36—44).—Experiments were carried out on cabbage leaves to show that the coagulation of a negative, hydrophile colloid by hydrogen-ions is counteracted by certain neutral salts. The kations investigated, in the presence of chlorine anion, have a counteracting influence in the following order: $\text{Ca} > \text{Mg} > \text{K} > \text{Na}$. In connexion with nitrate ions the calcium-ion effect is greatly diminished and magnesium and potassium ions produce no effect.

CHEMICAL ABSTRACTS.

Effect of different Kinds of Solar Radiation on the Formation of Essential Oils in Plants. E. CANALS (*Bull. Sci. Ind. Roure-Bertrand fils*, 1921, [iv], 3, 8—13; from *Chem. Zentr.*, 1922, i, 580—581).—Plants of *Thymus vulgaris* were grown under glass of different colours. Plants receiving white and blue light were little different from open-air plants. With red light, however, growth was altered and flowering inhibited. The essential oil from plants under red light contained 25.5% of thymol, from plants under blue light 36% of thymol, and under white light, 45% of thymol. The oil from open-air plants contained 52.5% of thymol. The thymol content of the oil decreases with the decrease in the xerophilous character of the plants.

G. W. R.

Capsella bursa pastoris, Moench. R. WASICKY (*Ber. deut. Pharm. Ges.*, 1922, 32, 142—153).—In order to determine whether *Capsella bursa pastoris* can serve as an ergot substitute, capsella plants in all stages of development were collected in both an infected and a fungus-free condition. The plants were extracted both with water and with alcohol of various concentrations, and fluid extracts were thus prepared from the whole plants and also after separation into their individual organs, such as leaves, stems, fruits, etc. Care was taken to avoid as far as possible any disturbing factors, such as high temperatures, infection, etc. The extracts were injected intravenously into rats, guinea pigs, and rabbits, and also into isolated frog's hearts and the intestines of rats, etc. It was shown that the action of the drug when free from fungus was only such as must be attributed to the potassium salts they contained. The fruits alone contained in addition choline or similar bases, but only in such quantity as to have a negligible influence on the therapeutic action. Infected plants had a more pronounced action probably on account of the presence of proteinogenous bases similar to those in ergot, but in any case the activity fell far below that of an ergot extract. Attempts to isolate acetylcholine according to the directions given by Boruttau and Cappenberg (A., 1921, i, 487) led to a negative result. It is maintained that the platinic chloride method of evaluating capsella extracts (*loc. cit.*) and Grimme's modification (A., 1921, ii, 720) are valueless, as the precipitates do not consist of choline compounds at all, but are potassium salts. Clinical

experiments confirm the uselessness of capsella preparations for staunching uterine bleeding, and it is concluded that the drug is quite useless as an ergot substitute. G. F. M.

Copal Oil, a New Fat of the Belgian Congo. J. PIERAERTS (*Mat. grasses*, 1922, **14**, 6094—6097).—The most important source of copal oil is from the fruit of the *Copaifera Demeusei*. The constants of the oil are: $d^{19.5}$ 0.9165; n^{40} 1.4601; saponification number, 196.2; iodine number, 59.5; Reichert-Meissl number, 0.67; Polenske number, 0.30; Hehner number, 94.6. A drying test made with the oil for one hundred and twenty days resulted in the major portion of the oil retaining its original consistency. The change in weight did not exceed 0.01%. The constants of the fatty acids are: solidifying point, 42°; n^{51} 1.4488; neutralisation number, 196.1; mean molecular weight, 286; iodine number, 62.9; solid acids, 55%, liquid acids, 45%. The constants of the solid acids are: solidifying point, 58.5 to 60°; iodine number, 40.2; neutralisation number, 153.9; saponification number, 171.2. The iodine number of the liquid fatty acids was 138.9.

CHEMICAL ABSTRACTS.

The Oils of Grape Seeds. The Solid Fatty Acids. Method of Separation of Stearic and Palmitic Acids. ÉMILE ANDRÉ (*Compt. rend.*, 1922, **175**, 107—109).—From the solid fatty acids obtained from the oil of grape seeds the author has isolated stearic, palmitic and melissic acids. The last-named acid probably comes from the waxy layer on the outer covering of the seeds. Palmitic and stearic acids may readily be separated for identification by fractional precipitation of their lithium salts from solution of the mixed acids in 95% alcohol. W. G.

Purging Nut Tree Oil. L. (*Mat. grasses*, 1922, **14**, 6099—6101).—The tree, *Jatropha curcas*, Linn., is related to the castor and croton oil plants. The dry seeds contain from 34 to 37% of oil. The constants of three samples of oil from different localities varied as follows: d^{15} , 0.9183 to 0.9207; saponification number, 191 to 193; iodine number, 95.6 to 104.3; acetyl number, 18.7 to 25.4; Reichert-Meissl number, 0.37 to 0.60; Polenske number, 0.22 to 0.24. Heating at 100° for twenty-two hours discolours the oil, and exposing to light and air for seven hours produces a slight drying. The cake contains purgative substances.

CHEMICAL ABSTRACTS.

Nitrogenous Metabolism of the Higher Plants. II. The Distribution of Nitrogen in the Leaves of the Runner Bean. ALBERT CHARLES CHIBNALL. (*Biochem. J.*, 1922, **16**, 344—362; cf. A., 1921, i, 482).—Extensive estimations have been made of the nitrogen content of the leaves of the runner bean, particularly to determine seasonal and diurnal variations and the results of starvation. The results indicate the synthesis of protein from nitric-nitrogen through monoamino-nitrogen, and then the degradation of protein to "other-nitrogen" followed by translocation from the leaf. W. O. K.

Organic Chemistry.

The Energy of the Atomic Linkings in Saturated and Unsaturated Hydrocarbons. J. P. WIBAUT (*Rec. trav. chim.*, 1922, **41**, 441—460).—A theoretical discussion in which it is pointed out that the energy of an ethylenic bond is, from thermochemical data, approximately 20 Cal. less than double the energy of the single bond. A similar relation may be deduced for aromatic hydrocarbons, and also for partly reduced substances derived from them, although in this class of compounds the difference between the energy of the two linkings is estimated at from 7 to 12 Cal. These deductions include accumulated errors, but are derived from a study of all the available data. From the work of Fajans (A., 1920, ii, 354), it appears that the value of a single carbon linking is at least 70 Cal., therefore the smallest value for a double bond is about 120 Cal. and for a triple bond about 160 Cal. By the combination of two CH_2 groups to form C_2H_4 , considerably more energy is evolved than by the combination of two CH_3 groups to form C_2H_6 . No value of the carbon-hydrogen linking is taken into account in the above inferences, so that the conclusions are drawn from the smallest value that can be assigned to a single carbon linking. It results from a consideration of the fact that the thermochemical data do not accord with the usual stereochemical view of the ethylenic bond, and its representation by means of a state of strain existing between the two carbon atoms thus bound.

H. J. E.

Preparation of Propylene in a Pure Condition. MAX TRAUTZ and KARL WINKLER (*J. pr. Chem.*, 1922, [ii], **104**, 44—52).—Propylene is prepared in very good yield by passing propyl, or, better, *isopropyl* alcohol over aluminium oxide or "graphit-tiegelmasse" (Ipatiev, A., 1902, i, 335) at 360° , preferably under diminished pressure. It is purified by passing through a receiver cooled in ice, then over calcium chloride and potassium hydroxide, through a vessel cooled in a mixture of toluene and solid carbon dioxide, and finally over calcium chloride. Pure propylene has the following constants: vapour density, 0—2% higher than corresponds with the molecular weight; d_4^{25} , 0.647; b. p. $-47.8^\circ/750$ mm.; it does not solidify in liquid air; n_{He} yellow 1.00102. The specific volume of a mixture of *cyclopropane* and propylene in the liquid condition is additive, and thus the measurement of the specific volume of such a mixture gives the proportion of the constituents.

W. O. K.

γ -Methyl- Δ^5 -pentene. HORTENSE VAN RISSEGHEM (*Bull. Soc. chim. Belg.*, 1922, **31**, 213—222).—Dehydration of methyl-diethyl-carbinol by means of *p*-toluenesulphonic acid yields a mixture of

the two stereoisomeric γ -methyl- Δ^7 -pentenes which may be separated by fractional distillation. The following physical constants were determined: for the fraction b. p. 65.1—65.7°, d_4^{15} , 0.7220; n_{Ha}^{15} , 1.3974; $n_{\text{H}\beta}^{15}$, 1.4058; $n_{\text{H}\gamma}^{15}$, 1.4108; n_{D}^{15} , 1.3997; for fraction b. p. 69.9—70.2°, d_4^{15} , 0.7022; n_{Ha}^{15} , 1.4047; $n_{\text{H}\beta}^{15}$, 1.4136; $n_{\text{H}\gamma}^{15}$, 1.4186; n_{D}^{15} , 1.4072. It is claimed that this is the first separation of isomeric ethylenic hydrocarbons that has been effected. Both substances are transformed into methyl ethyl ketone on oxidation with chromic acid. The action of bromine on each is merely additive, but aqueous hydrochloric acid acts on the fraction of lower boiling point as an isomerising agent. Like other ethylenic substances, these hexenes undergo spontaneous oxidation with formation primarily of peroxides and subsequently of aldehydic substances.

H. J. E.

The Explosion of Acetylene and Nitrogen. II. WILLIAM EDWARD GARNER and KICHIMATSU MATSUNO (T., 1922, **121**, 1729—1736).

The Chlorination of *n*-Butyl Alcohol. H. GAULT and R. GUILLEMET (*Compt. rend.*, 1922, **175**, 367—369).—An experimental study carried out under various conditions, in presence of metallic iron together with control experiments in absence of the catalyst, shows that the proportion of alcohol unattacked by chlorine is greater in the absence of iron. Chlorination of the heated alcohol yields a smaller proportion of products of high boiling point; this is due to the fact that increase of temperature tends to the formation of acetals and thus at the higher temperature the fixation of chlorine is less complete. The mechanism of the reaction seems to depend in the first place on the oxidation of the alcohol; this is followed by the conversion of the aldehyde into an acetal by the hydrochloric acid which is formed simultaneously. Four substances are produced in quantity, one of which, b. p. 138—140°/15 mm., has been studied. It appears to be a dibutyl acetal of a dichlorobutyraldehyde and forms 60—70% of the total yield. Little effect is produced on it by hydrolytic agents; concentrated sulphuric acid decomposes it almost quantitatively into *n*-butyl alcohol. Oxidation by chromic acid in acetic acid solution yields butyl acetate or, in dilute aqueous solution, butyl butyrate, and in both cases a butyl dichlorobutyrate of b. p. 110°/15 mm. Acetic anhydride yields butyl acetate. The authors conclude that the two atoms of chlorine that are fixed form part of the aldehyde chain, and they assign to the compound the formula $\text{C}_4\text{H}_6\text{Cl}_2(\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CH}_3)_2$.

H. J. E.

Derivatives of Trihalogen *tert*-Butyl Alcohols. IV. The Benzoyl Ester of Tribromo-*tert*-butyl Alcohol or Brometone Benzoyl Ester. T. B. ALDRICH and JULIA E. BLANNER (*J. Amer. Chem. Soc.*, 1922, **44**, 1759—1762; cf. A., 1916, i, 115; 1917, i, 77; 1919, i, 62; 1920, i, 611).—*Brometone benzoate* [*tribromo-tert-butyl benzoate*], monoclinic crystals, m. p. 90°, is prepared in excellent yield when molecular proportions of benzoyl

chloride and tribromo-*tert.*-butyl alcohol are heated together on a water-bath until hydrogen chloride ceases to be evolved. It is not readily saponified. In striking contrast to brometone, the halogen atoms are not readily removed by treatment with sodium hydroxide solution. Its insolubility probably accounts for its lack of physiological action. The interaction of the trihalogeno-*tert.*-butyl alcohols with the three nitrobenzoyl chlorides leads to the formation of the corresponding nitrobenzoates; the meta-compounds are also obtained by treatment of the parent esters with concentrated nitric acid. The following substances are described: *Trichloro-tert.-butyl o-nitrobenzoate*, monoclinic plates, m. p. 91°, *m-nitrobenzoate*, monoclinic plates, m. p. 87°, *p-nitrobenzoate*, flat needles, m. p. 145°; *tribromo-tert.-butyl o-nitrobenzoate*, monoclinic plates, m. p. 97°, *m-nitrobenzoate*, flat needles, m. p. 121°, *p-nitrobenzoate*, needles, m. p. 148°. The esters are not as active physiologically as the alcohols from which they are derived, possibly owing to their insolubility in water. H. W.

The Oxidation of Acetylcarbinol with Potassium Permanganate. WILLIAM LLOYD EVANS and ORA L. HOOVER (*J. Amer. Chem. Soc.*, 1922, **44**, 1730—1741; cf. A., 1916, i, 362; 1919, i, 514, 572).—The series of experiments described in this communication is designed to elucidate the following points: (1) the influence of the initial concentration of the alkali on the character and amounts of the products of the reaction; (2) the effect of variation of temperature on the nature and quantities of the products; (3) the mechanism of the change in neutral and alkaline solution.

Four general reactions, represented by the equations $[\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_3\cdot\text{CHO} + \cdot\text{CH}\cdot\text{OH}$; $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot + \text{H}\cdot\text{OH}$; $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{OH}$; $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}]$, are involved in the oxidation of acetylcarbinol in neutral or alkaline potassium permanganate solutions. The extent to which each reaction contributes to the general oxidation of acetylcarbinol depends on the initial concentration of the alkali used.

Carbon dioxide and acetic acid are the sole products of the oxidation with neutral permanganate solutions at 25°, 50°, 75°, and 100°. Oxalic acid is found in all alkaline solutions except those in which the concentrations of the base are exceedingly small.

The production of carbon dioxide at 50°, 75°, and 100° is in excess of that which corresponds with one gram atom equivalent of carbon. Acetylcarbinol is oxidised to give this excess of carbon dioxide through the following steps: pyruvaldehyde, (hydroxypyruvaldehyde), pyruvic acid, hydroxypyruvic acid, formylglyoxylic acid, and glyoxylic acid. The concentration of the alkali at the peaks of the carbon dioxide yields is approximately the same as that corresponding with the minimum yields for oxalic acid; the yield of carbon dioxide decreases as that of oxalic acid increases.

The general effect of the alkali is to increase the velocity of the oxidation, to convert pyruvaldehyde into lactic acid, to increase

the enolisation of pyruvic acid, to increase the enolisation of the acetylcarbinol according to the schemes : $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_3\cdot\text{C}(\text{OH})\cdot\text{CH}\cdot\text{OH}$ and $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OH} \rightleftharpoons \text{CH}_2\cdot\text{C}(\text{OH})\cdot\text{CH}_2\cdot\text{OH}$, and to lower the dissociation point of acetylcarbinol in accordance with the expression : $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_2\cdot\text{OK} \rightarrow \text{CH}_3\cdot\text{CO}\cdot\text{CH}\cdot + \text{KOH}$.

The yields of acetic acid reach a second maximum and those of oxalic acid a second minimum in solutions in which the initial concentration of potassium hydroxide is approximately 0.5*N*; these points are also a function of the temperature.

The effect of temperature on the yield of the products of oxidation varies in different regions of alkalinity. H. W.

Action of Bromine on Methylal. FRANZ FEIST (*Z. angew. Chem.*, 1922, **35**, 489—490).—The addition of bromine to methylal, cooled in a freezing mixture of ice and salt, leads to the formation of methyl bromide, dibromomethylal, $\text{CBr}_2(\text{OMe})_2$, and products of higher boiling point which could not be freed from an excess of bromine without undergoing decomposition, and have not been investigated further. Dibromomethylal is a colourless liquid with a somewhat unpleasant odour, b. p. 14.5—15°. It is very readily hydrolysed. It is highly reactive and, at 0°, effects the methylation of a series of substances which are not affected by methyl bromide under similar conditions. When treated with water, it gives methyl alcohol, hydrogen bromide, and carbon dioxide, together with formaldehyde and formic acid. With aniline dissolved in ether, it yields methylaniline hydrobromide and carbon dioxide. It converts β -naphthol into β -naphthyl methyl ether, ethyl sodio-malonate in the presence of light petroleum into ethyl methyl-malonate, and ethyl sodioacetoacetate into ethyl methylacetoacetate. Cinnamic acid is not esterified by dibromomethylal, whereas its sodium salt is converted into methyl cinnamate. H. W.

Vapour Densities at Low Pressures and over an Extended Temperature Range. I. Properties of Ethylene Oxide compared to Oxygen Compounds of Similar Molecular Weight. O. MAASS and E. H. BOOMER (*J. Amer. Chem. Soc.*, 1922, **44**, 1709—1728).—The vapour pressure, boiling point, melting point, surface tension, critical temperature, viscosity, and liquid density of pure ethylene oxide have been determined, and these physical constants compared with those of methyl ether, ethyl alcohol, and acetaldehyde. The following data are recorded : m. p. —111.3°, b. p. 10.73°, critical temperature, 192.0°, molecular heat of vaporisation, 6.00 Cal.; *K* (Ramsay and Shields), 1.79; surface tension at the boiling point, 25.8; total surface energy, 73.1; molecular volume at the boiling point, 49.9; molecular viscosity at slope 0.0000323, 0.0412; molecular viscosity at slope 0.0000987, 0.0785. The particularly good agreement of the surface tension data over the range —52.0° to +20.0° with the modern theory is pointed out. The comparison of the physical properties with those of the other substances mentioned emphasises the ring structure of ethylene oxide. The investigation of the oxonium compound formation, by means of freezing-point curves of the

binary systems between ethylene oxide and chlorine, bromine, water, hydrogen chloride, and hydrogen bromide, respectively, furnishes evidence of the existence of double compounds, $C_2H_4O.Cl$, $C_2H_4O.Cl_3$, $C_2H_4O.Br$, $C_2H_4O.Br_2$, $C_2H_4O.6H_2O$, and the probable existence of a compound with hydrogen bromide. The compounds with chlorine and bromine exist only at low temperatures, at higher temperatures an interatomic rearrangement taking place. The vapour density of ethylene oxide over the temperature range $14-100^\circ$, and the pressure range 0—1 atmosphere was measured, and it is pointed out that these data will serve for obtaining data on the relative molecular attraction. J. F. S.

Preparation of Water-soluble Derivatives of Aryl Ethers of Higher Aliphatic Alcohols. ELEKTROCHEMISCHE WERKE G. M. B. H., HEINRICH BOSSHARD, and DAVID STRAUSS (D.R.-P. 344878; from *Chem. Zentr.*, 1922, ii, 834—835).—Aryl alkyl ethers, obtained by condensation of naphthols or phenols with halogen-substituted aliphatic hydrocarbons containing at least sixteen carbon atoms, using appropriate catalysts, are sulphonated until they are soluble in water. *Monochloroparaffin*, obtained by chlorination of paraffin, is a white, wax-like substance having m. p. $35-40^\circ$; it gives, on heating with phenol, potassium carbonate, and carbon in a reflux apparatus, *phenoxyparaffin*, a soap-like mass having m. p. 60° . The corresponding *sulphonic acid* is a semi-solid, fat-like substance soluble in water. Its dilute aqueous solution may be used for tanning. Similar sulphonic acids may be obtained from *o*- or *p*-tolylloxyparaffin and cetylguaiacol. *Phenoxychloroparaffin*, obtained from *dichloroparaffin* (m. p. $40-60^\circ$) and phenol, and α - or β -*naphthoxyparaffin* are similar to phenoxy-paraffin. G. W. R.

The Reactivity of Alkyl Iodides with Sodium Benzyloxide and the Effect of Temperature on such Reactions. PERCY CHARLES HAYWOOD (T., 1922, 121, 1904—1921).

Action of Silver Sulphate in Sulphuric Acid Solution on certain Halogen Derivatives. E. A. SCHILOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1921, 4, 169—170).—A solution of silver sulphate in concentrated sulphuric acid acts on methyl iodide, ethyl chloride or bromide, or ethylene bromide more energetically than an alcoholic solution of silver nitrate of identical concentration. The reaction proceeds in 100% sulphuric acid, but is greatly influenced by the presence of water, the function of which has not yet been explained.

With ethyl bromide and a strong sulphuric acid solution of silver sulphate, the products obtained include silver bromide and ethylsulphuric acid, but not ethyl sulphate; the latter undergoes only slow conversion into ethylsulphuric acid under the influence of concentrated sulphuric acid and is hence not formed even as an intermediate product. The amount of ethylsulphuric acid separable as barium salt amounts to only about 77% of the calculated quantity. Since in the sulphuric acid solution the silver

probably exists as the complex ion AgSO_4' , the energetic action on alkyl haloids is scarcely compatible with Bruyn and Steger's theory (A., 1899, i, 745, 849), which assumes electrolytic dissociation of the silver salt and alkyl haloid. T. H. P.

The Autoxidation of Organic Sulphur Compounds. MARCEL DELÉPINE (*Bull. Soc. chim.*, 1922, [iv], **31**, 762—789; cf. this vol., i, 261).—A general survey of the subject in which the bearing of the work of Moureu and Dufraisse (this vol., i, 250) on organic sulphur compounds is discussed. The facts observed in studying the effect of pressure on oxidation of phosphorus (Jorissen, A., 1921, ii, 79, 688) are considered in their relation to the oxidation of sulphur compounds. As a provisional hypothesis, the author suggests that sulphur compounds form a group intermediate between those substances which are spontaneously inflammable in air or oxygen and others, such as benzaldehyde, which undergo oxidation with the formation of more stable compounds. H. J. E.

Behaviour of $\beta\beta$ -Dichlorodiethyl Sulphide. S. P. KRAMER (*Kolloid Z.*, 1922, **31**, 150—151).—When $\beta\beta$ -dichlorodiethyl sulphide is shaken with 5 c.c. of 1% sodium silicate solution, it is shown that in two hours each drop of the sulphide is surrounded by a sheath of colloidal silicic acid, and in forty-eight hours the whole tube is filled with colloidal silicic acid gel. The dichlorodiethyl sulphide is hydrolysed to dihydroxydiethyl sulphide, and the hydrochloric acid set free liberates colloidal silicic acid. By this change, the oil has lost its inflammatory properties and may be placed on the skin with impunity. A 10% solution of $\beta\beta$ -dichlorodiethyl sulphide in olive oil or cod-liver oil, when added to 1% sodium silicate solution, is immediately emulsified and on centrifuging the hydrolysed product separates. The above experiments furnish a method of treatment of burns produced by "mustard gas." The wound is washed and covered with olive oil or cod-liver oil and then washed with a 1% solution of sodium silicate. It is then covered with a compress moistened with 3% sodium silicate solution so long as it remains inflamed. J. F. S.

Improvements in the Process of Converting Organic Acids into Esters. ERNST ZOLLINGER-JENNY (Brit. Pat. 183897).—The conversion of organic acids, other than polyhydroxy-fatty acids, into esters is greatly simplified and accelerated by the use of zinc or tin or other metals of the periodic group including tin. The metal need not necessarily be in a finely-divided state; it may be introduced into the apparatus in the form of a regulus, or be applied to the floor or wall or to a body inserted into the vessel. As soon as the temperature of reaction is reached and maintained, the conversion sets in and proceeds with considerable speed until the mixture is neutral. It is not essential to have an excess of the alcoholic component; the mixture may be in stoicheiometrical proportions. Organic acids of the highest molecular weights, including resin acids, can be converted into esters in this way, and the process can be applied, not only to pure, free fatty acids,

but also to fatty acids mixed with fat or diluted with primary monohydric or other alcohols.
H. W.

The Solubilities of the Alkali Formates and Acetates in Water. NEVIL VINCENT SIDGWICK and JOSEPH ALFRED HECTOR ROBERTS GENTLE (T., 1922, 121, 1837—1843).

The Transformation of Sodium Formate into Oxalate. C. MATIGNON and [MLE] G. MARCHAL (*Bull. Soc. chim.*, 1922, [iv], 31, 789—796; cf. Merz and Weith, A., 1882, 1049).—A study of the reactions which take place on heating sodium formate to 440° shows that its decomposition is rapid. No appreciable difference is made in the yield of sodium oxalate by heating in a vacuum when compared with the results obtained by heating in air in presence of a catalyst. Sodium hydroxide when present to the extent of 4% is a satisfactory catalyst and increases the yield of oxalate from 50% to 85%; as it is normally present as impurity in commercial sodium formate, a better yield is obtained from the latter than from the pure substance. A method of isolating the oxalate from the reaction mixture is described.
H. J. E.

Preparation of Acetic Anhydride, Acetaldehyde, or Acetic Acid from Ethylidene Diacetate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 346236; from *Chem. Zentr.*, 1922, ii, 808).—Ethylidene diacetate is heated under reduced pressure in the presence of contact substances. The acetic anhydride thus formed is separated by distillation from paracetaldehyde with or without depolymerisation or oxidation of the latter. For example, after heating ethylidene diacetate (400 parts) with sulphuric acid (8 parts) at 70—80° under 100 mm. pressure, the resultant mixture of acetic anhydride and paracetaldehyde is either maintained at a medium temperature or heated with a depolymerising substance, whereby acetaldehyde is obtained and separated by distillation. Alternatively, the paracetaldehyde is oxidised to acetic acid by a stream of oxygen.
G. W. R.

Acetic Acid Esters of Multivalent Alcohols. I. Is there a Connexion between the Velocity of Saponification and the Method of Preparation of the Glycerol Acetins? L. SMITH (*Z. physikal. Chem.*, 1922, 102, 54—73).—After a short discussion on the constitution of the glycerides, the author draws the conclusion that all methods of determining the constitution of these substances which depend on the products of reaction with other substances and the subsequent examination of the products are worthless, and that for the determination of constitution some physico-chemical property must be employed which will allow the glyceride being studied "in statu." Of such physico-chemical properties, the velocity of saponification appears to be most suitable. The author has synthesised mono-, di-, and tri-acetin by a number of methods, and has used the various products to determine the velocity of saponification at 25°. The results show that the velocity of the acetins in alkaline aqueous solution is within

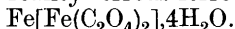
the limits of experimental error (1%), independent of the method of preparation.

J. F. S.

Decomposition of Methyl Oxalate by Acetic Acid. E. E. TURNER and F. H. H. WILSON (*Proc. Roy. Soc. New South Wales*, 1921, **55**, 63—64).—When methyl oxalate is heated with acetic acid in a reflux apparatus, it is more or less completely converted into methyl acetate and oxalic acid. Using acetic acid of 70% concentration, an 83% yield of methyl acetate is obtained; stronger and weaker acids give lower yields. Since methyl oxalate can be readily obtained in a pure state from commercial methyl alcohol, a convenient means is afforded for preparing pure methyl acetate.

E. H. R.

The Preparation of certain Ferrioxalates. G. J. BURROWS and E. E. TURNER (*Proc. Roy. Soc. New South Wales*, 1921, **55**, 263—265).—Barium ferrioxalate is obtained by heating in aqueous solution the calculated quantities of ferric sulphate, barium hydroxide, and oxalic acid, and extracting the barium ferrioxalate with boiling water. The salt crystallises in slender, pale green needles of the composition $\text{Ba}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]_2 \cdot 12\text{H}_2\text{O}$. Hydrates containing 7, 21, and 22 molecules of water have been described by various authors. Starting with ferric ammonium sulphate, a barium ammonium ferrioxalate was obtained in addition to the normal barium salt. It crystallises, by spontaneous evaporation of the filtrate from the barium salt, in bright green prisms of the composition $\text{NH}_4 \cdot \text{Ba}[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 3\text{H}_2\text{O}$. The yellow colour of ferrous oxalate, both in the solid state and in dilute sulphuric acid solution, suggests that it may be in reality ferrous ferro-oxalate,



Cinchonine ferrioxalate crystallises from dilute alcohol in pale green needles having the composition $(\text{C}_{19}\text{H}_{22}\text{ON}_2)_3 \cdot \text{H}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 6\text{H}_2\text{O}$. *Strychnine ferrioxalate*, $(\text{C}_{21}\text{H}_{22}\text{O}_2\text{N}_2)_3 \cdot \text{H}_3[\text{Fe}(\text{C}_2\text{O}_4)_3] \cdot 12\text{H}_2\text{O}$, forms pale green leaflets. Attempts to resolve ferrioxalic acid into its optically active components by recrystallisation of the strychnine salt were unsuccessful.

E. H. R.

The Formation and Stability of Spiro-compounds. IX. The Influence on Stability of Groups of High Molecular Weight. STANLEY FRANCIS BIRCH and JOCELYN FIELD THORPE (*T.*, 1922, **121**, 1821—1837).

A Method for the Preparation of $\alpha\beta\beta$ -Trialkylated Glutaric Acids. GEORGE ARMAND ROBERT KON and JOCELYN FIELD THORPE (*T.*, 1922, **121**, 1795—1803).

Ring-chain Tautomerism. III. The Occurrence of Tautomerism of the Three-carbon (Glutaconic) Type between a Homocyclic Compound and its Unsaturated Open-chain Isomeride. CHRISTOPHER KELK INGOLD, EDWARD ARTHUR PERREN, and JOCELYN FIELD THORPE (*T.*, 1922, **121**, 1765—1789).

Zirconyl Citrate. F. P. VENABLE and R. A. LINEBERRY (*J. Amer. Chem. Soc.*, 1922, **44**, 1708—1709).—The addition of ammonium or potassium citrate to solutions of zirconyl chloride gives precipitates, soluble in excess of ammonium citrate, which may be washed free from ammonium and potassium compounds. The precipitates are therefore not double citrates, as was stated by Harris (A., 1899, i, 262). Normal zirconyl citrate, $(\text{ZrO})_3(\text{C}_6\text{H}_5\text{O}_7)_2$, may be prepared by the slow addition of a 0.1*M*-solution of citric acid to a freshly prepared 0.1*M*-solution of zirconyl chloride. If the zirconyl chloride is boiled before precipitation, the basic compound, $3\text{ZrO}(\text{OH})_2(\text{ZrO})_3(\text{C}_6\text{H}_5\text{O}_7)_2$, is obtained. J. F. S.

Clupanodonic Acid. M. TSUJIMOTO (*Chem. Umschau*, 1922, **29**, 261—262).—The highly unsaturated acid to which the peculiar odour of fish oils is probably due has the formula $\text{C}_{22}\text{H}_{34}\text{O}_2$, and not $\text{C}_{18}\text{H}_{28}\text{O}_2$, although a small quantity of an acid having the latter formula occurs in Japanese sardine oil. Majima and Okada found that the acids obtained by the debromination of the ether-insoluble bromides from Japanese sardine oil gave mainly behenic acid on hydrogenation. Clupanodonic acid has been obtained almost pure by fractionating the methyl esters obtained from the highly unsaturated acids from Japanese sardine oil by the lithium-salt-acetone method. It is a pale yellow liquid not solidifying at -50° , and thick, like vaseline, at -78° . It has a fishy odour and the following characters: d_4^{20} , 0.9398; neutralisation value, 172.5; iodine value (Wijs), 390 (theoretically 384.3); n_D^{15} , 1.5040. The methyl ester has d_4^{15} , 0.9247; b. p. $222^\circ/5$ mm.; n_D^{15} , 1.4960. Clupanodonic acid is one of the most widely distributed compounds in nature, occurring in the oils of all fresh- and salt-water fish, reptiles, and amphibious animals. H. C. R.

The Oxidation of Hydrocarbons, with Special Reference to the Production of Formaldehyde. E. W. BLAIR and T. SHERLOCK WHEELER (*J. Soc. Chem. Ind.*, 1922, **41**, 303—310t).—The limited oxidation of ethylene by oxygen at high temperatures in presence and absence of a catalyst was studied with the object of discovering the most favourable conditions for the production and possible manufacture of formaldehyde. The conclusions of Willstätter and Bommer (A., 1921, i, 93) were confirmed, and to some extent amplified. When a catalyst (platinum gauze) was used, even when the temperature was so low and the time of contact so short that a reaction was barely perceptible, hydrogen and carbon monoxide were the main products. Traces of formaldehyde were detected, however, showing that the course of the oxidation is the same as in absence of a catalyst. Extending Willstätter's and Bommer's experiments without a catalyst, it was found that as the time of heating at any given temperature decreased, the ratio of acetaldehyde to formaldehyde increased; the percentage yield of aldehyde on ethylene increased, and at 540° , heating for 1.5 secs., no carbon monoxide was formed. Decreasing the proportion of ethylene in the mixed gases below the 20% used by Willstätter also increased the yield of formaldehyde. A number

of experiments were made in which the reacting gases were continuously circulated, and a yield of 75% theory of formaldehyde on the ethylene consumed was obtained at 575° with a heating time of 1 second, starting with a mixture containing 19.4% of ethylene and 15.8% of oxygen. It was not found possible to work with mixtures containing less than 14% of ethylene. These are inflammable, the ignition temperature being 546°. Below this temperature the reaction is very slow and the proportion of acetaldehyde formed increases. Ammonia was found to stabilise the formaldehyde as formed, by combining with it to form hexamethylenetetramine; using ammonia in the mixed gases, it was possible to isolate some formaldehyde in experiments in which a catalyst was used. Steam also had a stabilising effect, and experiments in which steam was used showed that formaldehyde is produced even when inflammation occurs. Steam and ammonia have also a protective action on the formic acid produced.

The frequent occurrence of acetaldehyde in the oxidation products, particularly when the reaction is slow, favours the view that it, and not dihydroxyethylene, is the chief intermediate product (cf. Bone and Wheeler, T., 1904, **85**, 1637). On the hydroxylation theory, the scheme $\text{CH}_3\cdot\text{CHO} \rightarrow \text{OH}\cdot\text{CH}_2\cdot\text{CHO} \rightarrow 2\text{CH}_2\text{O}$ is quite possible.

E. H. R.

A Solid Water-soluble Formaldehyde Preparation. ROBERT COHN (D.R.-P. 345145; from *Chem. Zentr.*, 1922, ii, 1007).—Calcium lactate is dissolved in 35% formaldehyde solution at about 90°. The white, crystalline mass obtained on cooling contains formaldehyde in the unpolymerised state and readily soluble in water. The product contains 12–14% of formaldehyde. It may be used in pharmaceutical preparations.

G. W. R.

Vapour Pressure of Acetaldehyde. ROBERT GILMOUR (*J. Soc. Chem. Ind.*, 1922, **41**, 293–294r).—The author has determined the boiling point of acetaldehyde corresponding with various pressures ranging from 100 mm. to 1011 mm. of mercury, employing the method devised by Wade and Merriman (T., 1911, **99**, 984; 1912, **101**, 2438). The sample of acetaldehyde was synthesised from acetylene and had b. p. (constant within 0.03°) 20.55°/771 mm. The following “smoothed” values were found for the vapour pressure in mm. of mercury at the respective temperatures: 27°, 981; 25°, 911; 23°, 846; 21°, 786; 20°, 757; 19°, 729; 17°, 676; 15°, 627; 13°, 580; 11°, 534; 9°, 490; 7°, 451; 5°, 414; 3°, 378; 1°, 346; 0°, 331; –1°, 317; –3°, 290; –5°, 264; –7°, 241; –9°, 219; –11°, 200; –13°, 181; –15°, 163; –17°, 147; –19°, 132; –21°, 119; –23°, 106. The following values for the density were determined: d_4^{20} 0.8058; d_4^{16} 0.7839. The value of the latent heat of vaporisation at 20°, calculated from the results by the method of Lewis and Weber (*J. Ind. Eng. Chem.*, 1922, **14**, 486), was 132 cal. per gram. The corresponding value of Trouton’s constant is 19.8.

J. S. G. T.

The Reverse Pinacolin Transformation. BERTIL NYBERGH (*Hyllningsskrift tillägnad Ossian Aschan*, 1920, 98–102).—When

heated with anhydrous oxalic acid, pinacolyl alcohol yields a neutral ester, m. p. 24° , b. p. $130^{\circ}/8$ mm., $252^{\circ}/760$ mm., d_4^{20} 0.9433, and an unstable acid ester. When heated with anhydrous oxalic acid, the esters yielded a distillate of which fractions had b. p. $65-69^{\circ}$, d_4^{20} 0.6970, n_D 1.40451, and b. p. $70-72^{\circ}$, d_4^{20} 0.7072, n_D 1.41230, respectively, an ester, b. p. $125-127^{\circ}$, of unknown constitution, and an unsaponifiable product, b. p. $180-200^{\circ}/8$ mm. Transformation temperatures were determined as follows: (1) pinacolyl alcohol and 5 mols. of anhydrous oxalic acid, 105° ; (2) acid oxalic acid ester (dissociation temperature 133°) and 4 mols. of oxalic acid, 105° ; (3) neutral oxalic acid ester and 4.5 mols. of oxalic acid, no transformation even at 135° . CHEMICAL ABSTRACTS.

Permeability of the Glomerulus Membrane for Isomeric Sugars. H. J. HAMBURGER (*Klin. Woch.*, 1922, **1**, 418; from *Chem. Zentr.*, 1922, i, 895).—Whilst the glomerulus membrane is impermeable to dextrose, it is permeable to fructose, mannose, and *l*-glucose. Experiments with a number of isomeric sugars showed that in some cases permeability is partial. The partial retention of *d*-galactose is held to be due to its occurrence in aqueous solution in two forms, one of which is retained and the other passed by the membrane. Quantitative separation of isomeric sugars by means of the glomerulus membrane was effected in the case of mixtures of dextrose and fructose and of dextrose and lactose.

G. W. R.

The Preparation of Lævulose. T. SWANN HARDING (*J. Amer. Chem. Soc.*, 1922, **44**, 1765—1768).—A solution of sucrose (2000 grams) in water (6000 c.c.) is acidified with glacial acetic acid (2 c.c.) and treated with such a quantity of invertase that hydrolysis is complete in about eighteen hours at $20-30^{\circ}$, the end of the reaction being judged by the initial and final polarimeter readings of the solution. A few grams of active decolorising carbon are added, and the solution is filtered. The clear, colourless filtrate is immediately concentrated in a vacuum to a syrup of about 90—95% total solids, care being taken to effect the operation at as low a temperature as is possible by the use of a good water pump. The thick syrup is mixed with two volumes of hot glacial acetic acid, cooled, seeded with dextrose, and allowed to crystallise at $15-20^{\circ}$ during three or four days. The dextrose is removed and washed thoroughly with glacial acetic acid; its weight should be 36—37.5% of that of the sucrose taken. The filtrate is diluted with two volumes of distilled water and concentrated to a thin syrup in a vacuum at a low temperature. The resulting thin syrup is again diluted with water and subsequently concentrated at a low temperature until it contains about 90—95% of total solids. The final syrup is mixed with an equal volume of hot glacial acetic acid, the mixture cooled somewhat, seeded with lævulose, and allowed to remain at $15-20^{\circ}$, crystallisation being usually complete in two or three days. The crystals are removed and washed with glacial acetic acid. The yield of crude sugar is 23.5—28% of the

k k* 2

weight of sucrose taken. Further purification is effected by dissolving the crude product (400 grams) in boiling ethyl alcohol (75%, 200 c.c.), adding absolute ethyl alcohol (300 c.c.) and decolorising with active carbon. The filtered solution is diluted further with absolute ethyl alcohol (100 c.c.), seeded with lævulose, and allowed to crystallise in a desiccator at the atmospheric temperature. The yield is 75–80% of the weight of crude sugar taken. Generally, a second crystallisation by the same method is necessary for the production of a pure material. H. W.

The Action of Hydrogen Peroxide on Pure Solutions of Dextrose, Lævulose, Sucrose, Lactose, and Maltose. C. W. SCHONEBAUM (*Rec. trav. chim.*, 1922, **41**, 503–508).—Previous workers on this subject appear to have obtained contradictory results. The author finds that hydrogen peroxide in dilute solution has practically no action on sugars, with the exception of sucrose, even when heated at 70°. At this temperature, sucrose undergoes partial inversion; this, however, does not occur if the solution is slightly alkaline. Sugars are decomposed by concentrated solutions of hydrogen peroxide. H. J. E.

Crystalline Glucose-ammonia and isoGlucosamine. ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (T., 1922, **121**, 1682–1688).

Crystalline Salts of some Physiologically Important Sugar Phosphates. C. NEUBERG and O. DALMER (*Biochem. Z.*, 1922, **131**, 188–192).—The salts of the phosphoric esters of the sugars prepared hitherto have been amorphous. By use of the alkaloids, crystalline salts can be obtained. The following are described. *Di-strychnine hexosemonophosphate* crystallises with 5H₂O, has no characteristic m. p., and gives $[\alpha]_D^{17} - 30.8^\circ$ in 50% alcohol. The *barium* salt regenerated from this has $[\alpha]_D^{17} + 2.89^\circ$. *Di-brucine hexose-monophosphate* crystallises with 9H₂O and decomposes about 160°. It has $[\alpha]_D - 26.85^\circ$ in 20% alcohol. The *cinchonidine* salt has also been prepared. *Di-strychnine hexose-diphosphate* crystallises with 2H₂O and has $[\alpha]_D^{18} - 20.4^\circ$ in 65% alcohol. *Di-strychnine sucrose-monophosphate* crystallises with 6H₂O, but shows no rotation. It is prepared from Merck's calcium saccharophosphate (hesperonal-calcium). H. K.

The Inversion of Sucrose by Alkaline Copper Solution. L. MAQUENNE (*Bull. Soc. chim.*, [IV], 1922, **31**, 799–806; cf. A., 1916, ii, 56, 156, and 202).—The author refers to his previous work on this subject and points out that Canals (this vol., ii, 592) has obtained incorrect results in ignoring this work. He repeats, with examples, the details of the method and technique developed by him. H. J. E.

The Constitution of the Disaccharides. VI. The Biose of Amygdalin. WALTER NORMAN HAWORTH and GRACE CUMMING LEITCH (T., 1922, **121**, 1921–1929).

The Action of Ozone on Pure Solutions of Maltose. C. W. SCHONEBAUM (*Rec. trav. chim.*, 1922, **41**, 501—502; cf. this vol., i, 223, 717).—Three hours' ozonisation of a 5% solution of maltose effects no decomposition even at 70°; in 0.1*N*-acid solution, no change occurs at the ordinary temperature, but rapid inversion takes place at 70°. In 0.1*N*-alkali solution, about 35% of the sugar is decomposed at the ordinary temperature, whilst at 70° it is rapidly destroyed, although complete decomposition requires considerable time. The products are similar to those in the other cases which have been studied, namely, water and carbon dioxide, with formic acid as an intermediate substance. H. J. E.

Pentosans. EMIL HEUSER (*J. pr. Chem.*, 1922, [ii], **104**, 80).—A reference to a paper of Salkowski (this vol., i, 323) bearing on the author's work (cf. this vol., i, 113). W. O. K.

Combination of Iodine and Starch. I. HANS VON EULER and STIG BERGMAN (*Kolloid Z.*, 1922, **31**, 81—89).—With the object of ascertaining the nature of the blue substance formed between soluble starch and iodine, the authors have carried out a number of partition experiments between a benzene solution of iodine and water, potassium iodide solution, 1% soluble starch solution, and starch solution containing various amounts of potassium iodide, respectively, at 6°, 15°, and 30°. It is shown that aqueous solutions of soluble starch dissolve more iodine than pure water and that the solubility of iodine in starch solutions containing potassium iodide is greater than the sum of the solubilities in starch solution and an aqueous solution of potassium iodide. That is, the power of starch to take up iodine is increased by the presence of potassium iodide. The absorption spectra of starch solution, starch iodide solution, and mixtures of these two respectively with various amounts of potassium iodide have been measured. The results show that there is a considerable displacement of the absorption of starch iodide by potassium iodide. The absorption is increased in the blue region by the addition of potassium iodide, and thereby the solution takes on a red colour. J. F. S.

Combination of Iodine and Starch. II. HANS VON EULER and STURE LANDERGREN (*Kolloid Z.*, 1922, **31**, 89—90; cf. preceding abstract).—The partition of iodine between starch solutions and a toluene solution of iodine has been investigated with the object of ascertaining the influence of the quantity of starch on the amount of iodine taken up by the starch. In all cases, soluble starch was employed. The results show that in solutions of varying concentrations of starch (0.27—1.9%) and constant concentration of potassium iodide (0.001*N*) the amount of iodine extracted from toluene solutions of iodine (1—8 gram per 100 c.c. of toluene) does not increase with increasing concentration of starch. J. F. S.

Plant Colloids. XIII. Synthetic Amylo-phosphoric Acids. M. SAMEC and ANKA MAYER (*Koll. Chem. Beihefte*, 1922, **16**, 89—98).—It is shown that when the erythroamyloses from the starch grains are esterified with phosphoric acid, a product

which corresponds in all points with amylopectin is obtained. By a similar treatment, the amyloamyloses are converted into a jelly-forming substance analogous to amylopectin. The iodine colour of these phosphorus-containing substances is the same as that of the starting materials, provided that during the esterification no fundamental change of the basal substance has taken place. The power of colouring with iodine is therefore to a large extent independent of the degree of hydration and the degree of association of the substance. The contradictory statements regarding the iodine colour of amylopectin are brought into line, and it is shown that a comparison of the phosphorus-containing starch hydrocarbons furnishes information with respect to the formation of jellies.

J. F. S.

Chemistry of the Manufacture of Artificial Silk. K. HESS (*Textilber. Wiss. Ind. Handel*, 1922, **3**, 41—46; from *Chem. Zentr.*, 1922, i, 738—739).—In the dissolution of cellulose by copper oxide-ammonia, the cellulose is supposed to be depolymerised to a simpler compound which combines with copper. On precipitation, the copper forms a normal salt, whilst the cellulose constituent polymerises by virtue of its residual affinity. By the action on cotton of acetyl chloride saturated with hydrogen chloride, the acetyl compound of a depolymerisation product of cellulose is obtained. It is probable that two molecules of this are combined in the cellulose molecule. A constitutional formula for cellulose is given.

G. W. R.

Saccharification of Cellulose. P. P. BUDNIKOV and P. V. ZOLOTAREV (*Bull. Inst. Polyt. Ivanovo-Voznesensk*, 1921, **4**, 119—128).—When dry filter-paper is saccharified by treating it with cold 72% sulphuric acid, then diluting the transparent solution obtained until it contains only 3% of acid, and heating this in an autoclave at 120° for two hours, the percentage of dextrose in the resulting liquid does not exceed 0.6. The concentration of the sugar may, however, be increased by diluting the strongly acid solution, not with water, but with dextrose solution previously obtained in the same way and freed from sulphuric acid. When a solution containing 1% of dextrose and 3% of sulphuric acid is introduced into the cathode chamber of an electrolytic cell and the anode chamber, separated by means of a porous pot, is charged with water acidified with sulphuric acid, electrolysis should result in the collection of all the acid in the anode chamber; with a suitable porous pot, as much as 91.5% of the acid was separated by this method.

T. H. P.

Cellulose Nitrate. A. ANGELI (*Z. ges. Schiess. u. Sprengstoffw.*, 1922, **17**, 113—115).—The action of pyridine on collodion-cotton (12% nitrogen) was studied with the object of elucidating the changes undergone by the basic organic stabilisers usually added to cellulose nitrate and glyceryl nitrate powders. The nitro-cotton was extraordinarily easily gelatinised by the pyridine,

forming a very viscous liquid, which, however, rapidly lost its viscosity and in a few days had the appearance of ordinary pyridine. On adding water to the solution, a white, resinous mass was precipitated, which tenaciously retained the odour of pyridine even after solution in sulphuric acid. The white powder obtained comprised 80% of the original nitro-cotton, was easily soluble in acetic acid, soluble in alcohol, but almost insoluble in ether and in benzene. The substance burnt much more slowly than the original nitro-cotton. Its nitrogen content varied between 9% and 10%, and it was similar to the product obtained by Berl and Fodor (A., 1911, i, 264) by the action of alkali hydroxides or carbonates on very dilute solutions of cellulose nitrate in alcohol and ether. When heated in a glass tube, the substance began to go brown at 165°, and became almost black at 250°. An alcoholic solution of the substance when poured into water gave a very stable, opalescent, colloidal solution, which was coagulated by sodium chloride, ammonium sulphate, or gelatin, but gave no precipitate with aqueous tannin. With benzene and sulphuric acid, nitrobenzene was produced, whilst sulphuric acid and mercury caused an evolution of nitrogen tetroxide. A small quantity of the solution poured on to a test-paper saturated with dimethylaminoazobenzene gave after a short time an intense red colour. The colloidal solution is insoluble in ammonia, but easily soluble in alkali hydroxides, the solution giving a voluminous white precipitate with acids. Ammoniacal silver nitrate is reduced by the colloidal solution, but Fehling's solution is almost unaffected. The substance reacts readily with phenylhydrazine. The development of acidity is ascribed either to the volatilisation of the pyridine or to hydrolysis of a pyridine salt.

H. C. R.

Copper Salts of Aminosulphonic Acids. MARCEL DELÉPINE and RENÉ DEMARS (*Bull. Sci. Pharmacol.*, 1922, 29, 14—20; from *Chem. Zentr.*, 1922, i, 634).—An investigation of the formation of complex salts of copper with amino-acids. Dimethylamino-sulphonic acid forms a simple *copper* salt, $[\text{Me}_2\text{N}\cdot\text{SO}_3]_3\text{HCu}\cdot 5\text{H}_2\text{O}$, light blue crystals. The *nickel* salt, $[\text{Me}_2\text{N}\cdot\text{SO}_3]_2\text{Ni}$, forms small, bluish-green crystals, m. p. 128—129°. Neither of these is a complex salt. The *acid* potassium hydrogen salt of aminomethane-disulphonic acid gives a *copper* salt, $[\text{NH}_2\cdot\text{CH}(\text{SO}_3\text{K})\cdot\text{SO}_3]_3\text{Cu}$, of deeper blue colour than copper sulphate but of lighter blue than copper salts of α -amino-acids. The *nickel* salt is pale blue. Among the β -amino-acids, taurine has no action on cuprous oxide. Phenyl-taurine dissolves cuprous oxide, giving a greenish-blue colour which soon changes to red and brown. Phenylmethyltaurine and phenylethyltaurine, also, do not give copper salts of constant composition.

G. W. R.

Syntheses of Alkylidenecyanoacetic Acids and of Substituted Succinic Acids. I. Acids containing Aromatic Residues. ARTHUR LAPWORTH and JOHN ALEXANDER McRAE (*T.*, 1922, 121, 1699—1712).

The Preparation of Methylguanidine, and of $\beta\beta$ -Dimethylguanidine by the Interaction of Dicyanodiamide, and Methylammonium and Dimethylammonium Chlorides Respectively. EMIL ALPHONSE WERNER and JAMES BELL (T., 1922, **121**, 1790—1794).

The Formation of Bromine Derivatives of Carbon Compounds without the Production of Hydrogen Bromide. BIRAJ MOHAN GUPTA and JOCELYN FIELD THORPE (T., 1922, **121**, 1896—1904).

Butenonitriles. II. P. BRUYLANTS (*Bull. Soc. chim. Belg.*, 1922, **31**, 225—230; cf. this vol., i, 817).—Vinylacetonitrile reacts readily with alcohols, yielding β -alkoxybutyronitriles, when a trace of the corresponding sodium alkoxide is present. In the case of the lower alcohols, the yield is diminished by reason of the polymerisation of the nitrile. The additive products, of the general formula $OR \cdot CHMe \cdot CH_2 \cdot CN$, are colourless liquids of pleasant odour; the following have been prepared: β -methoxybutyronitrile, b. p. 169—170°/759 mm.; d_4^{20} , 0.91643; n_{Ha}^{20} , 1.40664; n_D^{20} , 1.40938; $n_{H\beta}^{20}$, 1.41363; β -ethoxybutyronitrile, b. p. 175.5—176.5°/764.7 mm.; d_4^{20} , 0.89164; n_{Ha}^{20} , 1.40814; n_D^{20} , 1.41076; $n_{H\beta}^{20}$, 1.41537; β -propoxybutyronitrile, b. p. 192—193°/766.5 mm.; d_4^{20} , 0.88312; n_{Ha}^{20} , 1.41183; n_D^{20} , 1.41443; $n_{H\beta}^{20}$, 1.41908; β -isopropoxybutyronitrile, b. p. 182—183°/764.2 mm.; d_4^{20} , 0.87408; n_{Ha}^{20} , 1.40994; n_D^{20} , 1.41235; $n_{H\beta}^{20}$, 1.41759; β -allyloxybutyronitrile, b. p. 196—198°/768 mm.; d_4^{20} , 0.90165; n_{Ha}^{20} , 1.42176; n_D^{20} , 1.42441; $n_{H\beta}^{20}$, 1.42935; β -butoxybutyronitrile, b. p. 209.5—210.5°/757.5 mm.; d_4^{20} , 0.87785; n_{Ha}^{20} , 1.41765; n_D^{20} , 1.41961; $n_{H\beta}^{20}$, 1.42474; β -isobutoxybutyronitrile, b. p. 201—201.5°/763.5 mm.; d_4^{20} , 0.86876; n_{Ha}^{20} , 1.43123; n_D^{20} , 1.41573; $n_{H\beta}^{20}$, 1.42073. An attempt to prepare the phenol derivative was not successful, leading to the formation of a mixture of the two crotononitriles from the vinylacetonitrile; the author states that this is due to the formation of an additive product and its subsequent decomposition. The action of concentrated sulphuric acid on the nitrile results in the formation of isocrotonic acid, and the mechanism of the reaction is discussed. H. J. E.

Optically Active Diazo-compounds. II. H. M. CHILES and W. A. NOYES (*J. Amer. Chem. Soc.*, 1922, **44**, 1798—1810).—In a previous communication (Marvel and Noyes, A., 1921, i, 15), an account has been given of unsuccessful experiments undertaken in the hope of preparing optically active aliphatic diazo-compounds in which the only asymmetric carbon atom is combined with the two nitrogen atoms. Subsequently, Levene and Mikeska (A., 1921, i, 233) have described optically active ethyl diazosuccinate. Six such active compounds have now been prepared. The failure of former experiments is due to the fact that such compounds racemise very easily; it is necessary to carry through all operations very carefully and to distil the compounds under a very low pressure.

Ethyl d-glutamate hydrochloride, m. p. 96—98°, is dissolved in

water and the solution is mixed with sodium acetate, sodium nitrite, and ether and diazotised at -10° by the gradual addition of sulphuric or acetic acid. The product, which is a mixture of the corresponding diazo- and hydroxy-esters, is treated with a quantity of sodium methoxide dissolved in ether and methyl alcohol sufficient to unite with the hydroxy-ester, and the diazo-ester is subsequently distilled under greatly diminished pressure. As thus obtained, *ethyl α -diazoglutarate* has b. p. $92-93^{\circ}/0.1$ mm., $[\alpha]_D +0.87^{\circ}$ to $+1.68^{\circ}$. Hydrolysis of the optically active ester by dilute sulphuric acid gives an optically active product which is probably a mixture of ethyl glutaconate and ethyl 5-ketotetrahydrofuran-2-carboxylate. Saponification of the products of the hydrolysis of the diazo-ester yields an optically active sodium salt which rotates in the same direction as the original amino-acid. When the sodium salt is acidified and the mixture extracted with ether, the ethereal extract is optically active in the same sense as the original amino-acid. Ethyl *d*-diazoglutarate is reduced by aluminium amalgam in the presence of moist ether and the product is hydrolysed by acid to glutamic acid, the rotation of which is about 13% of that of the pure substance.

Ethyl *d*-glutamate is converted at $160-170^{\circ}/20$ mm. into ethyl 5-pyrrolidone-2-carboxylate, m. p. 54° after softening at $49-50^{\circ}$, $[\alpha]_D -2.45^{\circ}$ in aqueous solution (cf. Fischer and Bochner, A., 1911, i, 485).

Methyl d-glutamate hydrochloride, which could not be caused to solidify, is converted in a similar manner into *methyl α -diazoglutarate*, b. p. $86-87^{\circ}/0.5$ mm., $85-86^{\circ}/0.4$ mm., $82-83^{\circ}/0.2$ mm., $d_4^{20} 1.185$, $n_D^{20} 1.4753$, $[\alpha]_D^{22} +0.89^{\circ}$.

isoPropyl d-glutamate, a colourless, viscous liquid, b. p. $115-117^{\circ}/0.15$ mm., $d_4^{20} 1.023$, $n_D^{20} 1.4402$, $[\alpha]_D^{22} +5.08^{\circ}$ (the *hydrochloride* is non-crystalline) is transformed by nitrous acid into *isopropyl α -diazoglutarate*, $[\alpha]_D +1.24^{\circ}$, which could not be distilled without decomposition; the crude material is hydrolysed by sulphuric acid (20%) to *isopropyl α -hydroxyglutarate*, $n_D^{20} 1.4440$, $[\alpha]_D^{24} +1.12^{\circ}$ in ethereal solution.

An attempt to prepare *n*-butyl *d*-glutamate resulted in the production of *n-butyl 5-pyrrolidone-2-carboxylate*, a colourless liquid, b. p. $151-153^{\circ}/0.2$ mm., $d_4^{20} 1.1101$, $n_D^{20} 1.4773$, $[\alpha]_D^{22} -12.39^{\circ}$.

Ethyl *l*-aspartate hydrochloride, m. p. 95° , is converted by nitrous acid into ethyl α -diazosuccinate, b. p. $77-78^{\circ}/0.1$ mm., $d_4^{20} 1.139$, $n_D^{20} 1.4620$, $[\alpha]_D^{22} -1.23^{\circ}$. When hydrolysed with dilute sulphuric acid, it gives a product which has $[\alpha]_D^{24} -0.98^{\circ}$ in ethereal solution.

Ethyl *l*- α -amino-*n*-hexoate hydrochloride (cf. Noyes and Marvel, *loc. cit.*) is converted into *ethyl l- α -diazo-*n*-hexoate*, b. p. $54-55^{\circ}/0.35$ mm., $n_D^{20} 1.4543$, $d_4^{20} 0.974$, $[\alpha]_D^{24} -1.92^{\circ}$ when dissolved in anhydrous ether. When hydrolysed with dilute sulphuric acid, it gives a lævorotatory product from which a lævorotatory sodium salt is obtained after treatment with sodium hydroxide. The aqueous solution of the latter, when acidified and extracted with ether, yields a lævorotatory ethereal extract. *Ethyl d- α -diazo-*n*-hexoate*,

b. p. 54—55°/0.35 mm., d_4^{20} 0.97, n_D^{20} 1.453, $[\alpha]_D^{23}$ +1.84° in dry ethereal solution, is prepared similarly from ethyl *d*- α -amino-*n*-hexoate hydrochloride.

Ethyl α -diazoisohexoate, prepared from ethyl *L*- α -aminoisohexoate hydrochloride, has b. p. 49—50°/0.50 mm., d_4^{20} 0.961, n_D^{20} 1.4333, $[\alpha]_D^{24}$ -1.52° in ethereal solution.

The production of partly active hydroxy-esters by the treatment of diazo-esters with dilute acids together with the formation of partly active amino-esters by their reduction may indicate the existence of two forms of diazo-ester, possibly corresponding with the compounds indicated by the Curtius and Angeli-Thiele formulæ, respectively.

It seems impossible to reconcile the Curtius formula for active diazo-esters with the ideas of atomic structure and of non-polar valency proposed by Lewis and Langmuir. The Angeli-Thiele formula may be reconciled with these theories if it is assumed that the polar valency between an ammonium group and another atom is a definite bond located in a fixed position in the compound (cf. Noyes and Potter, A., 1915, i, 79).

H. W.

The β -Chlorovinylarsines. FREDERICK GEORGE MANN and WILLIAM JACKSON POPE (T., 1922, 121, 1754—1759).

Manufacture of Allylarsinic Acid. F. HOFFMANN-LA ROCHE & Co. (Brit. Pat. 167157).—*Allylarsinic acid*, $C_3H_5 \cdot AsO(OH)_2$, colourless needles or coarse prisms, m. p. 129—130°, is prepared by treating tertiary alkali arsenites in aqueous solution and in the presence of an excess of alkali with allyl haloids. The *silver salt*, *sodium hydrogen salt* (+aq), colourless, lustrous tablets which partly melt at 87—88°, the hygroscopic *disodium salt*, and the insoluble *zinc, lead, copper, cobalt, and iron salts* are described. The acid is not precipitated by the addition of magnesia mixture or calcium chloride to its cold ammoniacal solution, but, on being heated with these reagents, it precipitates a white *magnesium or calcium salt*.

H. W.

isoPropylstannonic Acid and its Derivatives. JOHN GERALD FREDERICK DRUCE (T., 1922, 121, 1859—1863).

Preparation of cycloPropane in a Pure Condition. MAX TRAUTZ and KARL WINKLER (*J. pr. Chem.*, 1922, [ii], 104, 37—43).—*cycloPropane* is conveniently prepared by the reduction of trimethylene bromide in amyl alcohol by zinc dust at 100—115°. The gas evolved is fractionated at a low temperature in an apparatus which is described, and pure *cyclopropane* obtained with the following constants: vapour density, 1.45—1.49; d_4^{20} of liquid, 0.720; m. p. -127°; b. p. -34.5°/750 mm.; n_{H_2} 1.000977.

W. O. K.

Problems of Organic Chemistry. I. The Velocity of Ring Fission in Gases. Isomerisation of cycloPropane. MAX TRAUTZ and KARL WINKLER (*J. pr. Chem.*, 1922, [ii], 104, 53—79).—As no case of intermolecular change in a gas has so far been studied kinetically, measurements have been made of the

reversible reaction, propylene \rightleftharpoons cyclopropane. The mixture resulting by passing pure cyclopropane or propylene through a tube at a definite temperature of about 600° or 700° is analysed by finding the density of the product in the liquid state at -79° (cf. this vol., i, 909). The result has to be corrected for the polymerised material also formed. The equilibrium mixture consists very largely of propylene. The isomerisation of cyclopropane to propylene is unimolecular, and its speed is influenced by the shape of the vessel and the material of which it is made, although these effects decrease in magnitude with rise of temperature. The heat of the reaction at 550—650° is calculated to be 63900 cal. At higher temperatures the reaction proceeds further and carbon, methane, and hydrogen are formed from propylene. W. O. K.

Application of the Octet Theory to Single Ring Aromatic Compounds. ERNEST C. CROCKER (*J. Amer. Chem. Soc.*, 1922, **44**, 1618—1630).—A theoretical paper in which the Lewis-Langmuir octet theory is considered as undergoing evolution, in that the original cubical octet has given way in certain cases to that of an octet which consists of four pairs of electrons arranged as are the points of a tetrahedron. The pairing tendency of electrons is considered as possibly due to the presence of magnetic properties in the electrons (magnetons). The Kekulé, Dewar, and centric formulæ of benzene are expressed in octet nomenclature and are considered as unstable forms. A stable arrangement is deduced and shown to be applicable, not only to benzene, but also to other aromatic compounds. In this arrangement, there is a ring of six carbon atoms, each singly linked to its neighbour on either side and to hydrogen. The remaining six electrons are situated between the carbon atoms in the plane of the ring, thus forming an octet for each carbon atom. These six "aromatic" electrons are considered as being in stable equilibrium only when paired up near carbon atoms 1, 3, and 5, or 2, 4, and 6 (or oscillating between these forms in benzene itself or in derivatives containing six identical substituents). Substituents on the carbons are considered as favouring the retention of one or other grouping of electrons, according to their electrical action on the adjacent or very near electrons, resulting in ortho, meta, or para patterns. Substituents with more than five kernel charges on the octet joining the ring plus its attached hydrogens are indicated as favouring the ortho and para patterns (as in toluene and chlorobenzene), and those with five or less charges as favouring the meta pattern (as in nitrobenzene and benzaldehyde). Substitution is considered as possible only when the hydrogens are lightly held ("open" positions of the adjacent aromatic electrons). The influence of these electrons is to "open" or "close" positions according to their attractive action on the hydrogen kernels. The relative ease of substitution into the various substituted benzenes is treated as a result of polarity considerations, which are developed as an essential consequence of the octet theory, and an addition to the above-mentioned aromatic structural considerations. Preference for substitution

in ortho- or para-positions is treated in like manner. Pyridine, thiophen, furan, and pyrrole are treated similarly and afford striking confirmations of the postulated structure in their behaviour. Addition of any kind is shown to be inconsistent with the retention of the aromatic structure in the remainder of the ring. J. F. S.

Conjugation and the Structure of Benzene. MAURICE L. HUGGINS (*J. Amer. Chem. Soc.*, 1922, **44**, 1607—1617).—A theoretical paper, in which on the basis of an assumed maximum in the force-distance curves, representing the repulsion between electrons, the probable mechanisms of the simplest types of organic reactions are given and explained. As intermediary steps in these reactions, bonds of three or four or more electrons surrounded by three, four, or more atomic nuclei are assumed. The reactivity of double and triple bonds is explained on this point of view. Conjugation is briefly considered and the structure of typical compounds given, some of these being similar to those put forward by Erlenmeyer. The relationship of keto-enol tautomerism to conjugation is also discussed. When this idea of conjugation is applied to benzene, a formula of the centroid type, as proposed by Körner, is obtained. The evidence for and against this structure is briefly considered. It is shown that the objections raised against it are all invalid or inconclusive. On the other hand, the known properties of benzene and its derivatives are very adequately represented by their centroid structures. Further, recent evidence from crystal structures proves that this benzene structure is the correct one.

J. F. S.

Oxidation of o-Toluenesulphonamide. A. V. PAMFILOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk*, 1921, **4**, 167—168).—In the oxidation of o-toluenesulphonamide to o-benzoic sulphinide ("saccharin") by means of potassium permanganate, the yield obtained is increased by 10—15% and the proportion of permanganate required diminished by nearly 50% if the alkali salt of the sulphonamide is used instead of the free sulphonamide. Electrolytic oxidation of the sulphonamide (*Chemische Fabrik vormals von Heyden*, D.R.-P. 85491), like that of p-toluenesulphonic acid (Sebor, A., 1903, i, 554), gives unsatisfactory results.

T. H. P.

The Formation of Derivatives of Tetrahydronaphthalene from γ -Phenyl Fatty Acids. II. ARNOLD STEVENSON and JOCELYN FIELD THORPE (*T.*, 1922, **121**, 1717—1722).

Absorption of Ultra-violet Rays by Naphthalene. VICTOR HENRI and PIERRE STEINER (*Compt. rend.*, 1922, **175**, 421—423).—A quantitative measurement of the absorption of solutions of naphthalene in hexane, ethyl ether, alcohol, and water reveals seventeen bands between $\lambda=3207$ and $\lambda=2563$ and one band in the extreme ultra-violet at $\lambda=2209$. The absorption curve of naphthalene is displaced towards the red with respect to that of benzene, and its absorption is more than ten times as strong as that of benzene. The frequencies of the naphthalene bands present

a double periodicity which corresponds with the fundamental intervals $a=921$ and $b=159$. The influence of the solvent on the spectrum of naphthalene is the same as in the case of benzene.

W. G.

Triphenylmethyl. XXX. Diphenyl- β -naphthylmethyl and the Colour of Free Radicles. M. GOMBERG and F. W. SULLIVAN, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 1810—1833).—Diphenyl- β -naphthylmethyl has been isolated in the crystalline state. The conductivity of the free radicle has been examined in sulphur dioxide and the conductivities of the chlorides and bromides of triphenylmethyl, diphenyl- α -naphthylmethyl, and diphenyl- β -naphthylmethyl have been determined in both sulphur dioxide and hydrogen cyanide. The results show that the property of electrolytic dissociation is general for this class of compound. The bromides give strongly conducting solutions with but little difference between the conductivities of the individuals. The chlorides are not such good conductors, and there is a variation among them. The conductivities of the chlorides are related in the same way as the dissociation of the corresponding free radicles, the order of diminishing conductivity being, diphenyl- α -naphthylmethyl chloride, diphenyl- β -naphthylmethyl chloride, and triphenylmethyl chloride. The latter has a large negative temperature coefficient of conductivity. The same relationship holds for the free radicles; diphenyl- β -naphthylmethyl is a better conductor than triphenylmethyl. The conductivity of the triarylmethyl haloids in hydrocyanic acid is uniformly greater than in sulphur dioxide. The bromides show molecular conductivities comparable to that of an aqueous solution of potassium hydroxide, or about twice the conductivity of the alkali haloids in water. The molecular weight of diphenyl- β -naphthylmethyl has been determined in carbon tetrachloride, ethylene chlorobromide, benzene, nitrobenzene, cyclohexane, *p*-bromotoluene, *p*-dichlorobenzene, and naphthalene, the freezing points of which cover the range -22° to $+80^{\circ}$. It is found that the hexa-arylethane is dissociated from 15% to 50%.

The effect of change in concentration of the free radicle on the dissociation and colour of the solutions has been examined. The resulting changes in colour intensity are independent of the changes in dissociation. Also the changes in colour intensity which result from variations in temperature are not parallel to the changes in dissociation which are thus produced. These facts point to the conclusion that the development of colour in solutions of free radicles is not due entirely to dissociation of the hexa-arylethane into the triarylmethyl. The most satisfactory explanation of the facts is in the hypothesis that, in addition to dissociation, there is also tautomerisation of the benzenoid triarylmethyl into the quinonoid form. The equilibrium between the bimolecular and unimolecular forms on the one hand, and that between the two unimolecular tautomerides on the other, are not equally influenced by changes either in concentration or in temperature.

Diphenyl- β -naphthylcarbinol, colourless crystals, m. p. 117.5° ,

is most conveniently prepared by the action of magnesium phenyl bromide on ethyl β -naphthoate in the presence of boiling toluene. It is reduced by zinc dust and acetic acid to diphenyl- β -naphthylmethane, m. p. 77—78°, which has properties differing from those described to it by Lehne (A., 1880, 478). *Diphenyl- β -naphthylmethyl chloride*, m. p. 94·5°, is prepared in almost quantitative yield by saturating an ethereal solution of the carbinol with hydrogen chloride in the presence of calcium chloride; it gives red additive products with stannic and mercuric chlorides. It is converted by an alcoholic solution of sodium ethoxide into *diphenyl- β -naphthylmethyl ethyl ether*, colourless crystals, m. p. 114°. *Diphenyl- β -naphthylmethyl anilide* has m. p. 158·5°. *Diphenyl- β -naphthylmethyl bromide*, colourless crystals, m. p. 136°, is prepared by the addition of acetyl bromide to a solution of the carbinol in benzene. *Diphenyl- β -naphthylmethyl*, a colourless or pale yellow, finely divided, crystalline powder, m. p. 135—140° to a red liquid, is obtained by the action of molecular silver on a solution of diphenyl- β -naphthylmethyl chloride in carbon disulphide. It appears to form an additive compound with methyl butyl ketone. It is transformed by oxygen into the corresponding *peroxide*, colourless crystals, m. p. 166°, the yield being 72% of that theoretically possible when an ethereal solution of the radicle is used, but only 46% in the presence of benzene as solvent. The free radicle is not very sensitive to light. It reacts with iodine in accordance with the scheme $2\text{CPh}_2\cdot\text{C}_{10}\text{H}_7 + \text{I}_2 \rightarrow 2\text{C}_{10}\text{H}_7\cdot\text{CPh}_2\cdot\text{I}$, but an equilibrium is attained before the change has proceeded to completion. H. W.

Metachromism of Toluidine-blue. ROBERT SCHWARZ and ERIKA HERRMANN (*Kolloid Z.*, 1922, **31**, 91—94).—The colloidal chemical properties of toluidine-blue have been investigated with the object of explaining the metachromatic behaviour of this substance. On diffusion of 0·2 to 0·002% solutions, it is found that separation into two diffusion zones takes place with velocities of 6 mm. and 9 mm., respectively, per twenty-four hours. The 9 mm. zone is considerably lighter in colour than the 6 mm. zone. The formation of the two zones is confirmed by ultrafiltration measurements, and both sets of results indicate that solutions of toluidine-blue constitute a polydisperse system which contains both colloidal as well as molecular disperse particles. Transport experiments bring about a separation, the cathode region becoming reddish-blue in colour and the anode pure blue. The behaviour of solutions of toluidine-blue with various colloidal substances has been examined. Thus α -silicic acid gel is coloured blue, whilst the β -gel is coloured red. Similar results were obtained with the various preparations of stannic acid, barium sulphate, aluminium hydroxide, and magnesium ammonium phosphate. The results all point to the one conclusion, namely, that the metachromism of toluidine-blue is due in the first place to the difference in the degree of dispersion of the adsorbent and in the second place to the electrical condition of the adsorbing surface, which is determined by the nature of the ions adsorbed on the surface. J. F. S.

The Condensation of Phenols with the Hydrochlorides of Cyanamides and Carbodi-imides, and its Relation to the Hoesch Reaction. WALLACE FRANK SHORT and JOHN CHARLES SMITH (T., 1922, **121**, 1803—1808).

The Solubility and Volatility of 3 : 5-Dinitrophenol. NEVIL VINCENT SIDGWICK and THOMAS WESTON JOHNS TAYLOR (T., 1922, **121**, 1853—1859).

The Migration of Acyl from Nitrogen to Oxygen. L. CHAS. RAIFORD and JOHN R. COUTURE (*J. Amer. Chem. Soc.*, 1922, **44**, 1792—1798).—In continuation of previous work (Raiford, A., 1920, i, 156), it is shown that, when the acetyl and benzoyl radicles are introduced into the *o*-aminophenols obtained from *o*- and *m*-cresol, respectively, the benzoyl radicle is found attached to nitrogen in each case, regardless of the order of introduction, thus confirming the observations reported previously.

o-Cresol is converted by bromine into 5-bromo-*o*-cresol, and the latter is converted by sodium nitrite and glacial acetic acid into 5-bromo-3-nitro-*o*-cresol, m. p. 90·5°, which appears to be the sole product of the change. The nitro-compound is reduced by Raiford's method (A., 1911, i, 993) to 5-bromo-3-amino-*o*-cresol hydrochloride. This substance is converted by acetic anhydride and fused sodium acetate into 4-bromo-2-acetyl-amino-*o*-tolyl acetate, pale brown, silky needles, m. p. 200°, which is slowly dissolved by aqueous sodium hydroxide solution with the formation of 4-bromo-2-acetyl-amino-*o*-cresol, colourless needles, m. p. 119°. Benzoylation of the latter compound with benzoyl chloride and sodium hydroxide gives 4-bromo-2-benzoyl-amino-*o*-tolyl acetate, slender, colourless needles, m. p. 168°, the constitution of which is established by the observation that it is hydrolysed by aqueous sodium hydroxide solution to 4-bromo-2-benzoyl-amino-*o*-cresol, rose-coloured needles, m. p. 194·5°, which is also formed by the action of benzoyl chloride on an ethereal solution of 5-bromo-3-amino-*o*-cresol. Acetylation of 4-bromo-2-benzoyl-amino-*o*-cresol with sodium acetate and an excess of acetic anhydride gives 4-bromo-2-benzoyl-amino-*o*-tolyl acetate, m. p. 167° (see above).

6-Bromo-4-nitro-*m*-cresol (cf. Raiford and Leavell, A., 1914, i, 1064) is reduced to the corresponding amine hydrochloride which is converted by sodium acetate and acetic anhydride into 6-bromo-4-acetyl-amino-*m*-tolyl acetate, colourless leaflets, m. p. 188°. The action of aqueous sodium hydroxide on the latter compound leads to the formation of 6-bromo-4-acetyl-amino-*m*-cresol, almost colourless needles, m. p. 199° (decomp.), which is transformed by benzoyl chloride in the presence of sodium hydroxide into 6-bromo-4-benzoyl-amino-*m*-tolyl acetate, slender, colourless needles, m. p. 157—158°. The constitution of the latter substance is established by the observation that 6-bromo-4-amino-*m*-cresol is transformed by benzoyl chloride in dry ethereal solution into 6-bromo-4-benzoyl-amino-*m*-cresol, almost colourless leaflets, m. p. 223° (decomp.), which is converted by anhydrous sodium acetate and acetic

anhydride into 6-bromo-4-benzoylamino-*m*-tolyl acetate, identical with the product described above. H. W.

Separation of Volatile Substances from Gases which are Absorbed with Difficulty. II. Use of Cresols. E. BERL and W. SCHWEBEL (*Z. angew. Chem.*, 1922, **35**, 189—192; cf. *ibid.*, 1921, **34**, 278, 369, 377).—Mixtures of cresol with ethyl ether, ethyl alcohol, and acetone give lower vapour tension values than the pure compounds; moreover, heat is developed when the substances are mixed; it is therefore concluded that molecular compounds are formed. In the case, however, of benzene and carbon tetrachloride (and therefore of hydrocarbons and chlorinated hydrocarbons in general), no such reduction of vapour tension takes place. The formation of molecular compounds, as detected by vapour tension measurements, does not take place between anisole and ethyl ether, ethyl alcohol, and acetone. A. A. E.

Formation of Additive Products between Cresols on the One Hand and Ethyl Ether, Ethyl Alcohol, Acetone, Benzene, etc., on the Other. C. and W. VON RECHENBERG (*Z. angew. Chem.*, 1922, **35**, 397—398).—As mixtures of cresols with ethyl ether, ethyl alcohol, acetone, carbon tetrachloride, benzene, and other volatile solvents, give perfectly smooth viscosity curves, which show no maxima, and the vapour-pressure curves likewise show no minima, the authors conclude that, contrary to the opinion of Berl and Schwebel (preceding abstract), no molecular additive compounds can be formed between these substances. G. F. M.

Additive Products between Cresols and Alcohols, etc. E. BERL and W. SCHWEBEL (*Z. angew. Chem.*, 1922, **35**, 398).—A reply to von Rechenberg (preceding abstract).

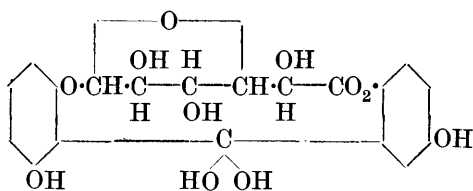
The authors maintain their view that molecular compounds are actually formed between cresols and ethyl alcohol or ether, and acetone; a vapour-pressure minimum is not necessarily to be expected when molecular compounds are formed. Further, the formation of molecular compounds does not necessarily cause a maximum in the viscosity curve, as the viscosity of the compound may be less than that of its components. G. F. M.

Chlorination of Quinol. ALFRED ECKERT and RUDOLF ENDLER (*J. pr. Chem.*, 1922, [ii], **104**, 81—84).—The chlorination of quinol in acetic acid yields a mixture of tetrachloroquinol, m. p. 226°, and 2 : 3-dichloroquinol, m. p. 143—145°, and a small quantity of 2 : 5-dichloroquinol, m. p. 165—168°. By chlorination in chloroform solution, 5 grams of 2 : 5-dichloroquinol may be obtained from 10 grams of quinol. W. O. K.

Researches on Residual Affinity and Co-ordination. IX. Cobaltammine Salts of the Nitro-Dyes. GILBERT T. MORGAN and HERBERT JOSEPH SEYMOUR KING (*T.*, 1922, **121**, 1723—1729).

The Precursor of Indian-yellow. K. GORTER (*Bull. Jard. bot. Buitenzorg.*, 1922, [iii], **4**, 260—267).—Euxanthogen, the substance isolated by Wiechowsky from the leaves of *Mangifera indica*

(cf. van Scherpenberg, A., 1916, i, 321), is preferably named *mangiferin*. The author has confirmed Wiechowsky's formula, $C_{19}H_{18}O_{11}$, whence the substance is isomeric with euxanthic acid, to which it gives rise in the organism. The precursor is best prepared from the bark, which is first exhausted with light petroleum and then with 60% alcohol, the latter giving a yield of 2.5% on evaporation. The leaves yield somewhat less readily 1.7%. The substance forms thin, pale yellow needles, m. p. 271° , $[\alpha]_D^{27} + 32.8^{\circ}$; unlike euxanthic acid, the substance does not at once liberate carbon dioxide from sodium hydrogen carbonate solution, whence the author concludes that it contains no carboxyl group. Ferric chloride gives in alcoholic solution a green coloration. Fehling's solution is reduced on prolonged heating, Bial's reagent gives a green colour. Diazomethane yields a *dimethyl* ether, $C_{19}H_{16}O_9(OMe)_2$, m. p. 276° . Mangiferin crystallises from dilute alcohol with $3H_2O$, of which $1H_2O$ is lost on exposure to air and the rest at 110° in a vacuum. It yields an amorphous *hepta-acetyl* derivative, $C_{19}H_{11}O_{11}(OAc)_7$, m. p. about 150° . Euxanthic acid under the same conditions yields a crystalline *tetra-acetyl* derivative, $C_{19}H_{12}O_{10}(OAc)_4$, m. p. 176° , although the substance contains six hydroxyl groups. After previous drying in a vacuum over sulphuric acid, this acetyl derivative loses $1H_2O$ at 80° in a vacuum over phosphorus pentoxide, apparently from a non-acetylated grouping, $C \begin{smallmatrix} \text{OH} \\ \text{OH} \end{smallmatrix}$. The author



proposes for mangiferin (=euxanthogen) the annexed constitution. The transformation to euxanthic acid would take place by addition of a molecule of water at the ester grouping, rotation of the ring on the left through 180° , and elimination of water to form the γ -pyrone ring. G. B.

Additive Compounds of Gold Haloids with Benzyl Sulphide. GEORGE MCPHAIL SMITH (*J. Amer. Chem. Soc.*, 1922, 44, 1769—1775).—The two compounds which are produced by the interaction of gold chloride with benzyl sulphide (Herrmann, A., 1905, i, 733) are additive compounds of gold monochloride and gold dichloride, respectively, with benzyl sulphide. They are conjugated compounds, probably constituted as shown in the formulæ, $[ClAu \dots S(CH_2Ph)_2]$ and $\left[\begin{smallmatrix} Cl \\ Cl \end{smallmatrix} > Au \dots S(CH_2Ph)_2 \right]$. Unlike the additive compounds with platinous chloride, $\left[\begin{smallmatrix} Cl \\ Cl \end{smallmatrix} > Pt < \begin{smallmatrix} SR_2 \\ SR_2 \end{smallmatrix} \right]$, which unite with further molecules of the organic sulphides to form interpolation compounds, such as $[Pt, 4SR_2]Cl_2$ (cf. Tschugaev and Benevolenski, A., 1913, i, 1149; Tschugaev and Kobljanski, A., 1913, i, 1149; Tschugaev and Chlopin, A., 1914, i, 479), the conjugate compounds of gold mono- and di-

chlorides appear to be incapable of yielding interpolation compounds by the further addition of benzyl sulphide. Dichloro-gold-benzyl sulphide probably exists in chloroform solution as a solvate of the formula $\text{Cl}_2\text{AuS}(\text{CH}_2\text{Ph})_2 \cdot \text{CHCl}_3$.

The compound $\text{Br}_2\text{AuS}(\text{CH}_2\text{Ph})_2$, prismatic needles of a dark maroon colour, is prepared by extracting an aqueous solution of chloroauric and constant-boiling hydrobromic acids with ether and addition of benzyl sulphide to the ethereal extract. It is transformed when heated with alcohol into the compound $\text{BrAuS}(\text{CH}_2\text{Ph})_2$, long, colourless, transparent needles. The substance $\text{I}_2\text{AuS}(\text{CH}_2\text{Ph})_2$, black, prismatic needles, is prepared similarly to the corresponding dibromo-compound; attempts to isolate the compound $\text{IAuS}(\text{CH}_2\text{Ph})_2$ were not successful. The substance $\text{ClIAuS}(\text{CH}_2\text{Ph})_2$ is also described. H. W.

Preparation of Symmetrical Aryl Alkyl Ethers. FARBEN-FABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 343930; from *Chem. Zentr.*, 1922, ii, 700).—Aryl alkyl haloids are heated with alkali hydroxides. *Dibenzyl ether* is prepared by heating benzyl chloride with potassium hydroxide at 180–200° or with sodium hydroxide at 90–120°. It is a colourless liquid with slight blue fluorescence, b. p. 285–290°. *Ditolyl dimethyl ether* has b. p. 300–310°. The products have uses as solvents. G. W. R.

The Solubility of the Alkali Salts of Benzoic and the Hydroxybenzoic Acids in Water. NEVIL VINCENT SIDGWICK and ELINOR KATHARINE EWBANK (*T.*, 1922, 121, 1844–1853).

The Reaction of Organomagnesium Compounds on Nitriles. Action of Magnesium Methyl Bromide on Phenylacetoneitrile. ALB. RONDOU (*Bull. Soc. chim. Belg.*, 1922, 31, 231–241).—Magnesium methyl bromide acts in an analogous manner to metallic sodium on the nitrile, producing new substances from it by polymerisation. Two of these have been obtained pure and examined. The chief product is a bimolecular polymeride, previously obtained by von Meyer (A., 1895, i, 582) as an oil, but now as crystals of m. p. 114·5–115°. It is stated that crystallisation is hindered by traces of impurities. The termolecular polymeride differs from those previously prepared, and an attempt to investigate its structure leads to the conclusion that it is 4 : 6-diamino-3 : 5-diphenyl-2-benzylpyridine (cf. Wedekind, A., 1911, i, 219). H. J. E.

The Action of Acetic Anhydride on some Benzyldene-anthranilic Acids. V. J. B. EKELEY, E. C. ROGERS, and MARGARET SWISHER (*J. Amer. Chem. Soc.*, 1922, 44, 1756–1758).—In previous papers (A., 1912, i, 211; 1913, i, 395; 1914, i, 576; 1915, i, 166), it has been shown that oxazine derivatives are produced when acetic anhydride reacts with benzyldeneanthranilic acids. The reaction has been extended further to a large number of aldehydes and appears to be of very general applicability. The acids are usually very readily prepared but, for some unexplained reason, the condensation of anthranilic acid with cuminol or β -naphtholaldehyde methyl ether could not be effected. Un-

expectedly, *o*-nitropiperonal gives two anthranilic acid derivatives which are convertible into different oxazines, thus indicating the possibility that *o*-nitropiperonal is in reality a mixture of two very similar nitration products.

The following benzylideneanthranilic acids are obtained by mixing molecular proportions of the requisite aldehyde and anthranilic acid in concentrated alcoholic or benzene solution at 0°. *3-Nitrosalicylideneanthranilic acid*, orange-red needles, m. p. 227°. *5-Nitrosalicylideneanthranilic acid*, orange-red needles, m. p. 270°. *2:4-Dinitrobenzylideneanthranilic acid*, mustard-coloured prisms, m. p. 153°. *m-Tolylideneanthranilic acid*, orange-red crystals, m. p. 202·5°. *p-Diethylaminobenzylideneanthranilic acid*, red needles, m. p. 154°. *Terephthalylideneanthranilic acid*, yellow crystals, m. p. 300°. *p-Ethoxybenzylideneanthranilic acid*, yellow needles, m. p. 117°. *o-Methoxybenzylideneanthranilic acid*, yellow needles, m. p. 130°. *β-Hydroxynaphthylideneanthranilic acid*, orange crystals, m. p. 252°. *4-Methoxy-3-methylbenzylideneanthranilic acid*, straw-coloured needles, m. p. 161°. *3:4-Dimethoxybenzylideneanthranilic acid*, pale yellow needles, m. p. 169°. *o-Carboxybenzylideneanthranilic acid*, colourless crystals, m. p. 225°. *Nitropiperonylideneanthranilic acid* (α-form), yellowish-brown crystals, m. p. 185° (decomp.). *Nitropiperonylideneanthranilic acid* (β-form), yellow crystals, m. p. 128°. *2:4:5-Trimethoxybenzylideneanthranilic acid*, orange-yellow crystals, m. p. 151°. *p-Homosalicylideneanthranilic acid*, red needles, m. p. 209°.

These acids yield the oxazine derivatives either by heating molecular proportions with acetic anhydride in xylene solution for several hours under a reflux condenser or by heating them with an excess of acetic anhydride and removing the excess by distillation. With terephthalylideneanthranilic acid, the reaction is effected in boiling nitrobenzene. The following individual substances are described: *4-Acetyl-3-3'-nitro-2'-acetoxypenyldihydro-2:4-benzoxazine-1-one*, $\text{C}_6\text{H}_4 \begin{smallmatrix} \text{CO}-\text{O} \\ | \\ \text{NAc} \cdot \text{CH} \cdot \text{C}_6\text{H}_3(\text{OAc})\text{NO}_2 \end{smallmatrix}$, colourless crystals, m. p. 190°. *4-Acetyl-3-5'-nitro-2'-acetoxypenyldihydro-2:4-benzoxazine-1-one*, colourless crystals, m. p. 178°. *4-Acetyl-3-2':4'-dinitrophenyldihydro-2:4-benzoxazine-1-one*, straw-coloured crystals, m. p. 110°. *4-Acetyl-3-2'-acetoxyl-4'-methoxyphenyldihydro-2:4-benzoxazine-1-one*, colourless crystals, m. p. 156°. *4-Acetyl-3-p-diethylaminophenyldihydro-2:4-benzoxazine-1-one*, colourless crystals, m. p. 170°. *4-Acetyl-3-p-phenylenebisdihydro-2:4-benzoxazine-1-one*, colourless crystals, m. p. 267°. *4-Acetyl-3-p-ethoxyphenyldihydro-2:4-benzoxazine-1-one*, colourless crystals, m. p. 182°. *4-Acetyl-3-o-methoxyphenyldihydro-2:4-benzoxazine-1-one*, colourless crystals, m. p. 178°. *4-Acetyl-3-β-acetoxynaphthyldihydro-2:4-benzoxazine-1-one*, colourless crystals, m. p. 198°. *4-Acetyl-3-p-methoxy-m-tolyldihydro-2:4-benzoxazine-1-one*, colourless crystals, m. p. 128°. *4-Acetyl-3-mp-dimethoxyphenyldihydro-2:4-benzoxazine-1-one*, colourless crystals, m. p. 183°. *4-Acetyl-3-o-carboxyphenyldihydro-2:4-benzoxazine-1-one*, colourless crystals, m. p. 134°. *4-Acetyl-3-nitro-3':4'-methylenedioxyphenyldihydro-2:4-benzoxazine-*

1-one (α -form), brownish-yellow crystals, m. p. 206°. 4-Acetyl-3-nitro-3':4'-methylenedioxyphenyldihydro-2:4-benzoxazine-1-one (β -form), colourless crystals, m. p. 165°. 4-Acetyl-2:4:5-trimethoxyphenyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 135°. 4-Acetyl-3-o-acetoxy-p-tolyldihydro-2:4-benzoxazine-1-one, colourless crystals, m. p. 166°. H. W.

Researches on Residual Affinity and Co-ordination. X. Salicylatotetramminocobaltic Salts and the Constitution of Oxonium Compounds. GILBERT T. MORGAN and J. D. MAIN SMITH (T., 1922, 121, 1956—1971).

New Synthesis of isoFerulic Acid [3-Hydroxy-4-methoxycinnamic Acid]. F. MAUTHNER (*J. pr. Chem.*, 1922, [ii], 104, 132—136).—3-Nitro-4-methoxycinnamic acid was prepared according to the instructions of Einhorn and Grabfield (A., 1888, 477), and found to melt at 248—249°, not 140°, as given by these authors. On reduction with ferrous sulphate and ammonia it yields 3-amino-4-methoxycinnamic acid, light, yellow crystals, m. p. 179—180°, which forms a diazo-compound, from which on boiling with dilute copper sulphate solution isoferulic acid, m. p. 228°, is obtained.

isoVanillin, prepared from protocatechualdehyde by partial methylation, condenses with malonic acid in presence of acetic acid, and at the same time carbon dioxide is eliminated and isoferulic acid formed. W. O. K.

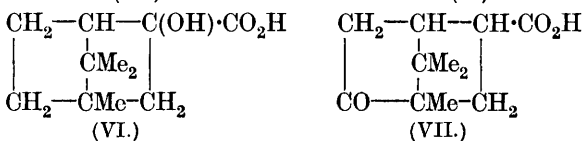
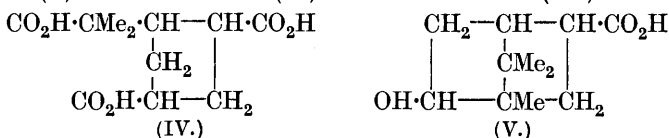
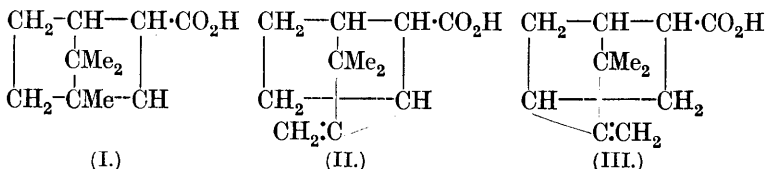
Formation and Properties of Fluorescein. O. FISCHER and MARTIN BOLLMANN (*J. pr. Chem.*, 1922, [ii], 104, 123—131).—In fluorescein as ordinarily prepared there is at most only traces of resorcinolphthalein, a fact no doubt due to the instability of this compound at the temperature of the reaction. In presence of boric acid, however, the more stable boric acid ester is formed, and fair yields of resorcinolphthalein, nearly colourless crystals, m. p. 208—209°, are obtained (monoacetyl derivative, colourless needles, m. p. 161°). This forms a hydrochloride, $C_{20}H_{12}O_5 \cdot HCl$, reddish-yellow leaflets, on passing hydrogen chloride into its ethereal solution, or on boiling with concentrated hydrochloric acid and then adding alcohol. This compound is useful in separating the fluorescein formed from the resorcinolphthalein. The hydrobromide, small leaflets, and hydroiodide, stellar aggregates of dark red needles, are formed in like manner. Fluorescein forms two mono- and two di-methyl ethers, one of each being coloured and one of each colourless. These yield the following salts: coloured monomethyl ether: hydrochloride, prisms, m. p. 242° (decomp.), hydrobromide; colourless monomethyl ether: hydrochloride, dark yellow leaflets, decomp. 170—173°, hydrobromide, yellow needles, in tufts; coloured dimethyl ether: hydrochloride, yellowish-red tufts of needles, decomp. 114°; hydrobromide, orange-red leaflets in bunches, decomp. 172°; colourless dimethyl ether: hydrochloride, dark coloured needles losing their colour at 140°; hydrobromide, orange leaflets, decomp. 92°, sulphate, reddish-yellow, microscopic prisms, m. p. 212°. W. O. K.

Camphene-*epi*-*sec.*-carboxylic Acids [[1:1-Dimethyl-6-methylene-(1:2:2)dicycloheptane-3-carboxylic Acid], their Preparation from Bornylene-*epi*-carboxylic Acid, and their Transformation into *sec.*- β -Hydroxycamphane-*epi*-carboxylic Acid [2-Hydroxy-3-methyl-*meso*-dimethyl-(1:2:2)dicycloheptanecarboxylic Acid] and δ -Hydroxycamphane-*epi*-carboxylic Acid [4-Hydroxy-3-methyl-*meso*-dimethyl-(1:2:2)-di-cycloheptanecarboxylic Acid] (*o*- and *p*-Borneolcarboxylic Acids). J. BREDT (*J. pr. Chem.*, 1922, [ii], 104, 1—27; cf. Bredt and Sandkuhl, A., 1909, i, 498).—It has been previously suggested (*loc. cit.*) that by intermolecular change, two camphenecarboxylic acids, (II) and (III), should be obtained from bornylene-carboxylic acid (I). The acid (II) has already been obtained as its isomeric lactone, and (III) is now prepared for the first time.

The tertiary hydrobromide of camphene-*epi*-*sec.*-carboxylic acid, m. p. 157° (previously known as α -hydrobromobornylenecarboxylic acid), is obtained by acting on bornylenecarboxylic acid with fuming aqueous hydrogen bromide, and this on treatment with alkali readily yields the tertiary hydroxy-acid, m. p. 176° (*loc. cit.*). This acid on dry distillation under reduced pressure, or on steam distillation, yields an acid, m. p. 76—77°. The same acid may be obtained directly from the hydrobromide by distilling in steam, or better, by warming with quinoline. This acid proves to be *camphene-epi-sec.-carboxylic acid*, b. p. 156—157°/13—14 mm., 132—133°/4 mm., 114°/1 mm. It crystallises from acetone or alcohol in plates. Treatment with hydrogen bromide yields the hydrobromide, m. p. 157°, from which the hydroxy-acid, m. p. 176°, and camphenecarboxylic acid, m. p. 76—77°, can again be obtained. With hydrogen bromide dissolved in acetic acid likewise, camphenecarboxylic acid hydrobromide is formed and no isomerisation to bornylenecarboxylic acid takes place. It forms a *silver* salt, $C_{11}H_{15}O_2Ag$, small leaflets, not hygroscopic, an *ethyl* ester, b. p. 121—126°/15 mm., 128—130°/22 mm., $[\alpha]_D + 4.04^\circ$, $n_D^{16.1}$, 1.47604. On treatment with mercuric acetate, a white *precipitate* soon separates, $C_{13}H_{20}O_5Hg$, indicating a terminal $-\dot{C}=CH_2$ group (Balbiano's reaction). It is oxidised by permanganate to *carboxycamphenecamphoric acid* (IV), nodular crystals, m. p. 234—236°. The *anhydride* of camphenecarboxylic acid is formed on treating the hydroxy-acid, m. p. 176°, with boiling acetic anhydride. It is a liquid, $C_{22}H_{30}O_3$, b. p. 260—270°/13—15 mm.

Camphenecarboxylic acid on treatment with acetic acid and a few drops of sulphuric acid yields a product which is separated by fractional distillation into a higher and a lower boiling fraction. From the lower boiling fraction has been separated *p*-borneolcarboxylolactone (*d*+*l*)-bornylene carboxylic acid, and an unsaturated acid apparently isomeric with bornylenecarboxylic acid. The higher boiling fraction consists of *acetyl- δ -hydroxycamphane-epi-carboxylic acid* (*acetyl borneol-p-carboxylic acid*), water-clear, prismatic crystals, m. p. 159°; on hydrolysis with potassium hydroxide solution, the above-mentioned *borneol-p-carboxylic acid* (V), leaflets, m. p. 180—181°, is obtained, and (*d*+*l*)-*sec.*- β -endo-

acetoxycamphane-epi-carboxylic acid [(d+l)-*acetylisoborneol-o-carboxylic acid*], hard, glistening prisms, m. p. 116°, yielding (d+l)-*isoborneol-o-carboxylic acid* (VI), small leaflets, m. p. 172°, on hydrolysis. With permanganate, borneol-*p*-carboxylic acid is oxidised to δ -*ketocamphane-epi-carboxylic acid* (*p*-*camphocarboxylic acid*) (VII), tufted needles, m. p. 133—134°, whereas (d+l)-*isoborneol-o-carboxylic acid* is unchanged, but is oxidised by nitric acid to camphoric acid. It is converted by acetic anhydride into (d+l)-bornylene *epi-carboxylic acid*, m. p. 110—111°, which is also formed on dry distillation of (d+l)-*acetylisoborneol-o-carboxylic acid*.



W. O. K.

Tropinonecarboxylic Acid Esters. R. WILLSTÄTTER, O. WOLFES, and H. MAEDER (U.S. Pat. 1419091).—Succindialdehyde is condensed with the mono-calcium salt of ethyl acetone-dicarboxylate and methylamine. The tropinone *ester* formed is an oily substance which hardens when exposed to air and takes up 2 mols. of water; m. p. 62—63° (*picrate*, m. p. 133—135°).

CHEMICAL ABSTRACTS.

Tropinonecarboxylic Acid Esters. O. WOLFES and H. MAEDER (U.S. Pat. 1419092).—An aqueous solution of succindialdehyde is added to a solution of an acetoacetic ester, alkali, and methylamine and the reaction product shaken with chloroform; the chloroform solution thus obtained is extracted with dilute sulphuric acid to obtain (on adding soda and extracting with chloroform) a tropinonecarboxylic acid ethyl ester, an oily substance which solidifies on exposure to the air for some time.

CHEMICAL ABSTRACTS.

Reduction of Acid Chlorides to Aldehydes by Means of Nickel Catalysts. H. SCHLIEWIENSKY (*Z. angew. Chem.*, 1922, 35, 483).—The preparation of aldehydes from acid chlorides by means of hydrogen in the presence of Kelber's nickel catalyst (A., 1917, ii, 215) has been described by Rosenmund (A., 1918,

i, 300). The author's attempts to repeat the preparation of benzaldehyde according to these directions have been unsuccessful. The reaction could not be effected in the presence of catalysts prepared from freshly precipitated basic nickel carbonate which was (a) ignited while moist in air to the oxide and subsequently reduced by hydrogen in an electric furnace at 310—320°, (b) directly heated in the tube at 310—320° and subsequently reduced at the same temperature, and (c) dried at 100° in air and then ignited and reduced in hydrogen at 310—320°. Failure cannot be attributed to inactivity of the catalyst which rapidly caused the hydrogenation of fats. H. W.

Reduction of Acid Chlorides to Aldehydes by Means of Nickel Catalysts. K. W. ROSENMUND (*Z. angew. Chem.*, 1922, **35**, 483).—In reply to Schlieviensky (preceding abstract), it is pointed out that attention has already been directed (A., 1918, i, 300) to the variability in the behaviour of palladium and nickel as catalysts in the conversion of acid chlorides into aldehydes by hydrogen. A trustworthy procedure has been given in the case of palladium (Rosenmund and Zetzsche, A., 1921, ii, 320); a modified method will be published in the case of nickel. H. W.

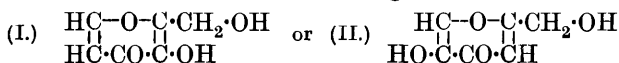
N-Oximino-ethers. II. N-Aryl Ethers of 2:4- and 2:6-Dinitrobenzaldoximes. FRED BARROW, EVAN DALTON GRIFFITHS, and EDWARD BLOOM (T., 1922, **121**, 1713—1717).

The Action of Sodium Methoxide and its Homologues on Benzophenone Chloride and Benzylidene Chloride. III. JOHN EDWIN MACKENZIE (T., 1922, **121**, 1695—1699).

Piperitone. IV. The Interaction of *dl*-Piperitone and Semicarbazide, and the Isolation of Pure *dl*-Piperitone. JOHN READ and HENRY GEORGE SMITH (T., 1922, **121**, 1863—1872).

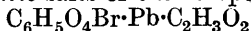
A New Organic Acid (Kojic Acid) Formed by *Aspergillus oryzae*. TEIJIRO YABUTA (*J. Chem. Soc. Tokyo*, 1916, **37**, 1185—1233, 1234—1269).—The substance is not only present in the organism, but is also formed abundantly when the latter is grown on steamed rice ("Koji") or in a 10% solution of dextrose with salts; in the latter case, one-tenth of the dextrose is converted according to the equation $C_6H_{12}O_6 + O = C_6H_6O_4 + 3H_2O$. The formula originally given (A., 1913, i, 180) must be halved, as the result of molecular weight determinations. Kojic acid thus differs by one oxygen atom from maltol, which is formed from carbohydrates on distillation (A., 1910, i, 719). Both substances are 3-hydroxy- γ -pyrones and give with ferric chloride a coloration similar to that given by salicylic acid; kojic acid gives this reaction even at 1:200,000. The acid forms colourless, anhydrous needles, m. p. 152°, subliming in a high vacuum without change, readily soluble in water, alcohol, or ethyl acetate, less soluble in ether, chloroform, or pyridine, scarcely at all soluble in most other solvents. The acid is precipitated by carbon dioxide from concentrated solutions of its sodium salt. It gives a red coloration

with *p*-diazobenzenesulphonic acid, and reduces Fehling's and ammoniacal silver solutions. The *copper* salt, $(C_6H_5O_4)_2Cu$, is the most characteristic of several crystalline salts, and is employed in the isolation of the substance. The *barium* salt has the composition $(C_6H_5O_4)_2Ba \cdot 2C_6H_6O_4$; the *calcium* and *strontium* salts have a similar composition, $+4H_2O$. The *diacetyl* derivative, $C_6H_4O_2(OAc)_2$, m. p. 102° , the *dibenzoyl* derivative, m. p. 136° , the *diphenylcarbamate*, $C_6H_4O_2(O \cdot CO \cdot NHPh)_2$, m. p. 170° , and the *monobenzoyl* derivative, $C_6H_5O_3(OBz)$, m. p. 135° , have been prepared, the latter by benzoyl chloride acting on the substance suspended in ether. The *dimethyl ether*, $C_6H_4O_2(OMe)_2$, prepared by diazomethane or methyl sulphate, m. p. 90° , is hydrolysed by boiling barium hydroxide solution into equimolecular proportions of formic acid, methoxyacetic acid, and methoxyacetone (acetylcarbinyl methyl ether). Ammonia transforms kojic acid into a *base*, $C_8H_{11}O_3N$, probably the dimethyl ether of a hydroxymethyl-hydroxy- γ -pyridone (comenamic alcohol?). This base was isolated as the *hydrochloride*, m. p. 180 — 181° , the *picrate*, m. p. 177° , and the *platinichloride*, m. p. 172° . The above facts suggest that kojic acid has either of the following constitutions:

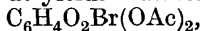


In the case of maltol, Peratoner and Tamburello (A., 1905, i, 807) decided between similar alternatives in favour of a formula analogous to I, and Peratoner and Palazzo (A., 1905, i, 806) assigned to comenic acid a constitution of the second type, because the latter does, and maltol does not, react with benzenediazonium acetate or amyl nitrite (only compounds of the second type can tautomerically furnish the $\cdot CH_2 \cdot CO \cdot$ grouping necessary for these condensations). Since kojic acid forms with benzenediazonium acetate a *benzeneazo*-derivative, $C_{12}H_{10}O_4N_2 \cdot H_2O$, m. p. (in sealed tube) 146 — 147° , the author considers that it is constituted according to formula II, so that it would be 3-hydroxy-6-hydroxymethyl- γ -pyrone, the alcohol corresponding with comenic acid. Various unsuccessful attempts at the conversion of kojic acid into known pyrone and pyridone compounds were made by oxidation and reduction.

Bromine water yields *monobromokojic acid*, $C_6H_5O_4Br$, m. p. 159 — 160° , furnishing a *copper* salt, $(C_6H_4O_4Br)_2Cu$, and with lead acetate and nitrate *double* salts of the compositions



and $C_6H_3O_4Br \cdot Pb \cdot NO_3$. It yields a *diacetyl* derivative,

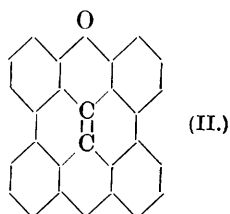
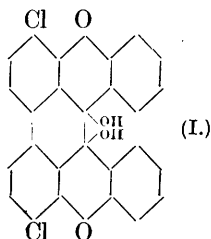


m. p. 94 — 95° , and a *dibenzoyl* derivative, $C_6H_4O_2Br(OBz)_2$, m. p. 133 — 134° . It is converted by barium hydroxide in poor yield into *hydroxykojic acid*, $C_6H_6O_5 \cdot \frac{1}{2}H_2O$, which gives with ferric chloride a transitory green or, in the presence of sodium acetate, a purple coloration. Hydroxykojic acid is probably 2:3-dihydroxy-6-hydroxymethyl- γ -pyrone and yields an amorphous *copper* salt, $C_6H_4O_5Cu$. When the lead double salt of bromokojic and acetic

acid (above) is treated with hydrogen sulphide, a *sulphide*, $(C_6H_5O_4)_2S$, m. p. 210—212°, results. (Cf. also, for maltol, A., 1894, i, 270; 1895, i, 80, and for *isomaltol*, A., 1910, i, 544; further, Brill, A., 1916, i, 876.) G. B.

Highly Condensed Derivatives of Xanthone. ALFRED ECKERT and GERTRUD ENDLER (*J. pr. Chem.*, 1922, [ii], **104**, 91—101).—Corresponding with anthraquinone, a *mesonaphthobi-anthrone* is known (Scholl, A., 1910, i, 494). The analogous *mesonaphthodixanthylene* is now described.

2 : 5-Dichlorophenol and *o*-chlorobenzoic acid are condensed by boiling methyl alcoholic potash in presence of copper powder to form *o*-2 : 5-dichlorophenoxybenzoic acid, a white, crystalline powder, m. p. 120—124°. Sulphuric acid converts this compound into 1 : 4-dichloroxanthone, long, colourless needles, m. p. 159—161°, which, when boiled with methyl alcoholic potash under a reflux condenser yields 4-chloro-1-methoxyxanthone, yellow needles, m. p. 156—158°. Aluminium chloride removes the methyl group from this, with the formation of 4-chloro-1-hydroxyxanthone, long, yellow needles, m. p. 156°. By treating 1 : 4-dichloroxanthone with copper powder in boiling naphthalene, 4 : 4'-dichloro-1 : 1'-dixanthonyl, long, colourless needles, m. p. 290°, is obtained, and this compound, on reduction with zinc dust in alcoholic potash, yields a *pinacone*, with the formula (I), yellow crystals, m. p. 276—278°. This substance can be very easily oxidised back to dichlorodixanthonyl with chromic acid. On further reduction with red phosphorus and hydrogen iodide, it yields *mesobenzdixanthylene*, golden-yellow plates, m. p. 236—237°. This substance on oxidation with chromic acid yields dixanthonyl, and when heated at 140—150° with aluminium chloride loses two atoms of hydrogen to form *mesonaphthodixanthylene*, yellow needles, m. p. 140—150° (II). It has not been found possible to carry out this last change by illuminating a solution of *mesobenzdixanthylene* in acetic acid.



W. O. K.

Preparation of Benzanthrone Derivatives. BRITISH DYE-STUFFS CORPORATION, LIMITED, ARTHUR GEORGE PERKIN, and GEORGE DOUGLAS SPENCER (Brit. Pat. 183351).—*Hydroxybenzanthrone* is obtained by heating a mixture of benzanthrone (50 parts), anthraquinone (50 parts), alkali hydroxide (300 parts), water (75 parts), and sodium chlorate or sodium nitrate (35 parts)

in an autoclave slowly at 250° and then maintaining the temperature during three hours between 250° and 265°. The product is digested with boiling water, and anthraquinone removed by filtration. Hydroxybenzanthrone is precipitated from the filtrate by carbonic acid or a stronger acid.

Aminobenzanthrone is prepared by gradually heating a mixture of hydroxybenzanthrone (25 parts) and ammonia (d 0.880, 500 parts) in an autoclave at 200° and subsequently maintaining the temperature at 220–230° during seven hours. The product is diluted with water and filtered, whereby aminobenzanthrone is isolated as dull red crystals; unchanged hydroxybenzanthrone can be recovered by acidification of the filtrate. H. W.

Introduction of Arylamino-groups into Aminoanthraquinones. BADISCHE ANILIN & SODA-FABRIK (Fr. Pat. 526686; Brit. Pat. 171292; Swiss Pat. 90480; from *Chem. Zentr.*, 1922, ii, 639).—Aminoanthraquinones or their substituted derivatives are treated with metallic compounds of primary aromatic amines, or with such metals or metallic compounds, especially metallic amides, which give with amines metallic arylamine compounds, in the presence of weak oxidising agents such as air. For example, by heating 1-amino-2-methylantraquinone with sodamide, or with sodium, magnesium, or aluminium anilides, 1-amino-4-anilino-2-methylantraquinone is obtained. 1-Amino-2-methylantraquinone and sodium *p*-toluidide similarly give 1-amino-4-*p*-toluidino-2-methylantraquinone, lustrous, metallic, dark violet prisms, *m. p.* 266°. Other compounds similarly prepared are the following. *s*-1:4-Dianilinoanthraquinone, lustrous, metallic, violet needles, *m. p.* 217°; *s*-1:4-Di-*p*-toluidinoanthraquinone; 1-amino-2-anilinoanthraquinone (?), violet, lustrous needles, *m. p.* 239°; 1-amino-4-anilinoanthraquinone, *m. p.* 192°; amino-*p*-toluidinoanthraquinone, *m. p.* 253°; amino-*o*-toluidinoanthraquinone, *m. p.* 206°; *s*-dianilinoanthraquinone, violet needles with slight metallic lustre, *m. p.* 152°; anthraquinonedihydro-5-phenylphenazine, *m. p.* 233° (cf. *A.*, 1921, i, 274); diaminophenylaminoanthraquinone, dark violet crystals. G. W. R.

Preparation of 1-Amino-2-anthraquinone Aldehyde. LEOPOLD CASSELLA & Co., (D.R.-P. 346188 and Swiss Pat. 73683; from *Chem. Zentr.*, 1922, ii, 638).—The condensation products obtained by heating 1-amino-2-methylantraquinone with aromatic nitro-compounds, with or without addition of primary aromatic amines in the presence of alkalis, are treated with acids. The condensation product of the composition $C_6H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>C_6H_2(NH_2) \cdot (CH:N-Aryl)^2$ obtained by the action of 1-amino-2-methylantraquinone on nitrobenzene in the presence of potassium carbonate or on β -naphthylamine in the presence of nitrobenzene, is heated with sulphuric acid or with acetic acid and strong hydrochloric acid. The 1-aminoanthraquinone-2-aldehyde thus obtained, $C_6H_4<\begin{smallmatrix} CO \\ CO \end{smallmatrix}>C_6H_2(NH_2) \cdot CHO$, forms lustrous,

metallic, red crystals, m. p. 231—233°. The solution in strong sulphuric acid gives a diazo-compound with sodium nitrite. When heated with primary amines, it gives an azomethine. G. W. R.

Picolinoylaminoanthraquinones. E. DE BARRY BARNETT (*Chem. News*, 1922, **125**, 143—144).—1-Picolinoylaminoanthraquinone, $C_{20}H_{12}O_3N_2$, a dark yellow, crystalline powder, m. p. 282—284° (decomp.), is prepared by the action of crude picolinoyl chloride on a solution of 1-aminoanthraquinone in tetrachloroethane. On alkaline reduction, it forms a red vat-dye, but the action takes place slowly and with considerable difficulty. 2-Picolinoylaminoanthraquinone forms almost colourless crystals, m. p. 257—258°. The compounds could not be caused to react with alkyl haloid with the formation of soluble, quaternary (pyridinium) salts. H. W.

Anthraquinone Derivatives. K. WILKE (U.S. Pat. 1417875).—By the action of fuming sulphuric acid on 1-nitro-2-alkylanthraquinones, products are formed which are insoluble in alkalis and are good starting materials for the manufacture of dyes. Conducting the reaction with exclusion of air gives products of greater purity. Elimination of the elements of water occurs between the nitro- and alkyl-group with formation of new isooxazole derivatives of anthraquinone. 1-Nitro-2-methylantraquinone yields 1:2-anthraquinoneisooxazole, m. p. about 250° (decomp.). 1:5-Dinitro-2-methylantraquinone yields greenish-yellow crystals of 5-nitro-1:2-anthraquinoneisooxazole. 1-Nitro-2-ethylantraquinone yields 1:2-anthraquinonemethylisooxazole, coarse, dark brown crystals, m. p. about 210°. 1-Nitro-2-methyl-5:6:7:8-tetrachloroanthraquinone yields 5:6:7:8-tetrachloro-1:2-anthraquinoneisooxazole, a greenish-yellow powder, m. p. about 242° (decomp.).

CHEMICAL ABSTRACTS.

Preparation of Camphene Hydrochloride. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 348484; from *Chem. Zentr.*, 1922, ii, 699—700).—Camphene is treated, in the presence of a suitable diluent, with hydrogen chloride at low temperatures. The hydrochloride (formula annexed) thus obtained forms branched snow-white crystals, m. p. 125—127°. It has a strong odour similar to that of menthol, but quite distinct from that of pinene hydrochloride and isobornyl chloride. It is unstable and readily loses hydrogen chloride, which results in the gradual formation of isobornyl chloride. This transformation takes place more quickly in the presence of acids. By shaking camphene hydrochloride with water, camphene hydrate is formed in quantitative yield. The reaction takes place more quickly in the presence of alkalis. G. W. R.

The Borneol obtained from the Magnesium Compound of Pinene Hydrochloride. G. VAVON and A. L. BERTON (*Compt. rend.*, 1922, **175**, 369—372).—Pinene hydrochloride when treated with

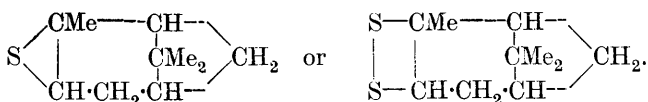
Grignard's reagent and then oxidised yields a mixture of borneol and isoborneol in different proportions depending on the temperature of oxidation. The authors state that their experiments yield no evidence as to the stage at which the formation of two isomerides takes place and suggest the possibility of the existence of isomerides in the pinene hydrochloride. H. J. E.

Phenylcamphenol. A. M. NORDSTRÖM (*Hyllningsskrift tillägnad Ossian Aschan*, 1920, 129—133).—Magnesium phenyl bromide and camphenol yield a viscid, oily substance, *phenylcamphenol*, b. p. 166—167°/15 mm., d_4^{20} 1.0620, n_D^{20} 1.55085, and a little diphenyl. Elimination of water yields a *compound*, probably of the annexed constitution, d_4^{20} 1.0002, n_D^{18} 1.54679. It does not form a nitrosochloride, but treatment with formic acid yields phenylapobornyl formate, a viscid oil, b. p. 183.5—185°/18 mm., d_4^{20} 1.0801, n_D^{20} 1.53461, by hydrolysis of the ester, of which there are obtained phenylapoborneol, b. p. 164.5—166°/7 mm., d_4^{20} 1.0583, n_D^{20} 1.55160, and an acid crystallising in fine needles, m. p. 164°. Phenylapoborneol on oxidation yields phenylapocamphor, b. p. 185—187°/20 mm., d_4^{20} 1.0716, n_D^{20} 1.55228 (semicarbazone, m. p. 214°); the latter on oxidation gives phenylapocamphoric acid, lustrous scales, m. p. 205° (anhydride, m. p. 118—119°; diethyl ester, b. p. 200—201°/7 mm., d_4^{20} 1.7028, n_D^{18} 1.50596). Phenylapoborneol yields, according to Chugaev, phenylapobornylene, b. p. 135°/13 mm., d_4^{20} 0.9907, n_D^{19} 1.54466 (nitrosochloride, m. p. 164°) and a substance, b. p. 70—74°/8 mm., d_4^{21} 0.9108, n_D^{17} 1.53619, which on oxidation gives benzyl alcohol and a ketone (semicarbazone, m. p. 199°).

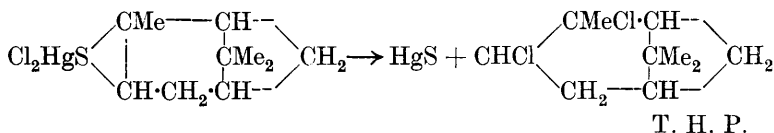
CHEMICAL ABSTRACTS.

Action of Sulphur and Sulphur Compounds on Terpenes. P. P. BUDNIKOV and E. A. SCHILOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk*, 1921, 4, 110—112).—When terpenes, b. p. 155—160°, are subjected to prolonged boiling with sulphur in a reflux apparatus and in an atmosphere of carbon dioxide, hydrogen sulphide and other gaseous products are formed together with a reddish-brown, oily liquid having a characteristic, acrid odour. Fractional distillation of this liquid at either ordinary or reduced pressure yields a number of products which all contain sulphur and form precipitates when treated with alcoholic solutions of mercuric chloride, auric chloride, and lead acetate. The mercury compound gradually decomposes with formation of mercuric sulphide and a red, oily liquid when boiled with water, and yields a distillate free from sulphur, but containing chlorine, when distilled in a current of steam. Hydrogen sulphide is also liberated when the fractions of the original product are treated with strong acids. Similar sulphur-containing products, giving precipitates with some of the heavy metal salts, are obtained when terpenes are treated with hydrogen sulphide under the conditions mentioned above.

Sulphur probably unites with terpenes at the double linking, giving a compound of the formula



In the compound formed with mercuric chloride, the latter probably unites with the sulphur, the subsequent decomposition by steam being represented by the equation :



The Composition of Beechnut Oil (*Oleum fagi sylvaticæ*). A. HEIDUSCHKA and P. ROSER (*J. pr. Chem.*, 1922, [ii], **104**, 137—160).—An exhaustive analysis shows the presence in this oil of 0.39% of α -linolenic acid, 9.19% of α -linolic acid, 76.69% of oleic acid, 4.88% of palmitic acid, 3.45% of stearic acid, and 0.82% of material which could not be saponified and was essentially phytosterol.

W. O. K.

The Essential Oil from Inchi Grass (*Cynopogon Cæsius*, Stapf.). K. L. MOUDGILL and K. R. KRISHNA IYER (*Perf. and Essent. Oil Rec.*, 1922, **13**, 292—295).—The constants for this oil (yield, 0.8%) are: d_4^{30} 0.9187; n_D^{30} 1.484; $[\alpha]_D^{30}$ -38.9° ; acid number, 1.7; saponification number, 5.6; acetyl number, 120; percentage of aldehydes (Bennett's hydroxylamine method), 4.2. The oil is not identical with any of the known commercial oils from allied grasses, and may be used as a substitute for palmarosa oil, which it resembles in odour. It contains *l*-borneol, *l*-camphene, *l*-limonene, *l*-terpineol, and unidentified sesquiterpene constituents.

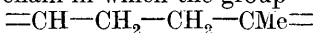
H. C. R.

Essential Oil of Juniper from Cyrenaica. V. MASSERA (*Riv. Ital. ess. profumi*, 1922, **4**, 23—24; from *Chem. Zentr.*, 1922, i, 1079).—A sample of essential oil of juniper from Cyrenaica had d^{15} 0.8715; $[\alpha]_D +6^\circ$; n_D^{20} 1.4732; acid number, 0.54; esterification number, 4.91; acetyl number, 11.92. α -Pinene and cadinene were present. A sample from another locality had similar properties.

G. W. R.

Empirical and Structural Composition of Natural and Synthetic Caoutchouc. F. KIRCHHOF (*Koll. Chem. Beihefte*, 1922, **16**, 47—87).—A critical discussion in which the author by means of an examination of the analytical data of Harries and his co-workers attempts to show that Para caoutchouc has the empirical formula $\text{C}_{10}\text{H}_{17}$. The African Congo caoutchouc has, like the synthetic isoprene and piperylene caoutchouc, the formula $\text{C}_{10}\text{H}_{16}$, which has been generally accepted for all forms of caoutchouc. These formulæ are in keeping with the behaviour of these substances during ozonisation and oxozonisation. Because of this new formula for Para caoutchouc, it must have a constitution different from

that put forward by Harries. The Para caoutchouc hydrocarbon must have an open chain in which the group

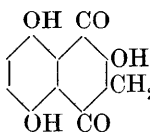


must appear, but in which other groups must also exist, as shown by the appearance of formic, carbonic, and succinic acids during the decomposition of the ozonide. Here, in part, is the difference between Para caoutchouc and synthetic isoprene caoutchouc. An attempt is made to build up structural formulae which shall represent the quantitative relationships of the ozonide decomposition, the depolymerisation in solution and the decomposition on distillation in a vacuum. Since the purely chemical structural formula is insufficient to represent both the chemical and physico-chemical facts, the author has advanced a spacial formula which, it is claimed, explains the colloidal, physico-chemical, and chemical properties of caoutchouc. J. F. S.

Anemonins. YASUHIKO ASAHINA and ATSUSHI FUJITA (*Acta Phytochim.*, 1922, **1**, 1—42).—A résumé in German of Asahina's work on anemonin, most of which has been published in Japanese only (cf. A., 1892, i, 241; 1896, i, 623; 1899, i, 930; 1914, i, 561; 1915, i, 1067; 1916, i, 401; 1920, i, 70, 321, 493, 678; 1921, i, 798).

W. G.

The Colouring Matter of *Lithospermum erythrorhizon*. RIKÔ MAJIMA and CHIKA KURODA (*Acta Phytochim.*, 1922, **1**, 43—65).—The colouring matter of shikon, the dried roots of *Lithospermum erythrorhizon*, has been isolated in a crystalline form and been shown to be a *monoacetyl* derivative, m. p. 85—86°, of shikonin. If the acetyl derivative is dissolved in dilute alkali and the solution is then acidified with dilute acid, *shikonin* itself, $C_{16}H_{16}O_5$, m. p. 147°, is obtained. It gives *sodium* and *copper* salts and on acetylation yields a *triacetyl* derivative, m. p. 113°, but if the acetylation is carried out in the presence of zinc dust, a *penta-acetyl* derivative of reduced shikonin, m. p. 90°, is formed, which on bromination gives a *bromo-compound*, $C_{16}H_{12}O_5BrAc_5 \cdot H_2O$, m. p. 123°. Shikonin also yields a *dibenzoyl* derivative, m. p. 168°, and an *oxime*, m. p. 163°. The constitution assigned to shikonin (annexed formula) is that of δ -methyl- Δ^7 -pentenyl-2:5:8-trihydroxy-1:4-naphthaquinone. In support of this view, it is shown that on heating, shikonin is partly converted into *shikazarin* (1:4-dihydroxy-8-methylanthraquinone), m. p. 232°, and on dry distillation gives 1- and 2-methylanthracenes. Shikazarin, if distilled with zinc dust, gives the same products. When oxidised with potassium permanganate in acetone solution, shikazarin gives 3-methylphthalic acid. Triacetylshikonin on oxidation with ozone yielded acetone, succinic acid, and 3:6-dihydroxyphthalic acid. W. G.

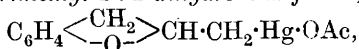


The Structure of the Compounds produced from Olefines and Mercury Salts: Mercurated Dihydrobenzofurans. ROGER ADAMS, F. L. ROMAN, and W. N. SPERRY (*J. Amer. Chem. Soc.*, 1922, **44**, 1781—1792).—Experimental evidence is adduced

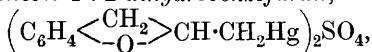
from the literature to disprove molecular formulæ, such as $\text{CH}_2\cdot\text{CH}_2\cdot\text{Hg}(\text{OH})\text{X}$, for the compounds from olefines and mercuric salts.

A series of mercurated dihydrobenzofurans of the general structure $\text{C}_6\text{H}_4\langle\text{CH}_2\text{O}\rangle\text{CH}\cdot\text{CH}_2\cdot\text{HgX}$, is described. These compounds are remarkably stable towards acids in comparison with other mercury salt-olefine compounds. They are converted by potassium iodide into the corresponding iodide and by treatment with sodium amalgam give compounds of the general type R_2Hg . No reasonable molecular formula for the mercurated dihydrobenzofurans can be written which will explain the structure and the chemical reactions of these compounds. The additive formula allows of a simple explanation of all the experimental facts.

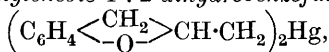
1-Acetoxymercurimethyl-1 : 2-dihydrobenzofuran,



colourless plates, m. p. $80-81^\circ$, is prepared by the gradual addition of an aqueous solution of mercuric acetate to a suspension of *o*-allylphenol in water. It is converted by sodium chloride solution into 1-chloromercurimethyl-1 : 2-dihydrobenzofuran, m. p. 137° , which is also obtained from *o*-allylphenol and mercuric chloride in the presence of water, ethyl alcohol, or *n*-butyl alcohol. If the reaction is effected in the presence of aqueous hydrochloric acid, an unstable intermediate compound, probably $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{HgCl}$, is also formed which, however, could not be isolated in a homogeneous condition. The acetoxy-compound is converted by hot potassium bromide solution into 1-bromomercurimethyl-1 : 2-dihydrobenzofuran, colourless, lustrous crystals, m. p. 122° , and by potassium iodide into 1-iodomercurimethyl-1 : 2-dihydrobenzofuran, colourless plates, m. p. $114-115.5^\circ$; the latter substance is also obtained from the chloromercuri-derivative and potassium iodide. 1 : 1-Sulphato-mercuridimethylenebis-1 : 2-dihydrobenzofuran,



m. p. 123° (decomp.), is prepared by the cautious addition of *o*-allylphenol to a solution of mercuric oxide in aqueous sulphuric acid. Reduction of 1-chloromercurimethyl-1 : 2-dihydrobenzofuran by sodium amalgam and ethyl alcohol leads to the production of 1 : 1-mercuridimethylenebis-1 : 2-dihydrobenzofuran,



colourless crystals, m. p. 93° .

o-Allylanisole reacts with an aqueous or methyl alcoholic solution of mercuric acetate with the formation of α -acetoxymercuri- γ -*o*-anisylpropan- β -ol, $\text{C}_6\text{H}_4(\text{OMe})\cdot\text{CH}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\cdot\text{Hg}\cdot\text{OAc}$, which could not be caused to crystallise. It is readily decomposed by hydrochloric acid with regeneration of *o*-allylanisole. It appears to be converted by sodium chloride into the corresponding chloride, which could not be caused to solidify. Mercuric chloride or sulphate does not react with *o*-allylanisole.

1-Iodomercurimethyl-1 : 2-dihydrobenzofuran is transformed by a hot solution of iodine in aqueous potassium iodide into 1-iodomethyl-1 : 2-dihydrobenzofuran, $C_6H_4<\begin{smallmatrix} CH_2 \\ -O- \end{smallmatrix}>CH\cdot CH_2I$, colourless crystals, m. p. 36.5—37.5°, b. p. 150—151°/13—15 mm., d_{25}^{24} 1.792 (liquid), n_D^{25} 1.614; the latter substance is reduced by granulated zinc and hydrochloric acid to 1-methyl-1 : 2-dihydrobenzofuran, b. p. 199—202°/744 mm., d_{25}^{24} 1.507, n_D^{25} 1.536. H. W.

The Relation between Vitali's Reaction and the Constitution of the Alkaloids which give it. PAUL HARDY (*J. Pharm. Chim.*, 1922, [vii], 26, 172—176).—It has been pointed out that Vitali's reaction is given by substances other than atropine and hyoscyamine. The author shows that it is a general reaction for esters of certain acids the constitution of which is analogous to that of tropic acid. The reaction is given by scopolamine and by *iso*-atropylcocaine but not by homatropine or veratrine. H. J. E.

Salts of Codeine : The Hydrobromide ; Preparation of Solutions for Injection. FELIX MARTIN (*J. Pharm. Chim.*, 1922, [vii], 26, 176—187).—Codeine hydrobromide crystallises with 2 mols. of water, which are not lost on exposure to the atmosphere; in dry air, $\frac{1}{2}$ mol. of water is lost at the ordinary temperature. At 100°, the salt is only partly dehydrated and must be heated at 115—116° before becoming anhydrous. The solubility in water at 97° is 2.04. Addition of sodium benzoate or salicylate increases its solubility at the ordinary temperature; this is considered to be due to double decomposition, as codeine salicylate may be extracted with ether from a mixed solution. Several analyses of commercial codeine indicate a product of a high degree of purity. H. J. E.

Harmine and Harmaline. VI. The Synthesis of N-Methyl-tetrahydronorharmine and the Constitution of Harmaline and of the Alkylated Harmines. WILLIAM OGILVY KERMACK, WILLIAM HENRY PERKIN, and ROBERT ROBINSON (*T.*, 1922, 121, 1872—1896).

Preparation of O-Alkyl Derivatives of Hydrocupreine. VEREINIGTE CHININFABRIKEN ZIMMER & Co., (D.R.-P. 344140; from *Chem. Zentr.*, 1922, ii, 812).—Hydrocupreine oxide, which may be obtained by oxidation of hydrocupreine, is alkylated by the usual methods and the products are reduced to the alkyl derivatives of hydrocupreine. Since the nitrogen atom which is alkylated is protected by an oxygen atom, ammonium bases are not formed. *Hydrocupreine oxide* (leaflets, m. p. 199°, obtained by the action of 30% hydrogen peroxide on hydrocupreine) is treated with ethyl sulphate, *ethyl hydrocupreine oxide sulphate*, thereby obtained, forms colourless needles. By heating with excess of sulphur dioxide under pressure, *ethyl hydrocupreine* is obtained. By treatment of hydrocupreine oxide with ethylene chloride and

reduction with sulphuric acid and sodium sulphite, *chloroethyl hydrocupreine* is obtained; it forms colourless needles, m. p. 164°. G. W. R.

The Isolation of Muscarine, the Potent Principle of *Amanita Muscaria*. HAROLD KING (T., 1922, 121, 1743—1753).

Arylated Pyridines and their Relations to the Corresponding Pyrylium Compounds. IV. WALTHER DILTNEY [with J. NÜSSELEIN, HEINR. MEYER, and H. KAFFER] (*J. pr. Chem.*, 1922, [ii], 104, 28—36; cf. A., 1921, i, 735).—It has been shown that whereas the salt-forming powers of pyrylium compounds are not much affected by the introduction of aryl groups, those of pyridine compounds are considerably weakened. It has now been found, however, that, under suitable conditions, penta- and tetraphenylpyridines form a picrate, and that pentaphenylpyridine forms a perchlorate, the basicity thus being rather stronger than had been suspected.

The following new compounds have been prepared: *Pentaphenylpyridine picrate*, nodular, yellowish-orange crystals or compact prisms, m. p. 233—237°, *perchlorate*, colourless crystals, m. p. 299°; 2 : 4 : 5 : 6-tetraphenylpyridine *picrate*, small, yellow needles, m. p. 192—193°; 4 : 5 : 6-triphenyl-2-(p-bromophenyl)pyridine, colourless needles, m. p. 172° (*picrate*, m. p. 226°); 4-phenyl-2 : 6-di-(p-bromophenyl)pyridine, colourless, silky needles, m. p. 196° (*hydrochloride*, citron-yellow needles, *picrate*, yellow prisms, m. p. 212°); 4 : 6-diphenyl-2-(4-methoxy-3-methylphenyl)pyridine, colourless needles, m. p. 112° (*hydrochloride*, greenish-yellow crystals like glass-wool, m. p. 100—104°); 4 : 6-diphenyl-2-(6-hydroxy-m-tolyl)pyridine, colourless needles, m. p. 151—152° (*picrate*, yellow needles, m. p. 232°); 4 : 6-diphenyl-2-(6-acetoxy-m-tolyl)pyridine, colourless prisms, m. p. 99—101° (*picrate*, nodular, yellow crystals, m. p. 126—127°).

W. O. K.

Preparation of Hydrogenated 1-Alkylpyridine-4-Carboxylates. E. MERCK (D.R.-P. 344028; from *Chem. Zentr.*, 1922, ii, 810).—Trigonelline (methylbetaine of pyridine-3-carboxylic acid), its 1-alkyl homologues, or the salts of these compounds are reduced by metals in alcoholic solution. Reduction of trigonelline chloride by tin and hydrochloric acid in methyl alcoholic solution gives *methyl 1-methylhexahydropyridine-3-carboxylate*, an oil, b. p. 92—94°/16 mm. The alkylhaloids have therapeutic uses. The *methiodide* has m. p. 190° (corr.). Ethyl 1-ethylhexahydropyridine-3-carboxylate, a basic-smelling, colourless oil, b. p. 108—110°/13 mm., is obtained by reduction of *ethyltrigonelline hydrochloride* (? *hydrobromide*). The latter is prepared by heating pyridine-3-carboxylic acid with ethyl bromide, sodium carbonate, and water in a closed vessel; it forms white, lustrous spangles, m. p. 227° (decomp.). G. W. R.

Preparation of Hydrogenated 1-Alkylpyridine-3-carboxylates. RICHARD WOLFFENSTEIN (D.R.-P. 346888; from *Chem. Zentr.*, 1922, ii, 811).—In the place of 1-alkylhaloids of alkyl pyridine-

3-carboxylates (this vol., i, 365), other quaternary ammonium salts are used. For example, methyl 1-methylpyridine-3-carboxylate methosulphate is reduced by tin and hydrogen chloride to methyl 1-methylhexahydropyridine-3-carboxylate, which is identical with the compound obtained by reduction of the corresponding 1-alkyl-haloids. *Ethyl 1-ethylhexahydropyridine-3-carboxylate*, similarly prepared, is a basic, oily liquid. G. W. R.

Preparation of Alkyl Salts of Hydrogenated 1-Alkylpyridine-3-carboxylates. RICHARD WOLFFENSTEIN (D.R.P. 346461 and 348379; from *Chem. Zentr.*, 1922, ii, 810—811; cf. this vol., i, 365).—Hydrogenated 1-alkylpyridine-3-carboxylates are treated with alkyl haloids or with other alkyl salts. By the action of methyl iodide on methyl 1-methylhexahydropyridine-3-carboxylate in the presence of a diluent, the corresponding 1-methiodide is obtained. It is a colourless or light yellow, crystalline powder of fish-like odour, having m. p. 185—188°. The 1-methobromide is a white, crystalline powder, m. p. 196°. The 1-methochloride is prepared by the action of silver chloride on the 1-methiodide. The *ethosulphate* forms white, lustrous leaflets, m. p. 90—96°. The *ethosulphate* of ethyl 1-methylhexahydropyridine-3-carboxylate is also mentioned. The products have therapeutic uses. G. W. R.

Preparation of 1-Alkylpyridine Carboxylates. E. MERCK (D.R.-P. 344029; from *Chem. Zentr.*, 1922, ii, 810).—Betaines of the pyridine series are esterified with alcohols by the usual methods in the presence of strong acids. The *chloride* of methyl 1-methylpyridine-3-carboxylate, $C_8H_{10}O_2NCl \cdot H_2O$, is prepared by heating trigonelline or trigonelline chloride with methyl alcohol containing hydrochloric acid. It forms colourless crystals, m. p. 101°. G. W. R.

Preparation of Betaines of the Pyridine Series. E. MERCK (D.R.-P. 344030; from *Chem. Zentr.*, 1922, ii, 810).—Pyridine-carboxylic acids are treated with methyl chloride in alkaline solution at about 100°. Trigonelline is thus prepared from pyridine-3-carboxylic acid. Pyridine-2 : 3-dicarboxylic acid (quinolinic acid) gives a *methyl pyridine-2 : 3-dicarboxylic acid* having m. p. 157°. G. W. R.

The 6-Alkyloxy-2-methylquinolines. GURNEY O. GUTEKUNST and H. LE B. GRAY (*J. Amer. Chem. Soc.*, 1922, **44**, 1741—1746).—The preparation of 6-alkyloxy-2-methylquinolines involves the production of relatively large quantities of the various *p*-amino-phenyl alkyl ethers, some of which are more conveniently obtained by the reduction of the corresponding *p*-nitrophenyl compounds, whereas others are derived more readily from the *p*-acetylaminophenyl alkyl ethers. The amines are transformed into the 2-methylquinolines according to the Doebner-Miller quinaldine synthesis.

p-Nitrophenyl butyl ether, slender, colourless needles, m. p. 32°, is prepared by the protracted heating of a solution of *p*-nitrophenol

in aqueous alcoholic (50%) potassium hydroxide solution with butyl alcohol and butyl iodide under a reflux condenser. *p*-Aminophenyl butyl ether, obtained by reducing the nitro-compound with stannous chloride and concentrated hydrochloric acid, is a pale yellow liquid, b. p. 143—144°/12 mm. *p*-Nitrophenyl isoamyl ether, a pale yellow liquid, b. p. 183°/18 mm., is reduced similarly to *p*-aminophenyl isoamyl ether, a pale yellow liquid, b. p. 149—150°/15 mm.

p-Acetylaminophenyl allyl ether, minute crystals, m. p. 88—89°, is prepared by the action of allyl bromide on a boiling solution of *p*-acetylaminophenol and potassium hydroxide in alcohol (75%). It is hydrolysed by sulphuric acid to *p*-aminophenyl allyl ether, a pale yellow liquid, b. p. 143—144°/13 mm., the sulphate of which, large, colourless plates, m. p. 244° (decomp.), is described. The following compounds have also been prepared: *p*-Acetylaminophenyl butyl ether, colourless needles, m. p. 112°; *p*-aminophenyl butyl ether, a pale yellow liquid, b. p. 143—144°/12 mm. [sulphate, large colourless plates, m. p. 270° (decomp.)]; *p*-acetylaminophenyl benzyl ether, colourless needles, m. p. 142°; *p*-acetylaminophenyl isobutyl ether, colourless needles, m. p. 80—81°; *p*-aminophenyl isobutyl ether, a colourless liquid, b. p. 145—146°/10 mm. [sulphate, large colourless plates, decomp. 251—252°]; *p*-acetylaminophenyl isoamyl ether, colourless plates, m. p. 103—103·5°; *p*-aminophenyl isoamyl ether, a pale yellow liquid, b. p. 149—150°/15 mm. [sulphate, colourless plates, m. p. 253—254° (decomp.)].

6-Propoxy-2-methylquinoline, a pale yellow liquid, b. p. 176—177°/16 mm., is prepared by the action of concentrated hydrochloric acid on a mixture of paracetaldehyde and *p*-aminophenyl propyl ether hydrochloride; the corresponding ethiodide crystallises in pale yellow needles, m. p. 147·5°. The following compounds are obtained in an analogous manner: 6-Allyloxy-2-methylquinoline, a red, oily liquid, and the corresponding ethiodide, small, yellow needles which could not be purified satisfactorily; 6-butoxy-2-methylquinoline, yellow nodules, m. p. 52° after softening at 48°, b. p. 182—183°/13 mm. (ethiodide, small, yellow needles, m. p. 186°); 6-isobutoxy-2-methylquinoline, a colourless, oily liquid, b. p. 171—172°/12 mm. (ethiodide, small, yellow needles, m. p. 142°); 6-isoamylloxy-2-methylquinoline, a pale yellow liquid, b. p. 182—183°/10 mm. (ethiodide, yellow needles, m. p. 201°). H. W.

Quinolines. I. Preparation of 6-Ethoxy-2:4-dimethylquinoline. S. PALKIN and M. HARRIS (*J. Ind. Eng. Chem.*, 1922, **14**, 704—705).—The method employed is a modification of that described by Mikeska, Haller, and Adams (*A.*, 1921, **i**, 54). The reaction product is distilled in steam for half an hour, cooled, decanted, and the tarry residue washed with dilute hydrochloric acid, which is added to the main liquid. Excess of sodium hydroxide solution is added and the oil which slowly rises to the surface is removed and distilled under reduced pressure (30—70 mm.). The oil is collected up to 225°/30 mm. The crude base is treated on a steam-bath with acetic anhydride and poured into water. Most

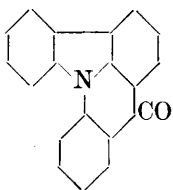
of the primary base and the hydro-base are thus removed as insoluble acetyl compounds. The filtrate is treated with excess of sodium hydroxide solution, and the solidified base removed, dissolved in twice its weight of hydrochloric acid, and diazotised.

On dilution with water, the hydrochloride of the base dissolves, leaving a residue containing phenacetin and the nitroso-compound. The filtrate is steamed for twenty minutes to decompose diazonium salts, filtered through cotton, and neutralised. The base solidifies and is collected on a filter and distilled in a vacuum. It is then recrystallised from 18% hydrochloric acid and the solution filtered in three stages—namely, at 40–50°, at room temperature, and at 0°. The product has b. p. 314–316° and m. p. 88–88.5°. Boiling range curves for the crude base and after the diazotisation process are given. A. G. P.

Preparation of Substituted Derivatives of Hydrogenated 2-Phenylquinoline-4-carboxylic Acid, and their Salts. FRITZ ZUCKMAYER (D.R.-P. 344501; from *Chem. Zentr.*, 1922, ii, 811).—An earlier patent (this vol., i, 574) is modified, whereby in place of 2-phenylquinoline-4-carboxylic acid, hydroxy-, amino-, or acetyl-amino-derivatives substituted in the quinoline group are used. By reduction of 7-acetylamino-2-phenylquinoline-4-carboxylic acid with sodium amalgam, 7-acetylamino-2-phenyltetrahydroquinoline-4-carboxylic acid is obtained; it forms yellowish-brown crystals, m. p. 210°, and gives a light yellow nitroso-compound. The potassium salt is a tasteless, yellow powder. Reduction of 6-hydroxy-2-phenylquinoline-4-carboxylic acid (a yellow mass, m. p. above 300°) yields 6-hydroxy-2-phenyltetrahydroquinoline-4-carboxylic acid; it is a white, tasteless powder, m. p. 248–250° (decomp.). The tetrahydro-compounds may be acetylated, and form nitroso-compounds. G. W. R.

Preparation of 2-ar-Tetrahydronaphthylquinoline-4-carboxylic Acids. CHEMISCHE FABRIK AUF AKTIEN (VORM. E. SCHERING) (D.R.-P. 344027; from *Chem. Zentr.*, 1922, ii, 811–812).—Isatins are condensed with ar-acetyltetrahydronaphthalenes in alkaline solution. 2-ar-Tetrahydronaphthylquinoline-4-carboxylic acid, from the condensation of isatin with ar-acetyltetrahydronaphthalene, forms dark yellow, transparent leaflets, m. p. 196–197.5°. With 6-bromoisatin, 7-bromo-2-ar-tetrahydronaphthylquinoline-4-carboxylic acid is obtained; it forms yellow crystals, m. p. 228–229.5°. G. W. R.

Phenylcarbazole. ALFRED ECKERT, FRITZ SEIDEL, and GERTRUD ENDLER (*J. pr. Chem.*, 1922, [ii], 104, 85–90).—Carbazole, when heated in a reflux apparatus with o-iodobenzoic acid in nitrobenzene solution in the presence of potassium carbonate and copper oxide yields carbazole-o-benzoic acid, white, lustrous needles, m. p. 184° (methyl ester, long needles, m. p. 138–140°). This decomposes at 350–400° to yield 9-phenylcarbazole, m. p. 94–95°, purified as the picrate, m. p. 126–129°. When heated with



zinc chloride at 280° , carbazole-9-benzoic acid yields an acridone *derivative* (annexed formula), crystals, m. p. 190° . This is also formed on boiling carbazole-9-benzoic acid in xylene solution with phosphorus pentachloride and then adding aluminium chloride. On reduction in alcoholic solution with sodium, the derivative yields the dihydroacridine *derivative*, $C_{19}H_{13}N$, yellow needles,

m. p. $158-160^{\circ}$.

W. O. K.

Preparation of an Unsaturated Ether of *p*-Dihydroxydiphenylacetamidine. SOCIETY FOR CHEMICAL INDUSTRY IN BASLE (Swiss Pat. 91728; from *Chem. Zentr.*, 1922, ii, 699).—*p*-Aminophenyl allyl ether is condensed with *p*-acetylaminophenyl allyl ether in the presence of phosphorus compounds such as phosphorus haloids, phosphoric oxide, phosphoryl chloride, or phosphoryl bromide, using benzene or toluene as diluting agents. The *diallyl* ether of *p*-dihydroxyphenylacetamidine thus obtained forms colourless crystals, m. p. $85-86^{\circ}$. The *hydrochloride* is crystalline, m. p. $152-153^{\circ}$. This product has a more powerful local anæsthetic action than the corresponding saturated ethers.

G. W. R.

Glyoxalinedicarboxylic Acid for the Recognition and Separation of Organic Bases. H. PAULY and E. LUDWIG (*Z. physiol. Chem.*, 1922, **121**, 165–169).—Glyoxalinedicarboxylic acid forms sparingly soluble and well crystallised mono-hydrogen salts with a number of organic bases. The hydrogen *salts* with the following bases have been prepared: Methylamine, m. p. $240-245^{\circ}$; dimethylamine, m. p. $238-239^{\circ}$; trimethylamine, m. p. $260-265^{\circ}$; ethylamine, m. p. $253-254^{\circ}$; diethylamine, m. p. 180° ; propylamine, m. p. 212° ; *n*-butylamine, m. p. $225-227^{\circ}$; piperidine, m. p. $221-222^{\circ}$; *d*-coniine, m. p. $208-209^{\circ}$; atropine, m. p. 93° ; the solubility of these being between 2 and 45 per cent., but with those of hydrazine, m. p. above 260° ; guanidine, m. p. $241-242^{\circ}$, glyoxaline, m. p. 245° , and *l*-histidine, m. p. $253-254^{\circ}$ (decomp.), the solubilities are very small. The ionisation constants for the two stages of ionisation are $K_1=0.00285$ and $K_2=6.44 \times 10^{-8}$.

H. K.

Glucosamine as the Basis of Formation of Heterocyclic Compounds. HERM. PAULY and ERNST LUDWIG (*Z. physiol. Chem.*, 1922, **121**, 170–176).—Glucosamine forms heterocyclic compounds of the glyoxaline and pyrrole type more easily than dextrose. By condensation with silver cyanate, *glucimidazolone* (5- $\alpha\beta\gamma\delta$ -tetrahydroxybutylglyoxal-2-one), $C_7H_{12}O_5N_2 \cdot \frac{1}{2}H_2O$, is obtained, m. p. $130-135^{\circ}$, and $[\alpha]_D^{20} -49.4^{\circ}$ in water, and from potassium thiocyanate in a similar manner, *2-thiolglucimidazole*, $C_7H_{12}O_4N_2S \cdot H_2O$, m. p. 168° , and $[\alpha]_D^{20} -17.9^{\circ}$ in water. On oxidation with hydrogen peroxide, the latter gives *glucinimidazole hydrochloride*, m. p. 162° , but when oxidised with dilute nitric acid an impure additive product of the silver salt and silver nitrate was

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obtained. Stronger nitric acid gave glyoxalinecarboxylic acid. Glucosamine condenses at 100° with acetoacetic ester or acetylacetone, giving, respectively, the *ethyl* ester of 2-methyl-5- $\alpha\beta\gamma\delta$ -tetrahydroxybutylpyrrole-3-carboxylic acid, m. p. 120° , and $[\alpha]_D + 49.7^\circ$ in water, and 3-acetyl-2-methyl-5- $\alpha\beta\gamma\delta$ -tetrahydroxybutylpyrrole, m. p. 98° , and $[\alpha]_D - 25.1^\circ$ in water. H. K.

Preparation of Aminoacetyl Compounds of 4-Amino-1-phenyl-2:3-dialkylpyrazolones. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (Aust. Pat. 86136; from *Chem. Zentr.*, 1922, ii, 575).—Aqueous ammonia is allowed to act on 4-chloroacetyl-amino-1-phenyl-2:3-dialkylpyrazolones, or the additive compounds of the latter with hexamethylenetetramine are treated with acids. 4-Chloroacetyl-amino-1-phenyl-2:3-dimethyl-5-pyrazolone, m. p. 187° , is prepared by the action of chloroacetyl chloride on 4-amino-1-phenyl-2:3-dimethyl-5-pyrazolone. The additive compound with hexamethylenetetramine gives by treatment with strong hydrochloric acid 4-aminoacetyl-amino-1-phenyl-2:3-dimethyl-5-pyrazolone (formula annexed). It forms a dihydrochloride, m. p. about 233° , and a monohydrochloride, m. p. $260-265^\circ$.

The aminoacetyl compound may also be prepared by the action of aqueous ammonia on the chloroacetyl compound. 4-Chloroacetyl-amino-1-phenyl-3-methyl-2-ethyl-5-pyrazolone (m. p. 186°) gives with aqueous ammonia 4-aminoacetyl-amino-1-phenyl-3-methyl-2-ethyl-5-pyrazolone. The hydrobromide has m. p. about 150° . The compounds have antipyretic properties.

G. W. R.

Hydantoins. Synthesis of the Soporific 4-Phenyl-4-ethyl-hydantoin [Nirvanol]. WILLIAM T. READ (*J. Amer. Chem. Soc.*, 1922, 44, 1746—1755).—The synthesis is effected in accordance with the scheme: $\text{COEtPh} \xrightarrow{\text{HCN}} \text{CN}\cdot\text{CEtPh}\cdot\text{OH} \xrightarrow{\text{NH}_3} \text{CN}\cdot\text{CEtPh}\cdot\text{NH}_2 \xrightarrow[\text{HCl}]{\text{KOON}} \text{CN}\cdot\text{CEtPh}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2 \xrightarrow{\text{H}_2\text{O}+\text{HCl}} \text{CO} \begin{array}{l} \text{NH}\cdot\text{CO} \\ \text{NH}\cdot\text{CEtPh} \end{array}$

The preparation of propionyl chloride by the action of chlorine on a mixture of propionic acid and sulphur monochloride is described. The optimal conditions for obtaining phenyl ethyl ketone from benzene, propionyl chloride, and aluminium chloride have been ascertained. Phenyl ethyl ketone does not react with ammonium cyanide in aqueous or dilute alcoholic solution, whilst the yields are poor in 95% alcoholic solution. Reasonably good results are obtained when an absolute ethyl alcoholic solution of ammonium cyanide (made by the action of ammonia on hydrogen cyanide dissolved in alcohol) is employed. The best results are secured when dry ammonium cyanide dissolved in a small amount of ethyl alcohol is allowed to react with phenyl ethyl ketone or when a mixture of hydrogen cyanide and phenyl ethyl ketone dissolved in alcohol is treated with ammonia. Under the best conditions, the yield of phenylethylaminoacetonitrile is 90% of

that theoretically possible, allowance being made for the recovered phenyl ethyl ketone, since the conversion is never complete. The yield does not appear to be affected by an excess of the reagent or the volume of solvent. The reaction is carried out at atmospheric temperature, the time being from one to four days.

Phenylethylaminoacetonitrile reacts with potassium cyanate in glacial acetic acid to form the nitrile of phenylethylhydantoic acid in 80% yield. When this compound is boiled with hydrochloric acid (20%), it is converted into 4-phenyl-4-ethylhydantoin, the yield being 85%. It is possible to prepare the latter substance by the procedure outlined above from phenyl ethyl ketone without isolating and purifying the intermediate products; the yield is 62% of that theoretically possible.

Potassium or ammonium thiocyanate does not react with phenylethylaminoacetonitrile in glacial acetic acid solution; phenylethylacetylaminopropionic acid or its nitrile is not acted on by potassium thiocyanate in the presence of acetic anhydride.

Phenylethylaminoacetonitrile is transformed by acetic anhydride into *phenylethylacetylaminopropionitrile*, $\text{NHAc}\cdot\text{C}_6\text{H}_5\cdot\text{CN}$, m. p. 147° ; *phenylethylacetylaminopropionic acid*, prepared by the action of dilute hydrochloric acid on the nitrile, has m. p. 225° (decomp.).

H. W.

The Preparation of 6 : 6'-Di- α -hydroxyisopropylindigotin from *p*-Cymene. MAX PHILLIPS (*J. Amer. Chem. Soc.*, 1922, **44**, 1775—1780).—*p*-Cymene is obtained by the distillation of spruce turpentine (cf. Schorger, A., 1917, i, 467) with steam, agitation of the distillate with sodium hydroxide solution and water, desiccation over calcium chloride, digestion over sodium, and fractional distillation. It is converted into mononitrocymene by a modification of the method described by Andrews (A., 1918, i, 339). The nitro-compound is oxidised by potassium permanganate in the presence of sodium hydroxide to *o*-nitro-*p*- α -hydroxyisopropylbenzoic acid, colourless crystals, m. p. 168° (corr.), which is reduced by tin and hydrochloric acid, ferrous sulphate, and ammonia or (preferably) ferrous sulphate and barium hydroxide to *o*-amino-*p*- α -hydroxyisopropylbenzoic acid, colourless plates, m. p. 158° (corr.). The latter is transformed by chloroacetic acid into *o*-aminoacetic-*p*- α -hydroxyisopropylbenzoic acid, $\text{CMe}_2(\text{OH})\cdot\text{C}_6\text{H}_3(\text{CO}_2\text{H})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, faintly yellow, probably triclinic, crystals, m. p. $232\cdot6^\circ$ (corr.). Fusion of the acid with potassium hydroxide at 180 — 230° , and subsequent oxidation of the aqueous solution of the melt by air, gives 6 : 6'-di- α -hydroxyisopropylindigotin, which closely resembles indigotin in appearance. It dyes cotton from a hyposulphite bath greenish-blue, and compares rather favourably with indigotin as regards fastness to light, acid, washing, and rubbing. It differs from indigotin notably in its solubility in most organic solvents.

H. W.

The Cyanine Dyes. V. The Virtual Tautomerism of the Thiocyanines. WILLIAM HOBSON MILLS and WALTER THEODORE KARL BRAUNHOLTZ (T., 1922, **121**, 1489—1495).

Dyes Derived from Phenanthraquinone. I. Phenanthra-naphthazines. ANUKUL CHANDRA SIRCAR and SIKHIBHUSAN DUTT (T., 1922, **121**, 1944—1951).

Dyes Derived from Phenanthraquinone. II. Naphtha-flavindulines. SIKHIBHUSAN DUTT (T., 1922, **121**, 1951—1955).

Synthesis of Substantive Azo-dyes derived from Naphthalene. N. N. VOROSHOV (Bull. Inst. Polyt. Ivanovo-Voznesensk, 1921, **4**, 95—109).—In so far as the formation of azo-colouring matters of substantive character is concerned, the analogues of benzidine in the naphthalene series are, not the bimolecular naphthidines, but the unimolecular naphthylenediamines with the two amino-groups in the 1:5-, 1:4-, 2:6-, and 1:6-positions. The scale of colours given by these colouring matters approximates to that obtained with the corresponding compounds of the benzidine series. T. H. P.

Attempts to prepare Red Sulphide Dyes. I. EDWIN ROY WATSON and SIKHIBHUSAN DUTT (T., 1922, **121**, 1939—1943).

The Constitution of the Products Arising from the Condensation of o-Aminoazo-compounds with Aldehydes. I. OTTO FISCHER (J. pr. Chem., 1922, [ii], **104**, 102—122).—The colourless bases obtained by Goldschmidt (A., 1890, 614; 1891, 839) by the action of aldehydes on o-aminoazo-compounds, and considered by him to be triazines, are now shown to be derivatives

of 1-aminobenziminazole, $C_6H_5 \begin{smallmatrix} & NH_2 \\ & \diagup \\ N & \\ & \diagdown \\ & CH \end{smallmatrix}$, as they are converted by hydrogen iodide into a derivative of benziminazole, and an amine, and also as they can be synthesised from such a benziminazole-derivative by heating the chloroimide, obtained from it on treatment with a hypochlorite, with a base. Moreover, it has in certain cases been found possible to isolate the Schiff's base compounds formed as intermediate stages in the condensation to Goldschmidt's bases, corresponding with the Schiff's base compounds obtained by the action of aldehydes on p-aminoazo-compounds.

[With WOLFGANG MEIER.]—From p-tolueneazo-β-naphthylamine and salicylaldehyde in methyl alcohol in presence of piperidine, tolueneazo-o-hydroxybenzylidene-β-naphthylamine is formed, deep red prisms, m. p. 162°, and this compound, on longer boiling in alcohol, acetic acid, formic acid, or alcoholic hydrogen chloride, or on heating with pyridine, further condenses to 1-p-toluidino-2-o-hydroxyphenylnaphthiminazole, white, compact crystals, m. p. 192° (diacetyl compound, white, compact crystals, m. p. 180° [decomp.]). Similarly, p-tolueneazo-β-naphthylamine yields with furfuraldehyde p-tolueneazofurfurylidene-β-naphthylamine, needles, m. p. 66°, which further condenses to 1-p-toluidino-2-furylnaphthiminazole, white needles, m. p. 215° (nitrosoamine, light yellow, compact crystals, decomp. about 150—160°); and with benz-

aldehyde, 1-*p*-toluidino-2-phenyl- α -naphthiminazole, needles, m. p. 208° (*nitrosoamine*, light yellow crystals).

The following compounds have been similarly prepared from *o*-aminoazo-*p*-toluene. 1-*p*-Toluidino-2-phenyl-5-methylbenziminazole, m. p. 231° (*nitrosoamine*, compact, yellow crystals, m. p. 129°); 1-*p*-toluidino-2-*o*-hydroxyphenyl-5-methylbenziminazole, white needles, m. p. 197—198° (*diacetyl* derivative, microcrystalline structure, but not crystallisable), 1-*p*-toluidino-2-furyl-5-methylbenziminazole, white, compact crystals, m. p. 227°.

[With H. SCHWAPPACHER.]—The following compounds are obtained similarly. From benzeneazo- β -naphthylamine and paraformaldehyde, 1-anilino- α -naphthiminazole, colourless prisms, m. p. 184° (*hydrochloride*, white needles, m. p. 254°, *picrate*, yellow, pointed crystals, m. p. 206—207°; *nitrosoamine*, long yellow needles, m. p. 120—121°). From *o*-tolueneazo- β -naphthylamine, compact prismatic dark red crystals, m. p. 125—126° (*acetyl* compound, fine, light red needles, m. p. 150—151°), and paraformaldehyde, 1-*o*-toluidino- α -naphthiminazole, yellow, crystalline powder, m. p. 166—167° (*nitrosoamine*, m. p. 130° [decomp.]) is formed. From *o*-tolueneazo- β -naphthylamine, with acetaldehyde, 1-*o*-toluidino-2-methylnaphthiminazole, colourless prisms, m. p. 169—170° (*acetyl* compound, small prisms, m. p. 117—118°); with benzaldehyde, 1-*o*-toluidino-2-phenyl- α -naphthiminazole, colourless needles, m. p. 210—211° (*picrate*, pointed, yellow crystals, m. p. 181—182°); with salicylaldehyde, 1-*o*-toluidino-2-*o*-hydroxyphenylnaphthiminazole, fine needles, m. p. 194—195°; with *p*-hydroxybenzaldehyde, 1-*o*-toluidino-2-*p*-hydroxyphenylnaphthiminazole, colourless, granular crystals, m. p. 228° (*nitrosoamine*, yellow, crystalline powder, decomp. 100°; *diacetyl* compound, coarsely granular crystals, m. p. 208°); with furfuraldehyde, 1-*o*-toluidino-2-furylnaphthiminazole, fine, colourless needles, m. p. 194—195° (*nitrosoamine*, yellow crystals, m. p. 147° [decomp.]).

[With H. KRACKER.]—On treating naphthiminazole with a hypochlorite 1-chloro- α -naphthiminazole, colourless, flat prisms, m. p. 198—199°, is obtained. This reacts with *p*-toluidine to yield 1-*p*-toluidino- α -naphthiminazole, short needles, m. p. 221—222°, identical with the base obtained by Goldschmidt from formaldehyde and *p*-tolueneazo- β -naphthylamine. In the same way, hypochlorite yields with 2-methyliminazole, 1-chloro-2-methyl- α -naphthiminazole, fine needles, m. p. 229°, which reacts with aniline to give 1-anilino-2-methylnaphthiminazole, m. p. 231—232°, identical with the substance formed from acetaldehyde and benzeneazo- β -naphthylamine, and with toluidine, to give 1-toluidino-2-methylnaphthiminazole, m. p. 197—198°, obtained from *p*-tolueneazo- β -naphthylamine and acetaldehyde.

W. O. K.

A New Fractionation Method for Proteins and their Derivatives. M. A. RAKUSIN (*Biochem. Z.*, 1922, **130**, 432—441).—The filtrates from a 95% alcoholic extract of a large number of animal and vegetable proteins and of enzymes were tested qualitatively by various colour reactions and found to contain

carbohydrate and nitrogenous substances in most cases. Pepsin-fibrin peptone can be fractionated by extraction with 95% alcohol and subsequent successive treatment of the filtrates with a 10% suspension of aluminium hydroxide for periods of twenty-four hours each, into a number of fractions which differ from one another in their colour reactions to various protein and carbohydrate reagents.

H. K.

Combined Action of Enzymes. A. J. J. VANDEVELDE (*Natuurwetenschapp. Tijdschr.*, 1921, **3**, 200—203).—The assumption that enzymic action in a living organism is due to the combined action of several enzymes is tested by experiment. The action of a mixture of invertase (extracted from yeast) and of amylase (extracted from malt) is compared with the action of each enzyme alone. No increased action could be observed although the experiment was repeated in various ways. There is no evidence of a difference in the action of enzymes alone and in mixtures.

CHEMICAL ABSTRACTS.

The Action of Chymosin and Pepsin. VII. Further Experiments on the Purification of the Enzyme of the Stomach. OLOF HAMMARSTEN (*Z. physiol. Chem.*, 1922, **121**, 240—260).—The starting material was prepared by extraction of the mucous membrane of the pig's stomach with 0.2% hydrochloric acid and precipitation of the "crude pepsin" as a hyaline mass by half saturation with sodium chloride. Preliminary experiments are described in which the sodium chloride is dialysed away in 0.2% hydrochloric acid solution and the solution kept at 37—38° to denature. The solution was then either (1) dialysed against water, (2) precipitated by half saturation with sodium chloride, or (3) precipitated by saturation with ammonium sulphate. A detailed account is to follow later. The present communication deals with the fractional extraction of the "crude pepsin" by water in a centrifuge, dialysis of the extracts and analysis of their contents in organic matter, pepsin, and chymosin. The successive extracts except the later ones compare favourably in activity with Pekelharing's pepsin, although the qualitative reactions are different. A comparison of the clotting time on milk (chymosin factor) and the digestive action by Mett's test (pepsin factor) of the author's preparation with Pekelharing's preparation showed no parallelism under any conditions. The author's solutions are stable, very faintly acid, and lose activity rapidly if neutralised.

H. K.

The Action of Chymosin and Pepsin. VIII. Relative Sensitiveness to Alkali of the Stomach Enzymes of the Calf and Pig. OLOF HAMMARSTEN (*Z. physiol. Chem.*, 1922, **121**, 261—282).—Michaelis and Rothstein (*A.*, 1920, i, 775) found that alkali destroyed chymosin and pepsin from the pig's stomach at the same rate, whilst the author (*A.*, 1915, i, 911) found that these enzymes when prepared from the calf's stomach were acted on by alkali at totally different rates. This is now ascribed to the influence of the use of different animals. Chymosin from the pig's

stomach is destroyed much more rapidly than from the calf's and the same probably applies to the pepsin. Moreover, the experiments show the distinct entities of chymosin and pepsin as they are destroyed at different rates. H. K.

The Proteolytic Enzymes of Malt. HARRY LUNDIN (*Biochem. Z.*, 1922, **131**, 193—218).—The optimum P_H for malt peptase is 3·7—4·3 in malt, and 3·2 in green malt. Malt peptase is not found in malt germ. The malt tryptase of green malt and of malt germ acts best at P_H 6·3. At the optimum P_H neutral salts have little action. The autolytic process in malt is conditioned by the various enzymes, each having their own optimum P_H . For the autolysis, the general optimum P_H is 4·3—5·0 in malt, 4·4 in green malt, and 6·3 in malt germ. H. K.

Inactivation of Saccharase by Small Quantities of Silver Salts. H. VON EULER and KARL MYRBÄCK (*Z. physiol. Chem.*, 1922, **121**, 177—182).—Euler and Svanberg (*ibid.*, 1919, **107**, 269, 302) had previously shown that whilst invertase was inhibited by silver salts in proportion to their concentration, mercuric salts behaved differently, the results lying on a curve. A re-examination of the effect with silver salts reveals, however, a parallelism with mercury salts, the previous results being due to the observation now recorded that the results depend greatly on the concentration of the enzyme. H. K.

Toxicity. The Combined Action of Quinine and of Narcotics on Invertase and on the Action of Arsenic Compounds on Maltase, and on α -Methylglucosidase. P. RONA, Y. AIRILA, and A. LASNITZKI (*Biochem. Z.*, 1922, **130**, 582—591).—The combined inhibitory actions of quinine and narcotics on invertase is less than the sum of their individual actions. Arsenious acid, arsenic acid, and atoxyl had no action on maltase or on α -methylglucosidase, but methylarsenious oxide was inhibitory. H. K.

Amylases of the Cereal Grains—The "Insoluble" Amylase of Barley. JULIAN LEVETT BAKER and HENRY FRANCIS EVERARD HULTON (*T.*, 1922, **121**, 1929—1934).

Emulsin. II. RICHARD WILLSTÄTTER and GERTRUD OPPENHEIMER (*Z. physiol. Chem.*, 1922, **121**, 183—194; cf. this vol., i, 282, 284, 390).—In continuation of previous work, it is found that those enzyme actions of the emulsin complex which proceed best in a decidedly acid medium follow the unimolecular law, as, for instance, the hydrolysis of salicin, arbutin, phenylglucoside, and helicin. By comparing the time at which 50% of the following glucosides have been hydrolysed, helicin, salicin, phenylglucoside, arbutin, methylglucoside, prunasin, and amygdalin, by nine totally distinct preparations of emulsin, it is found that the ratio of the time values for helicin, salicin, and phenylglucoside alone is the same in each case. This is the first quantitative demonstration that one enzyme of the emulsin complex can attack different substrates. This enzyme, phenylglucosidase, is most specific for helicin. H. K.

The Enzyme Hydrolysis of Benzyl Succinate. J. W. HOWARD (*J. Amer. Chem. Soc.*, 1922, **44**, 1763—1765; cf. Shonle and Row, A., 1921, i, 341; Christman and Lewis, A., 1921, i, 755; Volwiler and Vliet, this vol., ii, 41).—The lipase of the pancreas hydrolyses dibenzyl succinate only to benzyl hydrogen succinate; the latter is not hydrolysed by this enzyme. H. W.

The Chemical Action of Rennin. G. S. INICHOV (*Biochem. Z.*, 1922, **131**, 97—108).—There is no appreciable increase of acidity on addition of rennin to milk or caseinogen solutions under various conditions. Peptonisation does not therefore occur. The action of rennin is purely physical, the formation of casein being due to a change in the degree of dispersity of the solution under the influence of the ferment and in presence of bivalent ions and hydrogen ions. H. K.

Phosphatases. I and II. M. TOMITA (*Biochem. Z.*, 1922, **131**, 161—169, 170—174).—I. Saccharophosphatase. Animal organs possess a phosphatase which can hydrolyse saccharose monophosphate. The order of activity of the organs is: kidney, liver, spleen, pancreas, brain, and, least of all, muscle. The enzyme is thermo-labile.

II. Hexosemonophosphatase. The kidneys, spleen, liver, and muscle of cold- and warm-blooded animals can hydrolyse hexose monophosphate. Muscle extract exerts the weakest action. The action is more pronounced in each case than with saccharophosphatase. H. K.

Comparative Study of Ring-substituted Phenylphosphinic and Phenylarsinic Acids. D. R. NIJK (*Rec. trav. chim.*, 1922, **41**, 461—500).—A comparison of the aromatic derivatives of nitric, phosphoric, and arsenic acids shows that nitrobenzene, phenylphosphinic acid, and phenylarsinic acid are very stable compounds from which the acidic group is not easily removed. In the case of the two last-named, removal of the group may be effected by very energetic methods. However, on the introduction of an amino-group in the ortho- or para-position with respect to the acidic group, the stability of the resulting phosphinic or arsinic acid undergoes considerable modification, although no such change is observed in *o*-nitroaniline or *p*-nitroaniline, the nitro-group remaining quite stable. The author points out that *p*-aminophenylphosphinic acid is less stable than the corresponding arsenic compound. If the amino-group be introduced into the meta-position with respect to the acidic group, no such change of stability takes place; it is a matter of some difficulty to remove the acidic group from *m*-aminophenylphosphinic and *m*-aminophenylarsinic acids. The author considers that the compounds studied exhibit an alternation of properties in aromatic derivatives of the same type containing nitrogen, phosphorus, and arsenic.

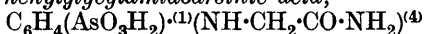
Full experimental detail of the work is given, and methods of preparation are described for 3-nitrophenylphosphinic acid, 3-amino-

phenylphosphinic acid, *p*-aminophenylarsinic acid, 5-nitro-2-amino-phenylarsinic acid, phenylarsinic acid, and 3-nitrophenylarsinic acid, which are claimed to be more satisfactory than those previously published. The nitration of phenylphosphinic acid was effected at 0°; it has been stated (Michaelis and Benzinger, A., 1878, 57) that a temperature of 110° is necessary. The method specified in the patent (D.R.-P. 264924) for the preparation of phenylarsinic acid is criticised.

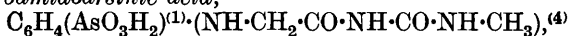
The following substances do not appear to have been previously described: 3-nitro-4-aminophenylphosphinic acid, deep yellow plates, m. p. 231° (decomp.); *m*-carbethoxyaminophenylphosphinic acid, thick, white plates, m. p. 140°, saponified on boiling in aqueous solution, cannot be diazotised, and gives no coloration with β -naphthol; nitro-3-carbethoxyaminophenylphosphinic acid, a bright yellow substance, explodes on heating; the aqueous solution does not react with nitrite, and is turned deep yellow by sodium hydroxide; 2-(?)nitro-3-aminophenylphosphinic acid, deep yellow needles, m. p. 185°. H. J. E.

The Crystalline Form of Atoxyl [Sodium *p*-Aminophenylarsinate]. G. GILTA (*Bull. Soc. chim. Belg.*, 1922, 34, 211—213).—Detailed measurements of the crystals were made in order to obtain a rapid method of distinguishing between this substance and sodium diaminodiphenylarsinate. Monoclinic, $a:b:c = 2.481:1:0.963$, $\beta = 97^\circ 40'$. The work of Melon (*Bull. Acad. Roy. Belg.*, 1922, 50) is criticised. H. J. E.

Preparation of Aromatic Aminoarsinic Acids. ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH (Dutch Pat. 6581; from *Chem. Zentr.*, 1922, ii, 873—874).— α -Halogenacylamides of the composition $X \cdot CHR \cdot CO \cdot NR_1R_2$ (where X=halogen, R=alkyl, aryl or hydrogen, R_1, R_2 =alkyl, aryl, substituted aryl, or hydrogen) are allowed to act on aminophenylarsinic acid, its homologues, its derivatives (substituted in the nucleus), or the salts of these compounds. *p*-Phenylglycylamidoarsinic acid,



is obtained by the action of chloro- or iodo-acetamide on the sodium salt of *p*-aminophenylarsinic acid; it forms colourless crystals, m. p. above 280°. The sodium salt forms colourless masses of crystals. By treating an alkaline solution of *p*-aminophenylarsinic acid with chloroacetylcarbamide, *p*-phenylglycylcarbamidoarsinic acid, $C_6H_4(AsO_3H_2)^{(1)}(NH \cdot CH_2 \cdot CO \cdot NH \cdot CO \cdot NH_2)^{(4)}$ is obtained. *p*-Phenylglycinearsinic acid is formed from this acid by hydrolysis; it has m. p. above 280°. The sodium salt contains two molecules of water of crystallisation. From α -chloroacetyl-methylcarbamide and *p*-aminophenylarsinic acid, *p*-phenylglycyl-methylcarbamidoarsinic acid,



is obtained; it forms colourless crystals, m. p. 232°. *p*-Phenylglycylanilinoarsinic acid, prepared similarly, using iodoacetanilide, forms a crystalline mass. *p*-Phenylglycyl-*m'*-aminophenolarsinic

acid is prepared by the action of 3*N*-chloracetyl-amino-1-hydroxy-benzene on *p*-aminophenylarsinic acid in alkaline solution. It forms small plates, m. p. above 230°. G. W. R.

Preparation of Aromatic Arseno-compounds. ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH (Dutch Pat. 6352; from *Chem. Zentr.*, 1922, ii, 573—574).—Aminophenylarsinic acids or aminophenylarsenoxides, unsubstituted in the aromatic nucleus, in which a hydrogen atom of the amino-group is replaced by an acylarylamino-group of the composition $-\text{CHR}\cdot\text{CO}\cdot\text{NHR}_1$ (R=alkyl, aryl, or hydrogen; R_1 =aryl with one or more acid groups such as hydroxyl, sulphonamide, carboxyl, or sulphonic acid) are reduced by ordinary methods to corresponding arseno-compounds. Phenylglycyl-*m'*-aminophenol-*p*-arsinic acid is reduced by hypophosphorous acid and hydriodic acid to the corresponding *arseno*-compound, which is a yellow powder, m. p. 180—190°. The *dihydrochloride* forms a light yellow powder, m. p. about 130°, which can only be kept in sealed vessels in the presence of indifferent gases, or in a vacuum. *Phenylglycyl-*m'*-aminophenol-*p*-arsenoxide*, $\text{AsO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$, is prepared by reduction of the corresponding arsinic acid with sulphur dioxide and hydriodic acid. It is a white powder with m. p. above 200° after softening at 130°. *Phenylglycylanthranilic acid-*p*-arsenoxide*, $\text{AsO}\cdot\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, is similarly prepared. The compounds have therapeutic uses in trypanosome and spirochæte infections. G. W. R.

Physiological Chemistry.

Preparation of Crystalline Oxyhæmoglobin. MICHAEL HEIDELBERGER (*J. Biol. Chem.*, 1922, **53**, 31—40).—The method described depends on the fact that the washed corpuscles from dog's or horse's blood crystallise almost completely in the presence of toluene when saturated with a mixture containing four parts of carbon dioxide to one part of oxygen. The oxyhæmoglobin so obtained may be recrystallised by dissolving in sodium carbonate solution and reprecipitating by saturation with the above mixture of gases. Salts may be removed from the recrystallised product by pressure dialysis. It is essential to perform all operations in the cold and in the presence of excess of carbon dioxide, and to prevent the oxyhæmoglobin becoming dry at any stage. Using this method, preparations with 96—100% of the theoretical oxygen capacity have been obtained. E. S.

Effect of Carbon Dioxide on Sugar in Blood. FRIEDRICH BINSWANGER (*Pflüger's Archiv*, 1922, **193**, 296—312; from *Chem. Zentr.*, 1922, i, 1053—1054).—Increase in the proportion of carbon dioxide in the air induces hyperglycæmia in rabbits, cats, and dogs.

Whilst increase in blood sugar is first observed in rabbits when 20% of carbon dioxide is present, 7% suffices to induce the condition in cats. The nature of the diet is without influence. Diminution of the pressure of carbon dioxide by forced respiration is without effect on the sugar content of the blood in man. Carbon dioxide hyperglycæmia is probably due to general cell injury, as it is accompanied by a marked fall in body temperature. G. W. R.

Adrenaline Hyperglycæmia. CH. ACHARD, A. RIBOT, and LÉON BINET (*Rev. méd.*, 1921, **38**, 447—456; *Ber. ges. Physiol.*, **11**, 319; from *Chem. Zentr.*, 1922, i, 987—988).—The percentage increase in blood-sugar and its duration depend on the amount of dextrose injected. With injection of dextrose and adrenaline, hyperglycæmia is more pronounced. Hypophysis extract exerts the same effect. With dextrose and aqueous pancreatic extract, the hyperglycæmia is less than with dextrose alone. Pancreatic extract partly neutralises the effect of adrenaline in adrenaline hyperglycæmia. G. W. R.

Partition of Urea in Blood. G. ETIENNE and M. VÉRAIN (*Compt. rend. soc. Biol.*, 1922, **86**, 394—395; from *Chem. Zentr.*, 1922, i, 1054).—Marked differences are found in the urea contents of blood and blood-clot. The amount of urea found in each component depends on the length of contact between clot and plasma. In experiments with liquids containing blood corpuscles, addition of trichloroacetic acid prevents diffusion of urea. G. W. R.

The Lipoids of the Blood in Tuberculosis. B. H. HENNING (*J. Biol. Chem.*, 1922, **53**, 167—170).—The blood of twenty-one tuberculosis patients was found to contain normal amounts of lecithin and of total fatty acid. When estimated without saponification, the content of cholesterol was also normal, but was uniformly low when the saponification method was employed. It is concluded that, in tuberculosis, the cholesterol of the blood is partly replaced by a related substance giving the same colour reaction. High values were obtained for "residual" fatty acid. E. S.

Biochemistry of Methyl Alcohol Poisoning. I. M. RABINOVITCH (*Arch. int. Med.*, 1922, **29**, 821—827).—In the case of a woman of seventy years, who lived for six days after taking methyl alcohol, the following results were observed: blood, increase of uric acid to 9.3 mg. per 100 c.c., urea to 144 mg., and creatinine to 4.5 mg., decrease in oxygen-saturation (15.5%); plasma, decrease in carbon dioxide (26%). On the last three days, the acid-soluble phosphorus content of the blood varied between 8.6 and 10.8 mg. per 100 c.c., and the dextrose content was 225 mg. per 100 c.c. The blood did not contain methæmoglobin. CHEMICAL ABSTRACTS.

Buffer Systems of Blood-serum. EDWARD A. DOISY, EMILY P. EATON, and K. S. CHOUKE (*J. Biol. Chem.*, 1922, **53**, 61—74).—Experiments on the increased binding power of serum for carbon dioxide with increased tensions of this gas have been

extended (cf. A., 1921, i, 753). Buffers due to the presence of the corpuscles are termed "loaned" buffers, and those independent of the corpuscles (phosphates, serum-proteins) "self-possessed" buffers. Average results from a number of experiments on defibrinated human and dog's blood indicate that, between the P_H range of 7.45 and 7.25, 16% of the base furnished for the increase of hydrogen carbonate in serum comes from self-possessed non-migrating serum buffers, 1 to 3% of this being supplied by phosphates, whilst loaned buffers supply 84%. Of the latter, 80% is due to the migration of hydrochloric acid into the corpuscles, and the remainder probably to the similar migration of other acids.

E. S.

Total Nitrogen and Residual Nitrogen Content of Oedematous Fluids. RUDOLPH STRISOWER (*Wiener Arch. inn. Med.*, 1922, 4, 115—120).—Normal values of the content of residual nitrogen in oedematous fluids lie between 0.02 and 0.05%; the content is parallel to the total protein content. The value is usually higher than that of the blood, and is increased in cardiac insufficiency, arteriosclerosis of the kidney and chronic parenchymatous nephritis. There does not appear to be any direct relation between the uræmia and the increase of residual nitrogen in the oedematous fluid.

CHEMICAL ABSTRACTS.

Solubility, Capillary Activity, and Hæmolytic Activity of Terpene Derivatives. HEINRICH RHODE (*Biochem. Z.*, 1922, 130, 481—496).—The above-named properties of camphor, borneol, menthone, menthol, α - and β -terpineol, and norcamphor have been determined without revealing a relation between the physical properties and the hæmolytic values. The hæmolytic value of a substance is the same above or below its melting point. H. K.

Effect of Ether on Anti-substances. J. FORSSMAN (*Compt. rend. Soc. Biol.*, 1922, 86, 495—497; from *Chem. Zentr.*, 1922, i, 1055).—When heated with ethyl ether at 56°, hæmolysin is destroyed whilst agglutinin is unaffected. Protective anti-substances behave normally. With sera, varying results are obtained owing to the presence of protective colloids. To this may be attributed the fact that anti-substances precipitated by ammonium sulphate behave differently from those precipitated by acetic acid and distilled water. G. W. R.

An Equilibrated Sterilisable Fluid of Physiological Hydrogen-ion Concentration. ALFRED FLEISCH (*Arch. exp. Path. Pharm.*, 1922, 94, 22—27).—The fluid has certain advantages over Ringer's or Tyrode's solutions. It possesses a constant P_H value of 7.52 at 37°, is isotonic with blood, is sterilisable, and contains potassium and calcium in a ratio which approximates to that in arterial blood. A similar relation exists between the total univalent and bivalent positive ions. The stock solution has the composition: sodium chloride, 10.5 grams; potassium chloride, 0.5 gram; calcium chloride, 0.3 gram; magnesium chloride, 0.1 gram; 5 c.c. of *N*-phosphoric acid, and 50 c.c. of water. This requires filtering. For use, 50 c.c. of the stock solution are mixed

with 1 litre of water, heated, and, after cooling, saturated with oxygen. Five c.c. of sterile *N*-sodium carbonate solution are then added. The heating may be omitted if a sterilised solution is not required. Modifications may be made to give fluids either richer or poorer in carbon dioxide. E. S.

[**Imperfect Digestion and**] the **Amino-acid Fractions and Hippuric Acid in the Urine of Pellagrins.** J. R. MURLIN (*U.S. Public Health Service, Hygienic Lab. Bull.*, 1920, No. 116, 45—72).—The imperfect gastric digestion, established in 50—60% of the cases of pellagra, might be expected to lead to imperfect assimilation of protein material and the production of toxic imperfectly resolved substances which might be eliminated in part unchanged in the urine. It is clearly suggested, by comparison of two subjects, one without free acid and pepsin in the stomach and the other with normal gastric juice, that the quantity of formol-titration nitrogen in the urine may depend on gastric conditions. The quantity of hippuric acid excreted by pellagrins, especially those kept on a maize-vegetable diet, is from twice to three times the quantity excreted by normal men on a general mixed diet. This may denote an intestinal condition capable of producing toxins which may have far-reaching somatic effects.

CHEMICAL ABSTRACTS.

Products of Prolonged Tryptic Digestion of Casein. SIGMUND FRÄNKEL and PAUL JELLINEK (*Biochem. Z.*, 1922, 130, 592—603).—When casein is digested with trypsin until the bromine reaction is negative for tryptophan, the filtrate after precipitation with Hopkins's reagent gives on removal of mercury and addition of alcohol racemic hydroxyproline in 0.8% yield. From the filtrate mercuric chloride precipitates *histidine anhydride dihydrochloride*, decomp. 285°, in minute quantity. The mercuric chloride precipitate from alkaline solution, however, contained ammonium chloride and methylamine hydrochloride. The presence of the latter is attributed to a decarboxylase action of the tryptic ferment on glycine. H. K.

Observations on Sugar Synthesis. II. An Abnormal Disturbance of Carbohydrate Exchange and its Relation to Diabetes Mellitus. RICHARD WAGNER and J. K. PARNAS (*Z. ges. expt. Med.*, 1921, 25, 361—384; from *Chem. Zentr.*, 1922, i, 893; cf. this vol., i, 487).—Further data are given with regard to the carbohydrate metabolism in a child with chronic interstitial hepatitis. Thyreoidin caused an increase in blood-sugar and a depression of acetone production, accompanied, however, by lipæmia, lipuria, and steatorrhœa. The production of sugar by degradation of body protein is held to be conditioned by thyroid activity, which is itself held in check by the pancreas as well as by mobilisation of liver carbohydrate. Conversely, excessive thyroid activity exerts an inhibitory effect on the pancreas.

G. W. R.

Effect of Radiothorium on Metabolism. K. MIYADERA (*Deut. med. Woch.*, 1922, **48**, 252—253; from *Chem. Zentr.*, 1922, i, 1049).—A single injection of radiothorium into the blood-stream causes a gradual disturbance of metabolism resulting in an increase in the total nitrogen output in urine and fæces and also in the excretion of uric acid. These changes are attributed to increased protein decomposition and decreased nitrogenous anabolism. Oxidative processes are also intensified. G. W. R.

Animal Calorimetry. XXII. The Production of Fat from Protein. H. V. ATKINSON, DAVID RAPPORT, and GRAHAM LUSK [with G. F. SODERSTROM and JAMES EVENDEN] (*J. Biol. Chem.*, 1922, **53**, 155—166).—From measurements of the respiratory quotient of dogs, it is concluded that, when the glycogen reservoirs of the body are full, the ingestion of large amounts of meat is followed by the production of fat from protein. E. S.

Lung Stones. A. SCHERER (*Beitr. klin. Tuberculose*, 1921, **49**, 17—27).—The chief constituents of lung stones are calcium carbonate and phosphates; magnesium carbonate, magnesium phosphate, fats, cholesterol, and traces of silicates are also present.

CHEMICAL ABSTRACTS.

Degradation of Bile Pigments by Anærobic Putrefactive Intestinal Bacteria. FRITZ PASSINI (*Wiener klin. Woch.*, 1922, **35**, 217—219; from *Chem. Zentr.*, 1922, i, 1057—1058).—Putrefactive anærobic intestinal bacteria rapidly break down biliverdin and bilirubin. Formation of urobilinogen or urobilin was not observed. Presence of sugar does not prevent the decomposition of bile pigments by typical putrefying bacteria. Anærobic fermentative bacteria have no effect on the bile pigments in substrates containing sugar. It is supposed that bile pigments are unaltered in those parts of the intestine where bacterial decomposition is mainly fermentative, their decomposition being confined to those parts where putrefactive action is predominant. G. W. R.

The Effects of Adrenal Feeding on the Iodine Content of the Thyroid Gland. E. M. BLACK, M. HUPPER, and J. ROGERS (*Amer. J. Physiol.*, 1922, **59**, 222—226).—The addition of various preparations of adrenal glands (ox) to the dietary of dogs causes an increase in forty-five days of 50·7—70·4% in the iodine content of the thyroid gland. The effect appears to be chiefly due to a substance other than adrenaline. CHEMICAL ABSTRACTS.

Probable Occurrence of Proteinogenic Amines in the Thyroid. UBALDO SAMMARTINO (*Biochem. Z.*, 1922, **131**, 219—225).—From 3 kilos of fresh thyroid glands, the author has isolated a trace of histamine picrate, tyramine picrate, and phenylethylamine picrate, as well as inositol. At an intermediate stage of the process of isolation, benzylation of the purified alcoholic extract was resorted to and the insoluble benzyolated products isolated and hydrolysed. In a shorter process, avoiding benzylation and using 400 grams of fresh horse thyroid and working very quickly

inositol was again isolated, but only potassium picrate and an unidentified picrate with m. p. above those of the picrates of the proteinogenic amines. H. K.

Keratin. I. A. HEIDUSCHKA and E. KOMM (*Z. physiol. Chem.*, 1922, **121**, 221—230).—Horn-clippings were heated at atmospheric pressure, in a vacuum, in sealed vessels, and with water or ammonia in sealed vessels. The temperature of initial partial degradation varies with the time of heating and the conditions of the experiment. Among the volatile products are hydrogen sulphide, ammonia, and sulphur compounds. H. K.

Beef Bone Fat and Neat's Foot Oil. HANNS ECKART (*Z. Unters. Nahr. Genussm.*, 1922, **44**, 1—29).—A table of analytical constants of bone fats, marrow fats, kidney fats, and neat's foot oils obtained from a well-nourished animal and as found in commerce is given. The rate of increase in free fatty acids shown by bone fat and neat's foot oil on storage depends on the conditions of storage, and is much more rapid if the sample is exposed to the action of light and air than if it is stored in the dark and sealed up. In the case of the solid fat exposed to light and air, an autocatalytic hydrolysis appears to take place whilst in the case of the oil the hydrolysis appears to be a unimolecular reaction. Measurements of the surface tension of neat's foot oil by the drop-pipette method gave values varying from 26·7 to 29·7 dynes/cm.² at 50°, according to the sample. The mixed ethyl esters of the fatty acids from bone fat were prepared and their analytical constants recorded. The compositions of beef bone fat and neat's foot oil are as follows: stearic acid, 19—21% and 2—3%; palmitic acid, 20—21% and 17—18%; oleic acid, 53—59% and 74·5—76·5%; glycerol, 5—10% in both cases; unsaponifiable substances, about 0·5% and 0·1—0·5%, respectively. The presence of cholesterol in the unsaponifiable substances was confirmed. Tristearin was definitely obtained as a constituent of beef bone fat. H. C. R.

Urinary Acidity. I. Some Effects of Drinking Large Amounts of Orange Juice and Sour Milk. N. R. BLATHERWICK and M. LOUISA LONG (*J. Biol. Chem.*, 1922, **53**, 103—109).—Orange juice produced alkaline urines with an increased organic acid and a decreased ammonia content; lactic acid milk, however, caused strongly acid urines due to an increased excretion of acid phosphate. No increase in the organic acid content of the urine was observed in the latter case. E. S.

Urine Iron, and Renal Function. RUDOLF EHRENBERG and ALFRED KARSTEN (*Pflüger's Archiv*, 1921, **193**, 86—92; from *Chem. Zentr.*, 1922, i, 650).—With moderate output of urine, the excretion of iron in man is smaller with large amounts, and larger with small amounts of urine eliminated; for example, 0·5 mg. in 1000 c.c. and 1·9 mg. in 500 c.c. per day. The amount excreted is a measure of total renal activity. G. W. R.

Periodicity in Chloride Excretion during Dropsical Nephritis. P. L. VIOLLE (*Compt. rend. soc. Biol.*, 1922, **86**, 362—363; from *Chem. Zentr.*, 1922, i, 1052).—In dropsical nephritis with marked retention of chlorides, the excretion of sodium chloride is constant, independently of the water balance. When the kidneys again become permeable to chlorides, variations in the daily output of chlorides occur. G. W. R.

Theory of the Retention and Excretion of Absorbed Bromine Salts, and the Halogen Content of the Organism. FR. BAUR and E. OPPENHEIMER (*Arch. exp. Path. Pharm.*, 1922, **94**, 1—21).—The known facts concerning the retention and excretion of bromides are explained by the assumptions that the organism is in halogen equilibrium and that the ratio of chloride to bromide in the urine is the same as that in the organism. Using these assumptions, expressions are deduced which give, in terms of the original chloride content of the organism, the amount of bromide and chloride which will be excreted on any day following the administration of one or several similar daily doses of bromide. These expressions may also be used to calculate the chloride content of the organism. E. S.

Fate of certain Sulphur Compounds when Fed to the Dog. CARL L. A. SCHMIDT and GUY W. CLARK (*J. Biol. Chem.*, 1922, **53**, 193—207).—Estimations were made of the sulphur and amino-nitrogen content of the urine following the administration of certain sulphur compounds. The following conclusions are drawn from the results: Cysteic acid is deaminised but is otherwise unattacked during its passage through the animal organism. In agreement with the results obtained with man (*A.*, 1920, i, 510), taurine does not combine with urea to form taurocarbamic acid, neither is its sulphur oxidised to any appreciable extent. The administration of isethionic acid does not lead to an increase in urinary sulphates. The greater part of the cystine absorbed undergoes oxidation. Urine is not a channel for the elimination of bile acids taken by the mouth. Appreciable amounts of sulphurous and thiosulphuric acids were found in the urine only after the ingestion of large quantities of sodium thiosulphate. E. S.

Genesis of Thiosulphuric Acid in Animals. SERAFINO DEZANI (*Arch. Farm. speriment. Sci. aff.*, 1922, **33**, 76—80, 81—91, 97—109).—The author discusses previous work on this subject, methods for detecting and estimating thiosulphuric acid in urine, and the various hypotheses which have been advanced to explain the occurrence of this acid in the animal organism. Salkowski's method for estimating thiosulphuric acid (*A.*, 1914, i, 455) leads to erroneous results. T. H. P.

Fat Excretion. ELSIE HILL and W. R. BLOOR (*J. Biol. Chem.*, 1922, **53**, 171—178).—The amount and composition of the fat in the faeces are to a large extent independent of the diet. These results favour the idea of a fat excretion from the intestine. E. S.

Cholesterol in Cerebrospinal Fluid. STANISLAO FABRIS (*Pediatrics*, 1921, **29**, 1057—1064; *Ber. ges. Physiol.*, **11**, 322; from *Chem. Zentr.*, 1922, i, 1058).—In normal children, 0.01% of cholesterol was found in cerebrospinal fluid. In hydrocephalic cases, cholesterol was absent, whilst in tubercular meningitis increased amounts were found.
G. W. R.

Scorpion Venom. WM. H. WILSON (*Bull. inst. Egypte*, 1921, **3**, 67—73).—An examination of the venom of *Prionurus citrinus* and *Buthus quinque-striatus*. The former has d 1.903, and contains 6.5% of mineral salts and 13.7% of other solid material, chiefly protein. It consists of a clear plasma containing numerous refractile granules of two types; solubility and precipitation reactions are described. In contrast with the venom of spiders and snakes, the activity of that of *P. citrinus* is not destroyed by putrefaction.

CHEMICAL ABSTRACTS.

The Wax of Corpses. S. GOY and E. WENDE (*Biochem. Z.*, 1922, **131**, 8—12).—The wax of two corpses buried five and one and a half years, respectively, consisted essentially of free fatty acids, free glycerol being present in very small quantity. A certain amount of the free fatty acids had become converted into calcium, magnesium, and ammonium soaps.
H. K.

Acetonuria of Diabetes. ROGER S. HUBBARD and SAMUEL T. NICHOLSON, jun. (*J. Biol. Chem.*, 1922, **53**, 209—230).—Based on certain assumptions, a formula has been developed by means of which the molecular ratio of ketogenic to antiketogenic substances in the diet of diabetic patients may be calculated. From a study of a number of cases, it has been found that acetone excretion varies inversely as the value of this ratio. The excretion of acetone is sometimes increased by the inclusion of additional fat in the diet, although the extra fat theoretically replaces fat which the patient had been drawing from his own reserves.

E. S.

Acute Yellow Atrophy of the Liver. MAX KAHN and JOSEPH BARSKY (*Arch. int. med.*, 1921, **28**, 142—150; *Ber. ges. Physiol.*, **11**, 303—304; from *Chem. Zentr.*, 1922, i, 991).—In acute yellow atrophy of the liver, the tissue shows a very high water-content and an increase in ash, particularly soluble constituents, chlorine, sulphur, and magnesium. Calcium, iron, and silicon show a decrease. The content of fat varies; lecithin, phosphatides, and sulphatides show decreases.
G. W. R.

Sugar Regulation in Paralysis Agitans. K. DRESEL and F. H. LEWY (*Z. ges. exp. Med.*, 1922, **26**, 95—103; from *Chem. Zentr.*, 1922, i, 897).—After administration of sucrose in paralysis agitans, blood-sugar remains normal for one and a half hours, but ultimately rises above the normal. After administration of dextrose, blood-sugar remains longer at a maximum than in normal cases.

G. W. R.

Effect of Primary Sodium Phosphate on Body Power. HERBERT HERXHEIMER (*Klin. Woch.*, 1922, **1**, 480—483; from *Chem. Zentr.*, 1922, i, 985—986).—Phosphoric acid given as sodium dihydrogen phosphate has a favourable effect on growth and energy production. G. W. R.

The Effect of Adrenaline on Healthy Individuals. ALFRED BJURE and JOHN SVENSSON (*Upsala läkareförenings förhandlingar*, 1921, **26**, 36 pp.; *Ber. ges. Physiol.*, **11**, 319; from *Chem. Zentr.*, 1922, i, 988).—Adrenaline, either in intramuscular or subcutaneous injections, produces increase in blood pressure and pulse frequency. Sugar in the urine does not increase, although an increase in blood-sugar occurs. The absolute amount of sodium chloride excreted in the urine increases, although the sodium chloride content of the urine decreases. G. W. R.

Behaviour of 5-Iodoguaiacol in the Human Organism. ITALO SIMON (*Arch. Farm. sperim. Sci. aff.*, 1922, **33**, 133—144).—5-Iodoguaiacol, administered gastrically, produces little effect in the animal organism. In the rabbit, a dose of 0.64 gram per kilo. causes no inconvenience; in the dog, 0.83 gram per kilo. leads only to slight albuminuria; in man, 0.25 gram per kilo. produces no harmful phenomenon, and 1 gram only transient diarrhoea. The compound is partly absorbed by the gastro-enteric tube and partly expelled with the faeces. A dose of 0.08 gram per kilo., administered to a dog, is eliminated in the urine in combination with sulphuric acid, whilst with a dose of 0.83 gram union occurs also with glycuronic acid. The elimination takes place rapidly. T. H. P.

Choline as Hormone of Peristalsis. K. ARAI (*Pflüger's Archiv*, 1922, **193**, 359—395; from *Chem. Zentr.*, 1922, i, 889).—In experiments with cats suffering from artificially induced peritonitis, peristalsis was produced by administration of choline chloride (0.01 gram per kilo.). G. W. R.

The Nature of Specific Poisons. PETER BERGELL (*Z. physiol. Chem.*, 1922, **121**, 231—239).—The author has investigated the question as to whether an animal dosed with tropine is especially sensitive to tropic acid, and, conversely, when dosed with tropic acid is sensitive to tropine, these components of the toxic alkaloid atropine being individually relatively harmless. Mice readily become acclimatised to tropine or tropic acid. After the injection of a succession of small doses of either of these substances, a subsequent injection of the other substance leads to death or very severe illness. H. K.

Physiology and Pharmacology of the Leech, *Hirudo medicinalis*. WERNER TESCHENDORF (*Pflüger's Archiv*, 1921, **192**, 135—162; from *Chem. Zentr.*, 1922, i, 893).—The musculature of the leech is comparatively little affected by an induction current, by variations in osmotic pressure, or by inorganic substances. It is sensitive to alkaloids, for example, nicotine. Small variations in hydrogen-ion concentration have little effect on the tonus; alcohol and chloroform increase tonus. G. W. R.

Chemistry of Vegetable Physiology and Agriculture.

Denitrification with Formates. Influence of the Kation. J. GROENEWEGE (*Bied. Zentr.*, 1922, **51**, 219—220).—With *Bacterium denitroformicum*, n. sp., using calcium formate as the exclusive source of carbon, denitrification does not take place in culture solutions containing potassium monohydrogen phosphate owing to reaction with the calcium formate whereby calcium phosphate and free formic acid are produced. When the culture solution is maintained neutral or slightly alkaline, denitrification takes place only on aëration. If, however, the calcium formate is replaced by potassium or sodium formate, denitrification takes place even under anærobic conditions. G. W. R.

Fermentation of Hexoses and Related Compounds by Certain Pentose-fermenting Bacteria. W. H. PETERSON, E. B. FRED, and J. A. ANDERSON (*J. Biol. Chem.*, 1922, **53**, 111—123).—The action on various sugars of four cultures of the group of pentose-fermenting organisms previously described (this vol., i, 201) has been determined. Dextrose, lævulose, lactose, raffinose, and melezitose were converted almost quantitatively into lactic acid, small quantities of carbon dioxide, which is regarded as a product of cell respiration, also being produced. With the last three sugars, the action was slow, and, when the cultures became old, a secondary fermentation began with the production of volatile acids. Mannitol was fermented differently from the sugars, thus showing the influence of the terminal alcohol group. With one exception, in which no volatile acids were formed, the products from this substance were lactic acid, ethyl alcohol, formic acid, and acetic acid. The action of the pentose-fermenting bacteria resembles that of *Streptococcus lactis*. The lactic acid produced by the former, however, is always optically inactive whereas that produced by the latter is active. E. S.

The Acetone and Butyl Alcohol Fermentation of Various Carbohydrates. GUY C. ROBINSON (*J. Biol. Chem.*, 1922, **53**, 125—154).—The fermentative ability of an organism of the *Granulobacter* type, isolated from a sample of fresh barley, towards various carbohydrates was studied. The course of fermentation was followed by making periodic estimations of the titratable acidity of the media and of the amount and, where possible, the composition of the carbohydrates present. The carbohydrates studied fell into two groups, according to the type of fermentation which occurred. In the first group, which consisted of dextrose, lævulose, mannose, sucrose, lactose, and starch, the acidity of the media, after reaching a maximum, showed a decided fall, whilst the carbohydrate was completely consumed. The second group comprised galactose, xylose, arabinose, raffinose, melezitose, inulin, and mannitol. In these cases, the high acidity persisted and the consumption was incomplete. Dextrin fell into the first or second

group, according as it was prepared by malt amylase hydrolysis or acid hydrolysis of starch. Trehalose, rhamnose, melibiose, and glycerol were not fermented. With mixtures containing dextrose and either sucrose or lactose, dextrose was preferentially consumed. Maltose, however, was fermented concurrently with dextrose, lævulose, or mannose. Galactose was more completely consumed in the presence than in the absence of dextrose. From the experimental data, it is concluded that the organism secretes the enzymes amylase, inulinase, and maltase, but not sucrase, lactase, or raffinase. Raffinose is hydrolysed to melibiose and lævulose by sucrase within the cell. E. S.

Decomposition of Inositol and Glycerol after the Manner of True Sugars by *Bacillus lactis aerogenes*. H. KUMAGAWA (*Biochem. Z.*, 1922, **131**, 157—160).—In presence of calcium carbonate and calcium sulphite, inositol is degraded by *B. lactis aerogenes* with production of acetaldehyde, lactic acid, and succinic acid. Glycerol gives acetaldehyde. H. K.

The Action of Tribromoxylanol on the Tubercle Bacillus. (MLLE) T. DUBOC (*Compt. rend.*, 1922, **175**, 326—328).—Emulsions of bovine, avian, and human tubercle bacilli were treated with tribromoxylanol. Part of the organisms was absorbed at once; the remainder formed a yellow, frothy layer on the surface of the liquid, gradually disappearing as the liquid cleared. After periods of nineteen to one hundred and forty-five days, varying with the nature and previous history of the organisms, all bacilli had disappeared and the liquid remained perfectly clear. Microscopic examination of organisms, periodically removed from treated emulsions, showed the gradual disappearance of acid-fast organisms, loss of structure, and finally complete solution. A. G. P.

Accelerators of Fermentation. HANS VON EULER and SIGNE KARLSSON (*Biochem. Z.*, 1922, **130**, 550—555).—Washed dry yeasts, free from co-enzyme, are not activated by juices and extracts containing much vitamin-B, but there is a marked acceleration of fermentation by washed dry yeast on addition of the co-enzyme. H. K.

Influence of Mineral Spring Water on the Carbohydrate Interchange in Yeast. PAUL MAYER (*Biochem. Z.*, 1922, **131**, 1—5).—The use of Karlsbad water as solvent for the sucrose in yeast fermentation leads to an increased production of glycerol and diminished production of alcohol. Solutions made up from Karlsbad salts (powder form), show this effect to an enhanced degree. H. K.

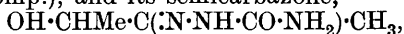
The Influence of Thyroxin on Alcoholic Fermentation. M. TOMITA (*Biochem. Z.*, 1922, **131**, 175—177).—Thyroxin has a slight, stimulating action on alcoholic fermentation. H. K.

Production of the Second and Third Forms of Fermentation with *Saccharomyces Saké*, *Zygosaccharomyces major*, and *Z. salsus*. H. KUMAGAWA (*Biochem. Z.*, 1922, **131**, 148—156).—The Japanese yeasts named can ferment sugar according to

the second and third modes. *Saccharomyces Saké* can withstand a greater proportion of sodium hydrogen sulphite than German yeasts, with the resultant production of increased yields, 19.6% of acetaldehyde, and 39.2% of glycerol, whilst the alcohol production was only 10%.

H. K.

Carboligase. V. The Binding of Carbon to Carbon Biosynthetically in the Aliphatic Series. JULIUS HIRSCH (*Biochem. Z.*, 1922, **131**, 178—187).—Yeast fermentation in presence of pyruvic acid leads to the production of optically active acetylmethylcarbinol, which is isolated and identified by its phenylosazone, m. p. 241—242°, its *p*-nitrophenylosazone, m. p. 308—310° (decomp.), and its semicarbazone,



m. p. 193—194°. This "acyloin" condensation is brought about by the carboligase.

H. K.

Ammonia as a Product of Protein Transformation caused by Mould Fungi and the Conditions of its Formation. V. S. BUTKEVICH (*Rec. d'articles dédié au Prof. C. Timriazev*, 1916, 457—499; *Abstracts Bact.*, **4**, 36).—The different species of fungi vary as regards their capacity to decompose proteins with formation of ammonia. The mould fungi are capable of utilising for the formation of ammonia not only amino- but also the amido-complexes. Both these reactions were studied, with the mycelium and with the expressed juice of *Aspergillus niger*. This fungus contains an enzyme which is capable of transforming the amido-group of asparagine into ammonia. An alkaline medium is most favourable for its action. The ammonification of the amino-group of amino-acids can only be observed with living cells.

CHEMICAL ABSTRACTS.

Formation of Citric and Oxalic Acids in *Citromyces* Cultures on Sugar and a Process for the Estimation of these Acids. WL. BUTKEWITSCH (*Biochem. Z.*, 1922, **131**, 327—337).—Various kinds of *Citromyces* were cultivated on 10% sucrose solutions deficient in nitrogen, and calcium carbonate was added. Citric and oxalic acids were formed, and were estimated. In each case, a large yield of oxalic acid means a diminished yield of citric acid, and vice versa. This is due to the formation of oxalic acid at the expense of the citric acid. These two acids may be estimated when present together in an approximately quantitative manner either (1) by extraction of the mixed calcium salts with dilute hydrochloric acid, or (2) by dissolving the salts in hydrochloric acid and adding sodium acetate which precipitates calcium oxalate alone. The main discrepancy falls on the citrate.

H. K.

Utilisation and Formation of Citric Acid in Cultures of *Citromyces glaber* on Sugar. WL. BUTKEWITSCH (*Biochem. Z.*, 1922, **131**, 338—350).—Citric acid is formed by *Citromyces glaber* when grown either on normal or on abnormal media. If citric acid or citrates be added to the nutrient media, oxalic acid

appears directly. In dilute solution, the "economic coefficient" of the utilisation of citric acid approaches that of dextrose, but in concentrated solutions it falls off. The combination dextrose-citric acid stimulates the productive metabolism. H. K.

Action of Selenium on the Metabolism of Plants in Presence of the Radioactivity of Air and of Soil. JULIUS STOKLASA [with P. KŘIČKA, J. PĚNKAVA, J. ZELENKA, J. CHMELÁŘ, and V. JÁNSKÝ] (*Biochem. Z.*, 1922, **130**, 604—643; cf. this vol., i, 613, 614).—The authors have investigated the action of ions containing selenium in the presence and absence of radium emanation on (a) the growth of *azotobacter*, (b) the germination of seeds, and (c) the development of plants. Sodium selenite is found to inhibit the growth of *Azotobacter chroococcus* but this inhibition is to some extent overcome by radium emanation. On the germination of seeds, both sodium selenite and selenate are detrimental, the selenite being the more powerful. Radioactive air accelerates the growth of seeds and inhibits the toxic action of selenites and selenates. A parallel behaviour is observed on the growth of plants, except that very minute quantities of selenates may stimulate growth. H. K.

The Diastatic Value of Malt. FR. DUCHÁČEK (*Chem. Listy*, 1922, **16**, 202—207).—The importance, in post-war brewing, of knowing the diastatic value (determined by the method of Windisch, *Woch. Brau.*, 1921, **38**, 149) of the malt used, is pointed out, and this value is given for numerous samples of last year's malt production in Czechoslovakia. From a comparison of the chemical and physical properties of these samples, it is concluded that none of these can alone allow of the estimation of the diastatic value of the sample in question, but that this value is more affected by the procedure in the germinator and in the malt-kiln. Particularly on the upper shelf of the latter is the diastase apt to be destroyed by inefficient drying, whilst efficient drying will sometimes double the diastatic value of a malt. R. T.

The Presence of the Antineuritic Substance, Water-soluble B, in Chlorophyll-free Plants. C. R. ORTON, E. V. MCCOLLUM, and NINA SIMMONDS (*J. Biol. Chem.*, 1922, **53**, 1—6).—Vitamin-B is present in small quantities in onion roots; it is therefore concluded that this vitamin is not associated with the chloroplasts in plant-tissue. The mushroom, *Agaricus campestris*, is a good source of vitamin-B; experiments with Indian-pipe, *Monotropa uniflora*, gave inconclusive results, whilst Gronovius's dodder, *Cuscuta Gronovii*, could not be tested owing to its toxic properties. E. S.

Preparation and Properties of Vitamin-B. SOGEN TSUKIYE (*Biochem. Z.*, 1922, **131**, 124—139).—The author has prepared an active vitamin-B preparation from an 80% alcoholic extract of 30 kilos of rice polishings and from an aqueous extract of 4 kilos. After cleansing with basic lead acetate, the vitamin is precipitated by phosphotungstic acid and the precipitate decomposed by barium

hydroxide. After removal of excess of barium hydroxide, a precipitation is effected in acid solution with silver and the filtrate made weakly alkaline with barium hydroxide, whereupon a second silver fraction is obtained containing the vitamin. The vitamin preparation is precipitated by tannin and picric acid and the picrate is soluble in alcohol and hot water. It is not soluble in the neutral state in alcohol of more than 80% strength, but is readily soluble in acidified alcohol and in water. H. K.

Glacial Acetic Acid as a Solvent for the Antineuritic Substance, Water-soluble B. VICTOR E. LEVINE, E. V. MCCOLLUM, and NINA SIMMONDS (*J. Biol. Chem.*, 1922, **53**, 7—11).—Glacial acetic acid is a good solvent for the extraction of vitamin-B from plant material. Impurities can be largely removed from such extracts by precipitation with ether. E. S.

Chemical Constituents of Green Plants. XIX. Occurrence of Lactic Acid and Succinic Acid in the Leaves of the Raspberry (*Rubus idaeus*). HARTWIG FRANZEN and EMMI STERN (*Z. physiol. Chem.*, 1922, **121**, 195—220).—The aqueous extract of raspberry leaves, after removal of substances precipitable by lead acetate, contains chiefly magnesium, calcium, and manganese salts of lactic acid with a little succinic acid. The content of lactic acid in the dried leaves is 1%. The isolation and characterisation of these acids is facilitated by fractionation of the esters, conversion into hydrazides, and condensation with benzaldehyde. H. K.

Nutmeg Butter. H. B. (*Mat. grasses*, 1922, **14**, 6099).—Nutmeg butter is composed of 1% butyrin, 19% olein, and the remainder myristin. It has m. p. 31°. CHEMICAL ABSTRACTS.

The Presence of Cobalt and Nickel in Arable Soil. GABRIEL BERTRAND and MOKRAGNATZ (*Compt. rend.*, 1922, **175**, 112—114).—In two samples of arable soils the authors have found respectively 0.00028% of cobalt and 0.00136% of nickel, and 0.00037% of cobalt and 0.00174% of nickel. W. G.

The Effect of Lime, Leaching, form of Phosphate, and Nitrogen Salt on Plant and Soil Acidity, and the Relation of these to the Feeding Power of the Plant. F. C. BAUER and A. R. C. HAAS (*Soil Sci.*, 1922, **13**, 461—480).—Soja-beans and maize were grown in sand cultures with suitable nutrient solutions and the rates of growth, together with the hydrogen-ion concentrations of the juices of various parts of the plants were compared. Limestone treatment, leaching, and the nature of the phosphate and nitrogen salts applied produced considerable effects on the acidity of the nutrient medium and of the plant juices. The acidity was closely related to the growth and feeding power of the plants. Limestone, by reducing soil acidity, reduced also the acidity of soja beans grown in the soil. In a few cases increased vigour of the plants resulted from liming and this was accompanied by increased acidity of the plant juices. The increased acidity of the nutrient medium by leaching usually resulted in increased

acidity of the juices of maize plants. Acid phosphates raised the acidity of the medium and of the plant juices more than did rock phosphates. The availability of rock phosphate to the plant increases with greater acidity of the medium. Ammonium nitrate increased the acidity of the soil and of the root juices of maize more than did sodium nitrate, but there was little difference apparent in the juices of the upper portions of the plants. The total acidity of soja-bean roots did not increase with increasing actual acidity. On the other hand, the total acidity of the maize plant increased with the actual acidity of the juices of both roots and tops. The total acidity of maize tops was usually greater than that of the roots. Sodium nitrate produced greater acidity than ammonium nitrate in maize tops. Limestone reduced the actual acidity of soja bean nodules below that of the roots on which they grew. Variations in the acidity of soja-bean nodules due to liming followed those of the juices of the upper portions of the plant.

A. G. P.

Acid Soils. III. The Influence of Calcium Carbonate, Calcium Oxide, and Calcium Sulphate on the Soluble Soil Nutrients of Acid Soils. R. H. ROBINSON and D. E. BULLIS (*Soil Sci.*, 1922, **13**, 449—460).—The acid soils examined responded very differently in field trials, when limed to the requisite extent to satisfy the Veitch "lime requirement." Examination of the water-soluble constituents of laboratory samples showed the chief difference to be a rapid formation of nitrates in those soils which responded to lime in the field. Treatment with calcium sulphate increased the soluble potassium and magnesium in all soils. [See also *J. Soc. Chem. Ind.*, 1922, 677A].

A. G. P.

Influence of Salts on Azofication in Soil. J. E. GREAVES, E. G. CARTER, and YEPPA LUND (*Soil Sci.*, 1922, **13**, 481—499).—Soil was treated with varying amounts of the chlorides, sulphates, carbonates, and nitrates of sodium, potassium, magnesium, calcium, iron, and manganese, and their effects on the rate of nitrogen fixation were compared. The toxicity of the salts is specific, and is not governed by the electronegative ion. All the salts examined were less toxic to the nitrogen-fixing organisms than to the nitrifiers or ammonifiers. The toxic quantity of any particular salt varied with the type of soil. No sodium salts were toxic in quantities up to 460 parts of sodium per million of soil. Potassium chloride and carbonate, manganese carbonate, and ferric sulphate did not stimulate nitrogen fixation under any conditions examined. All other salts had a stimulating effect. The common soil alkalis would not affect nitrogen-fixing organisms, even if present in sufficient quantities to retard ammonification, nitrification, and plant growth, provided the soil is not acid and contains the necessary nutrients. Nitrogen-fixing bacteria are much more resistant to the salts than are ammonifiers, nitrifiers, and many higher plants.

A. G. P.

Organic Chemistry.

The Ozonides of Petroleum. RUDOLF KOETSCHAU (*Z. angew. Chem.*, 1922, **35**, 509—513; cf. Molinari and Fenaroli, A., 1908, i, 933).—A Texas transformer oil, *d* 0.915, was found to have a molecular weight of 293, whilst the ozonide, of which 25% was produced from the oil, had a molecular weight of 663. A solution of this ozonide in benzene, after keeping for a few hours, had a molecular weight of 606 only, and after two days a molecular weight of 479, showing that decomposition into compounds of lower molecular weight had taken place. The figure 663 corresponds closely with that of a dimeric diozonide (688). The molecular weights of mineral oils determined in camphor are generally lower than those determined in benzene. The ozonides from Texas and Pennsylvanian spindle oils have a characteristic pungent odour, and separate as white, flocculent precipitates, which gradually change to a red resin at temperatures of 20° and above. Oils poor in sulphur give more stable ozonides of a lighter colour. The curves of ozone absorption are very steep at their commencement, and the maximum increase of weight is 16—17%. "White oils" show no formation of ozonides, but a considerable increase in viscosity when exposed to the action of ozone.

The ozone value is subject to too great variations for employment in analysis, but a "splitting number" determined by taking the acidity of an ozonised oil which has been boiled for half an hour with water is of utility in the examination of used transformer oils.

H. M.

Hydrogenation of Unsaturated Hydrocarbons. CHEMISCHE FABRIK GRIESHEIM-ELEKTRON (D.R.-P. 350429; from *Chem. Zentr.*, 1922, ii, 1026).—In the hydrogenation of unsaturated hydrocarbons by passing them, mixed with hydrogen, over metallic catalysts, a better utilisation of the hydrogen is obtained by diluting with methane, ethane, or ethylene. For example, in the preparation of pure ethane from acetylene the mixture is diluted with ethane until the acetylene content of the mixture amounts to less than 30% by volume. Similarly, in the preparation of a mixture of ethylene and ethane the mixture is diluted with ethane or ethylene until the acetylene content is less than 35% by volume.

G. W. R.

The Formation of Butadiene from Ethylene. J. E. ZANETTI, J. R. SUYDAM, jun., and M. OFFNER (*J. Amer. Chem. Soc.*, 1922, **44**, 2036—2041).—The formation of butadiene from ethylene has been studied at temperatures varying from 550° to 850°. The temperature of maximum formation has been shown to be 750°, above which the decomposition of ethylene into methane, hydrogen, and carbon occurs very rapidly. The maximum quantity of ethylene transformed into butadiene is 0.0096 litre per litre of ethylene.

It is suggested that the formation of aromatic hydrocarbons from ethylene takes place, at least in part, through the intermediate formation of butadiene. Attention is directed to the formation of an aliphatic hydrocarbon of higher boiling point from one of a lower boiling point and to the possible rôle of similar reactions in the cracking of oils. H. W.

The Addition of Hydrogen Haloids to Isoprene. H. STAUDINGER, W. KREIS, and W. SCHILT (*Helv. Chim. Acta*, 1922, 5, 743—756).—When isoprene combines with 1 mol. of hydrogen bromide, addition takes place at the α - and δ -positions with formation of *dimethylallyl bromide* [α -bromo- γ -methyl- Δ^{β} -butene], $\text{CMe}_2\text{CH}\cdot\text{CH}_2\text{Br}$, the constitution of which was established in the following manner. It condenses readily with sodium ethyl malonate, forming *ethyl γ -methyl- Δ^{β} -butenylmalonate*,

$$\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{CH}(\text{CO}_2\text{Et})_2,$$

b. p. 127°/11 mm. When hydrolysed with alcoholic sodium hydroxide, this gives *γ -methyl- Δ^{β} -butenylmalonic acid*, m. p. 95·5—96°. The fact that the crude acid has a sharp melting point proves that the compound of isoprene and hydrogen bromide is a uniform product. γ -Methyl- Δ^{β} -butenylmalonic acid when heated at 160° loses carbon dioxide with formation of *dimethylallylacetic acid* (δ -methyl- Δ^{γ} -hexenoic acid), a colourless oil, b. p. 103—105°/10 mm. The constitution of this compound is fixed by its oxidation with permanganate to the known δ -dimethyl- δ -hydroxylævulic acid and eventually into acetone and succinic acid.

The halogen of α -bromo- γ -methyl- Δ^{β} -butene is specially reactive, on account of the double bond in the $\beta\gamma$ -position. With guaiacol, it condenses in alcoholic sodium hydroxide solution to give *guaiacyl- γ -methyl- Δ^{β} -butenyl ether*, a viscous, nearly colourless oil, b. p. 140°/10 mm., which, by heating at 220°, changes into *p- γ -methyl- Δ^{β} -butenylguaiacol*, b. p. 148—149°/12 mm. The latter was methylated with methyl sulphate to *p- γ -methyl- Δ^{β} -butenylveratrole*, b. p. 140°/10 mm., which gave veratric acid on oxidation. The great reactivity of bromomethylbutene was shown by its behaviour with magnesium, when very little Grignard compound could be detected since it reacted almost at once with more of the bromide to form *tetramethyldiallyl* [$\beta\eta$ -dimethyl- $\Delta^{\beta\delta}$ -octadiene], b. p. 45—50°/11 mm. A similar reaction was observed by Rupe and Burgin (*A.*, 1910, i, 161) with styryl bromide. They also obtained, besides the normal distyryl, an isomeric compound which, from its oxidation products, must be a diphenylallyl, that is $\alpha\delta$ -diphenyl- Δ^{α} -hexadiene, $\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{CH}\cdot\text{CH}_2$, not $\alpha\delta$ -diphenyl- Δ^{α} -hexene, as they supposed. Evidence was obtained of the formation of a second hydrocarbon, $\text{CMe}_2\text{CH}\cdot\text{CH}_2\cdot\text{CMe}_2\text{CH}\cdot\text{CH}_2$, in a similar manner from α -bromo- γ -methyl- Δ^{β} -butene. The presence of this compound would account for the observed formation of dimethylsuccinic acid among the oxidation products of the mixed hydrocarbons obtained from bromomethylbutene and magnesium. With magnesium phenyl bromide, bromomethylbutene reacts to form γ -methyl- Δ^{β} -butenylbenzene. By the action of magnesium on

α -bromo- γ -methyl- Δ^{β} -butenyl bromide in presence of carbon dioxide, a small quantity of pyroterebic acid was formed. E. H. R.

Isoprene Dibromide. H. STAUDINGER, O. MUNTWYLER, and O. KUPFER (*Helv. Chim. Acta*, 1922, 5, 756—767).—The dibromide formed by addition of bromine to isoprene is $\alpha\delta$ -dibromo- γ -methyl- Δ^{β} -butene, since on oxidation it gives bromoacetic acid. The compound therefore contains two reactive bromine atoms (cf. preceding abstract). Attempts to obtain a cyclopentene derivative by condensing it with sodium ethylmalonate were not successful. Only one atom of bromine reacted with the malonate, the other being lost as hydrogen bromide. The condensation product was not a uniform substance but appeared to consist principally of *ethyl δ -methyl- $\Delta^{\alpha\delta}$ -pentadiene- $\alpha\alpha$ -dicarboxylate*. On reduction, it united with four atoms of hydrogen and the resulting ester, after hydrolysis, was converted into a monocarboxylic acid which was identified as δ -methylhexoic acid. The condensation product must consequently contain the ester, $\text{CH}_2\cdot\text{CMe}\cdot\text{CH}_2\cdot\text{CH}\cdot\text{C}(\text{CO}_2\text{Et})_2$. By hydrolysing the condensation product before hydrogenating, and distilling after removing carbon dioxide, there were obtained a methylpentadienecarboxylic acid and a lactone of a hydroxy-methylpentenecarboxylic acid which were not identified with certainty. The lactone may be that of γ -hydroxy- δ -methyl- Δ^{δ} -pentene-carboxylic acid; it is a colourless liquid, b. p. 105—110°/12 mm.; it is oxidised by permanganate or by hydrogen peroxide to succinic acid. Besides these two products were isolated a *lactonic acid*, m. p. 119—122°, giving a *monoethyl* ester, m. p. 85—86°, and a mixture of substances formed by the action of 1 mol. of isoprene dibromide on 2 mols. of ethyl malonate.

From isoprene tetrabromide was obtained a new *dibromoisoprene*, b. p. 78—83°/12 mm., a liquid of pleasant odour. *Isoprene dibromide*, from isoprene and bromine in carbon disulphide solution, is an unpleasant smelling liquid, b. p. 90—96°/12 mm., and has the constitution given above. When incompletely oxidised with permanganate, it forms $\alpha\delta$ -dibromo- $\beta\gamma$ -dihydroxy- β -methylbutane, $\text{CH}_2\text{Br}\cdot\text{CMe}(\text{OH})\cdot\text{CH}(\text{OH})\cdot\text{CH}_2\text{Br}$, m. p. 127°. From isoprene dibromide by treatment with alcoholic sodium methoxide was obtained a mixture of bromoisoprenes difficult to separate. Unlike isoprene itself, the mono- and di-bromoisoprenes do not polymerise to form caoutchouc-like products, but decompose when heated.

E. H. R.

Electrolytic Oxidation of Alcohols. I. *iso*Amyl Alcohol. SHUNZO KOIZUMI (*Mem. Coll. Sci. Kyoto*, 1922, 5, 359—382).—The material used in the investigation had b. p. 130—132°, d 0.811, and was obtained by fractional distillation of technical *iso*amyl alcohol; it possibly contained a small quantity of optically active amyl alcohol. The experiments were made in a divided cell, the cathode being of nickel gauze or sheet lead and the cathode solution being sulphuric acid or dilute sodium hydroxide solution. Lead peroxide acted most effectively as anode material. The products

m m 2

of the oxidation were *isovaleric acid*, *isovaleraldehyde*, and carbon dioxide. In alkaline solution, the acid formed was always accompanied by the aldehyde; the current efficiency increased with decreasing current density. In a sulphuric acid solution, aldehyde was produced only when the current density fell below 1 amp. per 100 sq. cm. For the electrolytic preparation of *isovaleric acid*, the most suitable current density was found to be 1—1.4 amp./sq. dem., if the solution remained stationary and about 2 amp./sq. dem. when it was stirred. The most favourable concentration of sulphuric acid was 10—20%. The temperature should be maintained below 30°. Vanadium pentoxide, cerium sulphate, potassium dichromate, and ferrous sulphate were found to be effective oxygen carriers.

A convenient and rapid electrolytic method for preparing *isovaleric acid* without involving the use of a diaphragm is described in detail.

H. W.

Preparation of Glycerol from Sugar. VEREINIGTE CHEMISCHE WERKE AKT.-GES. (D.R.-P. 343321; from *Chem. Zentr.*, 1922, ii, 1085).—The fermentation of sugar to form glycerol is carried out with addition of salts of acid or neutral reaction as well as nutrient salts. As examples of the salts added, ferrous sulphate, aluminium sulphate, ammonium chloride, and calcium chloride are mentioned. Ammonium sulphate, sodium phosphate, potassium sulphate, and magnesium sulphate are used as nutrient salts. The addition of neutral or acid salts increases the yield of glycerol. The yeast is also less harmfully affected than is the case in alkaline solution.

G. W. R.

Preparation of Glycerol from Sugar. VEREINIGTE CHEMISCHE WERKE AKT.-GES. (D.R.-P. 347604; from *Chem. Zentr.*, 1922, ii, 1086).—In the formation of glycerol from sugar, the fermentation is allowed to reach its maximum intensity and, without interruption of the process, a further addition of sugar is made together with smaller amounts of yeast and nutrient salts than in the initial mixture. A larger yield of glycerol and a quicker fermentation are thereby obtained. In an example given, the yield of glycerol was 23% of the sugar used.

G. W. R.

The Action of Epichlorohydrin on Normal Sodium Phosphate in Aqueous Solution and the Stability of a Diglyceromonophosphoric Diester. OCTAVE BAILLY (*Bull. Soc. chim.*, 1922, [iv], 31, 848—862; cf. A., 1921, i, 299, 493).—On attempting to prepare sodium α -glycerophosphate by using epichlorohydrin in place of the α -monochlorohydrin, the fact that one of the -ONa groups of the sodium phosphate behaves in a somewhat similar manner to the same group in sodium phenoxide (cf. Fourneau, A., 1910, i, 246) causes other reactions to take place simultaneously. When normal sodium phosphate is treated in aqueous solution with an equimolecular quantity of epichlorohydrin, formation of sodium monoglycidophosphate and diglycidophosphate occurs, and at the same time sodium α - γ -monoglycero-

monophosphate and $\alpha\gamma$ -monoglycerodiphosphate are formed. The two first-named substances are readily hydrolysed to α -glycerophosphate and $\alpha\alpha$ -diglyceromonophosphate, respectively. It is pointed out that the latter is extremely stable. An attempt was made to convert potassium diallyl phosphate into $\alpha\alpha$ -diglyceromonophosphate but this substance was only obtained in solution and in an impure condition; all attempts at crystallisation failed. Like the sodium salt, it is very stable and is not hydrolysed by prolonged boiling at 120° under pressure (cf. Fischer and Pfähler, A., 1920, i, 807). H. J. E.

Hydrolysis of $\beta\beta'$ -Dichlorodiethyl Sulphide. Synthesis of Divinyl Sulphide and the Preparation of a Non-vesicant Isomeride of $\beta\beta'$ -Dichlorodiethyl Sulphide. SIDNEY HARTLEY BALES and STANLEY ARTHUR NICKELSON (T., 1922, 121, 2137—2139).

Monothioethylene Glycol. GEORGE MACDONALD BENNETT (T., 1922, 121, 2139—2146).

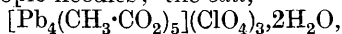
The Constitution of Soap Solutions. Hexadecanesulphonic (Cetylsulphonic) Acid and other Sulphonates. MABEL HARRIET NORRIS (T., 1922, 121, 2161—2168).

Complex Compounds of Lead Acetate. R. WEINLAND and RUDOLF STROH (*Ber.*, 1922, 55, [B], 2219—2225).—A series of salts in which the lead-acetate ion functions in all probability as kation has been prepared by the action of perchloric or nitric acid on lead oxide and acetic acid or on lead acetate under conditions which are precisely described in the original. The kation is considered to be produced by the union of the lead atoms and the acetate residue by means of the subsidiary valencies of the oxygen

atoms thus, $\left[\text{Pb} \begin{array}{c} \text{O}:\text{CMe}:\text{O} \\ \text{O}:\text{CMe}:\text{O} \end{array} \text{Pb} \right]$ and $\left[\text{Pb} \begin{array}{c} \text{O}:\text{CMe}:\text{O} \\ \text{O}:\text{CMe}:\text{O} \\ \text{O}:\text{CMe}:\text{O} \end{array} \text{Pb} \right]$. The

salts are without exception beautifully crystalline. The perchlorate acetates explode violently when strongly heated or when struck; occasionally they appear to explode violently without obvious cause. Their electrical conductivity is in harmony with the conception that they are complex salts.

The following individual compounds have been prepared: The salt, $[\text{Pb}_2(\text{CH}_3\text{CO}_2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$, colourless, rhombic plates, formed by the action of perchloric and glacial acetic acids on a thin paste of lead monoxide and water; the salt, $[\text{Pb}_2(\text{CH}_3\cdot\text{CO}_2)_3](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$, colourless, microscopic needles; the salt,



aggregates of needles or thick, hexagonal rods (this is the only salt of the series which can be crystallised unchanged from aqueous

solution); the salt, $[\text{Pb}_3(\text{CH}_3\cdot\text{CO}_2)_4](\text{ClO}_4)_3 \cdot \text{CO}_2$, large, rhombohedral crystals; the salt, $[\text{Pb}_3(\text{CH}_3\cdot\text{CO}_2)_4](\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, microscopic needles; the salt, $[\text{Pb}_2(\text{CH}_3\cdot\text{CO}_2)_3]\text{NO}_3 \cdot \text{H}_2\text{O}$, small needles. H. W.

Complex Salt of Mercuric Acetate and Sulphide. A. MIOLATI (*Gazzetta*, 1922, 52, ii, 27).—The compound, $\text{HgS} \cdot \text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$, described by Bernardi and Rossi (this vol., i, 421), was prepared by Palm (1862) in another way, and is referred to in current handbooks. With other mercuric salts, such as the chloride or iodide, mercuric sulphide gives salts containing a complex kation of which the mercuric sulphide forms part (cf. Borelli, A., 1908, i, 515; ii, 1039; 1909, i, 452). T. H. P.

Saponification of Oils and Fats. H. M. LANGTON (*J. Oil and Colour Chemists' Assoc.*, 1922, 5, 41–75).—Large scale experiments were carried out on the hydrolysis of various oils and fats under a steam pressure of eight atmospheres, using 2.5% of the weight of oil of calcium or magnesium oxide as catalyst. The resulting curves obtained are of the exponential type in every case, the greater part of the oil or fat being hydrolysed in the first four hours and the velocity of the reaction thereafter falling to a very low rate. In most cases, magnesium oxide was more effective weight for weight than calcium oxide as a catalyst. H. C. R.

The Action of the Brush Discharge on Fatty Acids and their Glycerides. EGON EICHWALD (*Z. angew. Chem.*, 1922, 35, 505–506).—If oleic acid is subjected to the action of the brush discharge, the iodine value steadily falls, the mean molecular weight steadily rises, and stearic acid is produced. The increase in molecular weight per unit fall in iodine value increases from 6.3 at the beginning of the treatment to 43.5 after twenty-two hours' treatment. About 11% of the acid is converted into stearic acid in an atmosphere of air or nitrogen and 15% in an atmosphere of hydrogen. It is considered that the bombardment of the molecules causes hydrogen atoms to become detached in a highly active state, and that they immediately saturate the double bonds of other molecules of oleic acid, leaving some highly unsaturated molecules, which polymerise and cause the increase in molecular weight. Glycerides show similar effects under the brush discharge, the glyceryl part of the molecule being unaffected. The resulting polymerised oils have high viscosities and flat viscosity-temperature curves, and are of value as lubricants. Owing to the possibility of intramolecular saturation of double bonds in the case of glycerides, the increase in molecular weight in this case becomes even more apparent in the later stages of treatment than in the case of the free fatty acids. H. C. R.

The Transformation of Methyl α -Elæostearate into Methyl β -Elæostearate. R. S. MORRELL (*J. Soc. Chem. Ind.*, 1922, 41, 328T).—Polemical, pointing out that Bauer and Herberts (this vol., i, 806) failed to acknowledge the author's work (A., 1918, i, 372), in which it was shown that methyl α -elæostearate is transformed into the β -variety when distilled in a vacuum. E. H. R.

Brassicidic Anhydride, and Anhydridisation by means of Carbonyl Chloride. D. HOLDE and K. SCHMIDT (*Z. angew. Chem.*, 1922, 35, 502–503).—Brassicidic acid, brassidic anhydride,

and ethyl brassidate were prepared from erucic acid and its corresponding derivatives by isomerisation by means of nitrous acid. *Brassicidic anhydride* crystallises from alcohol in small needles, m. p. 64°, and gives the theoretical iodine value with the Hanus reagent. It has d_4^{20} 0.835. *Ethyl brassidate* forms leaflets, m. p. 30—30.5°, n_D^{25} 1.4587. The anhydrides of the fatty acids of train oil were prepared in an impure condition, containing chlorine, by the action of carbonyl chloride on their alkali salts. They formed pasty products of higher melting point than the corresponding glycerides and acids. The difference frequently observed between the acid and saponification values of the acids of fatty oils may possibly be explainable by the observation that they are often accompanied by a proportion of anhydrides, which, as in the case of erucic, brassidic, and other higher anhydrides, do not react normally with cold alcoholic hydroxide solutions. G. F. M.

Promoters of the Hydrogenation of Oils. I. SEIICHI UENO (*J. Chem. Ind. Japan*, 1922, **25**, 777—783; cf. *ibid.*, 1918, **21**, 898, and 1920, **23**, 1216).—In the hydrogenation of herring and cotton-seed oils with hydrogen, using nickel or nickel sulphate (0.3—0.5% as nickel) as a catalyst, the presence of 2—3% of palmitic, oleic, stearic, or benzoic acid promotes the reaction.

K. K.

Perilla Oil. K. H. BAUER and R. HARDEGG (*Chem. Umschau*, 1922, **29**, 301—305).—Experiments were made to separate and identify the saturated and unsaturated fatty acids of perilla oil, obtained from the fruit of the East Asian labiate *Perilla ocymoides*. The oil had the following constants: d_4^{20} 0.9280; n_D^{20} 1.4830; saponification number, 187.4; iodine number, 204.0; mean hexabromide number, 50.8%. The m. p. of the hexabromide was 180°. The oil contained 12% of saturated and 88% of unsaturated fatty acids. By fractional precipitation of the magnesium salts and crystallisation of the acids from the different fractions, palmitic acid was identified in the saturated acids; a second saturated acid of higher m. p. than palmitic appears also to be present. The unsaturated acids were investigated by oxidising with cold potassium permanganate in alkaline solution and extracting the oxidation product with different solvents. From the water-soluble portion were obtained the two hexahydroxystearic acids, linusic acid, m. p. 201°, and isolinusic acid, m. p. 173—175°. From the water-insoluble portion was isolated a tetrahydroxystearic acid, m. p. 135—140°, which may be identical with the acid obtained by Nicolet and Cox through the dichloro- and dibromo-dihydroxystearic acids (this vol., i, 320).

Attempts were made to separate the mixed hexahydroxystearic acids by fractional crystallisation of the methyl esters. It was not possible in this way to separate linusic and isolinusic acids. By extraction of the mixed esters with ethyl acetate, however, an ester soluble in this solvent was obtained, m. p. 158—160°, which when hydrolysed gave what appears to be a new hexahydroxy-

stearic acid, m. p. 165°. *Methyl linusate* forms colourless, microscopic crystals, m. p. 195°. E. H. R.

Direct Oxidation of Esters of Hydroxy-acids by Oxygen or Air. L.-J. SIMON (*Compt. rend.*, 1922, 175, 489—491; cf. Fenton and Jones, T., 1900, i, 69; also Ciusa and Piergallini, A., 1914, ii, 604).—Ethyl lactate is spontaneously oxidised in contact with air, ethyl pyruvate being formed. The action is slow in the cold, but is accelerated by shaking or by the influence of light. On heating in a current of air, this ester, and also the methyl, butyl, and amyl esters of lactic acid, yield the corresponding ester of pyruvic acid; after some hours, sufficient oxidation has taken place to admit of detection of methyl or ethyl pyruvate by the formation of phenylhydrazones, whilst in twenty-four to forty-eight hours the transformation has taken place to the extent of 5 to 10%. Rise of temperature facilitates the change, but after a certain point other and more complex reactions take place. In the case of butyl lactate, heating for twenty hours at 180° gave a yield of 9% of butyl pyruvate. A second oxidation reaction of ethyl lactate occurs at the ordinary temperature, the products being acetaldehyde and carbon dioxide; it is stated that this is one type of reaction which prevents larger yields of pyruvate being obtained. Direct oxidation of ethyl glycolate to ethyl glyoxylate has also been observed and the question is raised as to the generality of this reaction with α -hydroxy-acids. H. J. E.

Inorganic Complex Salts. Crystallographic and Optical Study. I. ISABEL ELLIE KNAGGS (T., 1922, 121, 2069—2079).

Preparation of Maleic Acid. CHARLES R. DOWNS (U.S. Pat. 1374720; from *Chem. Zentr.*, 1922, ii, 1055; cf. A., 1921, i, 216—217).—For the preparation of maleic acid, benzene in a state of vapour is mixed with a gas containing oxygen and passed over vanadium oxide, as catalyst, at about 400°. In order to limit the oxidation, a constant temperature is maintained by the dispersion of mercury vapour in the zone of reaction.

G. W. R.

Ethyl α -Cyano- β -methylglutaconate and its Methyl Homologues. EDWARD HOPE (T., 1922, 121, 2216—2223).

The Addition of Hydrogen Cyanide to Derivatives of Glutaconic Acid. I. The Addition of Hydrogen Cyanide to Ethyl α -Cyano- β -methylglutaconate and its Homologues. EDWARD HOPE and WILFRID SHELDON (T., 1922, 121, 2223—2235).

Action of Uranyl Acetate on some Organic Substances. I. Action of Uranyl Acetate on Tartaric Acid and its Salts. FRITZ KOPATSCHEK (*Anal. Asoc. Quím. Argentina*, 1922, 10, 133—151).—An investigation of the effect of uranyl acetate on tartaric acid and tartrates, alone and in the presence of sugars, as shown by polarimetric determinations. Uranyl acetate combines with hydroxylic compounds but not with hydroxy-aldehydes. The compounds formed are optically active, the optical activity being

probably due to the formation of new asymmetric atoms or to the formation of new complex compounds of greater rotatory power. The formation of such compounds depends on the presence of one or more central hydroxyl groups. The reaction in the case of tartaric acid and tartrates is influenced by concentration. The use of uranyl acetate in the estimation of tartaric acid is suggested. The supposed compounds are sensitive to light and unstable.

G. W. R.

Keto-enolic Tautomerism. H. P. KAUFMANN (*Ber.*, 1922, 55, [B], 2255—2257).—A preliminary account of experiments with ethyl diacetylsuccinate (cf. Knorr and Kaufmann, this vol., i, 220), the details of which will be published subsequently.

The ferric chloride reaction is given only by the α -ester (dienol, m. p. 45°) and the $\alpha_2\beta$ -ester (semi-enol, m. p. 20°); the $\alpha_1\beta$ -ester (liquid semi-enol), on the other hand, does not give a coloration with ferric chloride when quite pure; the brown coloration previously attributed to it is due to the presence of small amounts of the isomeric $\alpha_2\beta$ -ester. It appears, therefore, that the ferric chloride reaction is not common to all enols.

The α - and $\alpha_2\beta$ -esters do not react with bromine under the conditions of K. H. Meyer's bromine titration method, which, however, may be applied to the $\alpha_1\beta$ -ester. It is, however, found that the direct and indirect methods lead to considerably different results. The cause of the discrepancy lies in the use of aqueous potassium iodide solution, since the presence of water causes secondary reactions which prevent the complete elimination of iodine. (The formation of ethyl diacetylfumarate by loss of hydrogen bromide from the additive compound primarily formed with bromine has been established.) The difficulty can be overcome by replacing the aqueous potassium iodide by a 10% solution of sodium iodide in alcohol, and this modification of the original process appears generally advisable.

The proportions of $\alpha_1\beta$ -, $\alpha_2\beta$ -, and β - and γ -esters in equilibrium in alcoholic solution has been determined by a combination of the bromine titration and colorimetric methods.

H. W.

The Addition of Ethyl Sodiocyanoacetate and Ethyl Sodiomalonnate to Ethyl Muconate. ERNEST HAROLD FARMER (*T.*, 1922, 121, 2015—2022).

Determination of the Three Dissociation Constants of Citric Acid. A. BAIRD HASTINGS and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1922, 53, 269—276).—On the basis of the theoretical considerations previously outlined (this vol., i, 893), the three dissociation constants of citric acid have been calculated from the results of the electrometric titration of 0.1*M*-citric acid with *N*-sodium hydroxide. The values obtained are: $K'_1 = 8.3 \times 10^{-4}$, $K'_2 = 4.1 \times 10^{-5}$, $K'_3 = 3.2 \times 10^{-6}$.

E. S.

Decomposition of Aliphatic Ketones. ALPHONSE MAILHE (*Bull. Soc. chim.*, 1922, [iv], 31, 863—867).—A continuation of the author's work (this vol., i, 803) on the behaviour of aliphatic ketones

*m m**

when heated at 600° in presence of copper-aluminium. The substances here dealt with are methyl *isopropyl* ketone, methyl *isobutyl* ketone, methyl *butyl* ketone, methyl *isoamyl* ketone, *diisopropyl* ketone, *isopropyl isobutyl* ketone, and *dihexyl* ketone, and the results obtained show that decomposition readily occurs under the conditions of experiment with formation of products which are chiefly gaseous. The molecule is disrupted at the ketonic group with formation of carbon monoxide and liberation of the two residues. The latter react, by gain or loss of hydrogen, to yield either a saturated or an ethylenic hydrocarbon. When the residues are of a certain degree of complexity, they are further decomposed into simpler substances; this occurs with the *butyl*, *isoamyl*, *isobutyl*, and heavier groups. The composition of the gaseous products obtained varies with small increments of temperature, a rise of 20° to 30° being sufficient to bring about a marked change.

H. J. E.

Diacetylacetone. JOHN NORMAN COLLIE and AMY ADA BEATRICE REILLY (T., 1922, **121**, 1984—1987).

Solubility of Dextrose in Water. R. F. JACKSON and CLARA G. SILSBEE (*U.S. Bureau of Standards, Sci. Papers*, 1922, No. **437**, 715—724).—The equilibria in the system dextrose–water have been determined. At temperatures below 90°, three solid phases are capable of existence, namely, ice, α -dextrose monohydrate, and anhydrous α -dextrose. The freezing-point curve was computed from the data of Roth and of Abegg. The cryohydric point, determined graphically, lies at -5.3° (31.75% dextrose). The solid phase, α -dextrose monohydrate, which occurs in lustrous plates, is stable between -5.3° and 50° . Its solubility shows a very high temperature coefficient. Thus, at 0.5° , 100 parts of water dissolve 54.32 parts; at 50° , 243.76 parts of dextrose. The observed m. p., 80 – 90° , although located far from the extrapolated solubility curve, is shown to be compatible with the measurements, on the theory that β -dextrose is present in the saturated solution and absent during a m. p. determination. Above the transition point, 50° , the anhydrous form becomes stable. The solubility measurements of this phase in the metastable state were continued down to 28° .

CHEMICAL ABSTRACTS.

Carbohydrate-sulphates. IV. HEINZ OHLE (*Biochem. Z.*, 1922, **131**, 601—610).—By the action of chlorosulphonic acid in chloroform at -10° on dextrose in pyridine and subsequent acetylation, the crystalline sodium salt of *tetra-acetyldextrose- ζ -monosulphate* is obtained. It has m. p. 137° (decomp.) and $[\alpha]_D +12.45^\circ$ in water. The *pyridine* salt has $[\alpha]_D +11.71^\circ$ and m. p. 158 – 160° . On hydrolysis with baryta, *dextrose- ζ -monosulphate* is isolated as the *brucine* salt, m. p. 184° , and $[\alpha]_D$ initially -4.07° , and after twelve hours -6.28° . Tetra-acetyldextrose on sulphonation gave the *pyridine* salt of *tetra-acetyldextrose- α -monosulphate*, m. p. 127° , $[\alpha]_D -4.65^\circ$ in water. The *sodium* salt has m. p. 149 – 151° and $[\alpha]_D -6.23^\circ$ in water. By the action of silver sulphate on aceto-

bromoglucose in pyridine solution, a *substance* is obtained of doubtful constitution. It has m. p. 143—144° and $[\alpha]_D -13.99^\circ$ in chloroform, and loses the whole of its sulphur as sulphate instantly on treatment with baryta. The *sodium* salt of *triacetyl* β -methylglucoside-monosulphate has m. p. 141—142° and $[\alpha]_D -5.1^\circ$ in water, and on hydrolysis with baryta gave β -methylglucoside monosulphate. The *brucine* salt has m. p. 136—155° and $[\alpha]_D -32.5^\circ$ in water.

H. K.

The Constitution of Acetone Derivatives of Glucose and Fructose. JAMES COLQUHOUN IRVINE and JOCELYN PATTERSON (T., 1922, 121, 2146—2161).

γ -Methylfructoside. ROBERT CHARLES MENZIES (T., 1922, 121, 2238—2247).

Phosphoric Esters of some Substituted Glucoses and their Rate of Hydrolysis. P. A. LEVENE and G. M. MEYER [with I. WEBER] (*J. Biol. Chem.*, 1922, 53, 431—435).—In previous papers on this subject (A., 1920, i, 712; 1921, i, 845), incorrect positions were assigned to certain groups in two of the esters. The substances described as phosphoric ester of ζ -benzoyl- $\alpha\beta$ -monoacetoneglucose and ζ -phosphoric esters of α -, β -, γ -, ϵ -diacetoneglucose were, in reality, the ϵ - or ζ -phosphoric ester of γ -benzoyl- $\alpha\beta$ -acetoneglucose and the γ -phosphoric esters of α -, β -, ϵ -, ζ -diacetoneglucose, respectively. When these corrections are made, it appears that the more resistant esters are those with the phosphoric acid group in the ϵ - or ζ - (probably the latter) position. *Benzylidene-monoacetone glucose*, m. p. 141—142°, $[\alpha]_D^{25} +22^\circ$, was prepared from monoacetoneglucose. With phosphoryl chloride, it gave the ζ -phosphoric ester of $\alpha\beta$ -monoacetoneglucose, isolated in the form of its amorphous barium salt. The hydrolysis constant of this was 17×10^{-3} . The abnormal results previously obtained with the β -phosphoric ester of $\gamma\epsilon\zeta$ -trimethyl methyl glucoside are now attributed to admixture with the ζ -phosphoric ester of $\beta\gamma\epsilon$ -trimethyl methyl glucoside.

E. S.

Sulphuric Esters of some Substituted Glucoses and their Rates of Hydrolysis. P. A. LEVENE and G. M. MEYER [with I. WEBER] (*J. Biol. Chem.*, 1922, 53, 437—440).—The γ -sulphuric ester of α -, β -, ϵ -, ζ -diacetoneglucose, isolated in the form of its amorphous barium salt, was obtained by the action of sulphuryl chloride on diacetoneglucose. The ϵ - or ζ -sulphuric ester of $\alpha\beta$ -monoacetoneglucose was similarly obtained from γ -benzoyl $\alpha\beta$ -monoacetoneglucose. These substances gave hydrolysis constants of 60×10^{-3} and 40×10^{-3} , respectively.

E. S.

Methylation of Xylose. ALBERT CARRUTHERS and EDMUND LANGLEY HIRST (T., 1922, 121, 2299—2308).

A New Depolymerisation Product of Starch. AMÉ PICTET and R. JAHN (*Helv. Chim. Acta*, 1922, 5, 640—644).—By heating potato starch in glycerol at 200—210°, distilling off the glycerol

m m* 2

under reduced pressure at the same temperature, and purifying the residue by dissolving in water and precipitating by means of alcohol, a new decomposition product of starch was obtained having the formula $(C_6H_{10}O_5)_3$. It forms a white, amorphous, slightly hygroscopic powder, $[\alpha]_D$ in water $+162.2^\circ$. It does not give a coloration with iodine, and is identical neither with Pringsheim's triamylose or isotriamylose (A., 1913, i, 1156) nor with Karrer's β -hexamylose (this vol., i, 435), which may be identical with triamylose. It does not reduce Fehling's solution at the boiling temperature, and when hydrolysed with hot dilute sulphuric acid gives dextrose. It forms a *nona-acetyl* derivative, $[C_6H_7O_5(Ac)_3]_3$, m. p. $153-154^\circ$. The name *trihexosan* is proposed provisionally. The existence of the compound confirms the presence in the starch molecule of $C_6H_{10}O_5$ units combined in groups of three, and cannot be reconciled with the idea that starch is a polymeride of an anhydride of maltose. E. H. R.

Preparation and Properties of Cellulose Solutions. P. WAENTIG (*Papierfabr.*, 1922, 20, 359—361; from *Chem. Zentr.*, 1922, ii, 1063—1064).—Viscose solutions, suitably prepared, do not change so quickly as copper solutions. Cellulose, artificially prepared, is very sensitive to time, temperature, and method of bleaching, and to treatment with acids and alkalis. Heating with dilute alkaline solutions increases the viscosity of viscose solution. The changes in viscosity are conditioned by colloidal as well as by chemical changes. It may be assumed that there is a difference in constitution between cotton and artificial cellulose, the latter probably consisting of molecular aggregates of differing sizes. Treatment with boiling dilute alkaline solutions results in a simplification of larger aggregates and a solution of smaller aggregates. G. W. R.

Reactions of Cellulose with Sodium Chloride and other Neutral Salt Solutions. I. Preliminary Survey. HELEN MASTERS (T., 1922, 121, 2026—2034).

Cellulose. VII. Cellulose Copper Compounds. KURT HESS and ERNST MESSMER [in part with FR. E. JAGLA] (*Ber.*, 1922, 55, [B], 2432—2443).—It has been pointed out previously (A., 1921, i, 401) that the enhanced specific rotation of cellulose in ammoniacal copper hydroxide solutions is probably due to the formation of a complex copper compound. Measurements are now recorded of the specific rotations of such solutions with increasing concentration of copper and constant concentration of cellulose, and conversely with increasing cellulose and constant copper content. The concentration of ammonia, which within wide limits does not affect the specific rotation appreciably, was kept uniform throughout. The results, particularly in the case of the first series of measurements, are in harmony with the hypothesis of the union of the molecules $C_{12}H_{20}O_{10}$ and $Cu(OH)_2$. Similar experiments are recorded with the biose anhydride, obtained from cellulose by means of acetyl chloride and hydrogen chloride, which

in Schweizer's reagent has a specific rotation of the same order as cellulose. Apparently, on account of dissociation, the results are not easy to interpret; this suggestion is supported by the observed influence of sodium hydroxide on the specific rotation of the solutions.

Indications of the nature of the copper complex are found in the observation that the blue zone wanders towards the anode when a solution of the biose anhydride in Schweizer's reagent is subjected to electrolysis in the presence of sodium hydroxide, whereas, in the absence of the latter the copper wanders towards the cathode. Cathodic copper thus appears to be displaced into the anion by sodium hydroxide (similar results are recorded with solutions of glycerol and mannitol), and, in addition, the dissociation of the sodium copper salt is depressed by the excess of alkali. This is in complete harmony with the observation that a copper-biose anhydride solution gives a *precipitate* when treated with an excess of sodium hydroxide which contains copper, sodium, and carbon in the atomic ratio 1 : 2 : 12.

Similar experiments with cellulose show that the specific rotations of solutions of the latter in Schweizer's reagent are increased in a similar manner by the addition of sodium hydroxide, that copper is displaced from the kation to anion by the addition of the alkali, and that a compound containing copper, sodium, and carbon in the atomic ratio 1 : 2 : 12 is also formed.

The capacity of the biose anhydride for combining with copper in solution is not exhausted when the substances are present in the proportion $1\text{Cu} : 1\text{C}_{12}\text{H}_{20}\text{O}_{10}$. H. W.

The Reduction of Lignin and of Carbohydrates with Hydrogen Iodide and Phosphorus. R. WILLSTÄTTER and L. KALB (*Ber.*, 1922, 55, [B], 2637—2652).—The behaviour of lignin towards hydrogen iodide and phosphorus is so closely similar to that of carbohydrates that the substances must be considered as nearly related in constitution. The formulæ for lignin proposed by Cross and Bevan and subsequently by Klason, which involve a relationship to aromatic substances, appear therefore to be improbable, whereas the authors' views in their more important features coincide with those of Fuchs (*A.*, 1921, i, 309) and Jonas (*A.*, 1921, ii, 554).

The lignin is obtained from pine and red beech, respectively, by treatment with hydrochloric acid (*d* 1.21), in accordance with the method of Willstätter and Zechmeister (*A.*, 1913, i, 955). It is converted by boiling hydriodic acid (*d* 1.96) and red phosphorus into a granular product which contains iodine; dehalogenation can only be effected incompletely with zinc dust in boiling glacial acetic acid solution. The final material is a pale grey or yellow resin; it is not homogeneous, and appears to consist mainly of two substances of faintly acidic character. A more promising material is obtained by treating lignin under pressure at about 250° with red phosphorus and hydriodic acid (*d* 1.7); the products from pine and red beech lignins resemble one another closely, but

differ in the relative quantities of their constituents. The portion of the product which does not dissolve in ether is a pale grey, non-homogeneous mass, which melts at a very high temperature with decomposition and distillation of difficultly-volatile oils. The portion which dissolves in ether is separated by treatment with alkali into an acidic material (C=76.50%, H=10.39%), an almost colourless, brittle resin, and a mixture of hydrocarbons. The latter is separated by successive treatment with acetone and glacial acetic acid into a solid and a liquid portion both of which are free from oxygen. The composition of the mixture approximates to a mean value which corresponds with the formula $\text{CH}_{1.6}$; the liquid portion is somewhat richer, the solid portion somewhat poorer in hydrogen. The liquid hydrocarbons have d 0.9—1.0 for the fractions of lowest and highest boiling point. The lowest observed molecular weight is 167, the highest 842 (for the solid portion). The two mixtures are an interrelated analogous (not homologous) series the properties of which are reminiscent of that of hydroaromatic hydrocarbons.

The four different fractions thus obtained have been separately subjected to further treatment with hydriodic acid and phosphorus. The purified residue, which is insoluble in ether, is almost completely converted into the mixture of solid hydrocarbons. The acid substance yields mainly solid together with some liquid hydrocarbons, the approximate ratio being 3 : 1. The liquid and solid hydrocarbon mixtures are practically unaffected.

[With G. VON MILLER.]—Hexitol, dextrose, xylose, and cellulose yield mixtures similar to those derived from lignin when treated with hydriodic acid and phosphorus under exactly similar conditions. The analogy extends to the production of the feebly acidic material and a product which is insoluble in all media. Xylose and cellulose yield larger proportions of compounds of high molecular weight than do dextrose and hexitol. These are also obtained in quantity from the humus-like material prepared by treating dextrose with hydrochloric acid. The known convertibility of hexitol into *n*-hexyl iodide suggests the possibility that the haloid is an intermediate product in the change; this cannot, however, be the case, since it does not give a mixture of hydrocarbons under the experimental conditions actually used. It appears more probable that the intermediate compound is a derivative of furan or a di-olefine.

H. W.

Catalytic Synthesis of Hexamethylenetetramine. LAWRENCE E. ROMBAUT and JULIUS A. NIEUWLAND (*J. Amer. Chem. Soc.*, 1922, **44**, 2061).—Hexamethylenetetramine is formed in small amount when a mixture of carbon monoxide, hydrogen, and ammonia at the atmospheric pressure is passed over a mixture of equal parts of reduced, finely-divided nickel and very pure diatomaceous earth heated to 250—280°. A trace of ammonium cyanide and a relatively large quantity of ammonium carbonate are also produced, the latter undoubtedly resulting from the reaction, $2\text{CO} \rightarrow \text{C} + \text{CO}_2$, since a deposition of carbon is noticed

in the reaction chamber. Reaction does not occur when the nickel catalyst is replaced by platinised asbestos. The effectiveness of a catalyst in this synthesis undoubtedly depends on its ability to form an unstable carbonyl.

H. W.

Preparation of Hexamethylenetetramine Derivatives.

J. D. RIEDEL, AKT.-GES (D.R.-P. 346383; from *Chem. Zentr.*, 1922, ii, 1081).—Ethylene halogenhydrins are allowed to act, with or without solvents, on hexamethylenetetramine. The additive compound of hexamethylenetetramine and ethylene chlorohydrin forms crystals, m. p. 135° (decomp.). The additive compound of hexamethylenetetramine with ethylene iodohydrin forms rod-like prisms, m. p. 149° (decomp.).

G. W. R.

Preparation of Additive Products of Hexamethylene-tetramine with Esters of Monohalogen Fatty Acids.

J. D. RIEDEL, AKT.-GES (D.R.-P. 346462; from *Chem. Zentr.*, 1922, ii, 1081; cf. A., 1921, i, 774).—Hexamethylenetetramine is allowed to act on monobromoacetic esters of alcohols or phenols which are insoluble or slightly soluble in water. The additive compound of bornyl bromoacetate and hexamethylenetetramine is a white, crystalline powder from which borneol separates gradually on warming with water. The additive compound of thymyl bromoacetate (from thymol, bromoacetic acid, and phosphoryl chloride, a yellow, heavy oil, b. p. 153—157°/4 mm.) and hexamethylenetetramine forms colourless needles, m. p. 155—157°. Thymol is liberated on warming the aqueous solution. At body temperature, these compounds break up into the alcohol or phenol and the antiseptic additive compound of bromoacetic acid and hexamethylenetetramine.

G. W. R.

Preparation of Amino-alcohols.

PAUL KARRER (D.R.-P. 347377; from *Chem. Zentr.*, 1922, ii, 1137—1138).—Ethyl α -acetyl-amino- γ -methylvalerate, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NHAc})\cdot\text{CO}_2\text{Et}$, mixed with ethyl alcohol, is allowed to act on metallic sodium with occasional heating. After heating for two to three hours and adding ethyl alcohol, water is added and the alcohol distilled off. On extraction with ether, β -amino- δ -methylamyl alcohol, $\text{CHMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{OH}$, is obtained as a colourless oil of basic odour, b. p. 194°. It forms crystalline salts with acids, for example, the hydrosulphate or hydrochloride, m. p. 148—150°. An optically active (lævorotatory) β -amino- δ -methylamyl alcohol may be obtained by starting from optically active leucine. β -Amino- γ -phenylpropyl alcohol, $\text{CH}_2\text{Ph}\cdot\text{CH}(\text{NH}_2)\cdot\text{CH}_2\cdot\text{OH}$, prepared from the ethyl ester of acetylphenylalanine, is a viscid oil with basic odour having b. p. 150—160° in a vacuum. It forms crystalline salts with acids; the hydrochloride has m. p. 128°. By acetylation of the products of hydrolysis of casein and subsequent reduction with sodium and ethyl alcohol, a mixture of amino-alcohols is obtained having b. p. 50—240°/16 mm. By fractionation, the following may be obtained. Up to 175°/16 mm., colamine, alaninol, etc.; 105—190° [? 175—190°]/16 mm., valine alcohol, leucine

alcohol, phenylalanine alcohol; and a fraction distilling over at 190—235°/16 mm. The products have therapeutic uses and serve as intermediate products.

G. W. R.

Preparation of Cystine. CARL L. A. SCHMIDT (*Proc. soc. exp. biol. med.*, 1921, **19**, 50—52; from *Chem. Zentr.*, 1922, i, 1277).—Human hair, or wool, from which fat has been extracted, is hydrolysed with twice its weight of concentrated hydrochloric acid until the biuret reaction has almost or completely disappeared. This takes place in approximately twelve hours, longer heating being undesirable. The greater part of the liquid is then distilled off in a vacuum at 60—70°. Water is added up to the original volume and a thick suspension of calcium hydroxide is added, avoiding rise in temperature, until a chocolate-brown colour is obtained. After filtering and washing with water, the filtrate, which should be clear and of light brown colour, is partly neutralised with hydrochloric acid and finally acidified with acetic acid. On keeping in an ice-chest, cystine separates. It is purified by dissolving in the least possible quantity of 5% hydrochloric acid, decolorising with animal charcoal, and again precipitating by the addition of sodium acetate until the liquid is no longer acid to congo-red. After filtering and washing with water until tyrosine is completely removed, a yield of cystine amounting to 6.3% is obtained.

G. W. R.

Preparation of Carbamide. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 301279; Brit. Pat. 145060; from *Chem. Zentr.*, 1922, ii, 1135—1136).—Carbon dioxide and ammonia are heated together under pressure and the product is maintained at the necessary temperature sufficiently long for the ammonium carbamate to be changed into carbamide (for example, two hours at 135°). The mixture of carbon dioxide and ammonia disengaged on removal of the product from the autoclave is again led back into the autoclave under pressure, whilst the carbamide is obtained free from ammonium salts.

G. W. R.

The Constitution of Carbamides. XIV. The Decomposition of Urea by Sodium Hypobromite in Alkaline Solution, and an Improved Procedure for the Estimation of Urea by this Means. EMIL ALPHONSE WERNER (*T.*, 1922, **121**, 2318—2325).

Preparation of Bromodialkylacetylcarbamides. FARBEN-FABRIKEN VORM. FRIEDRICH BAYER & Co. (D.R.-P. 347609; Swiss Pat. 92296; from *Chem. Zentr.*, 1922, ii, 1111—1112).—Dialkylmalonic acids of the general formula $\text{CO}_2\text{H}\cdot\text{CR}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$ (R=alkyl) are treated with bromine with or without addition of solvents, or diluents, or bromine carriers. The reaction proceeds at 100° with elimination of carbon dioxide. For example, diethylmalonic acid is heated with an equal weight of bromine and some aluminium chloride at 100° under a reflux apparatus until the evolution of hydrogen bromide and carbon dioxide is completed.

From the residue, *bromo- α -ethylbutylcarbamide*, m. p. 118—120°, is obtained with 80—85% of the theoretical yield. G. W. R.

Preparation of Carbamide from Cyanamide. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 301278; from *Chem. Zentr.*, 1922, ii, 1135).—Cyanamide is warmed in acid solution with the sediment, consisting of ferrosiferrous oxide, obtained from the reduction of nitro-compounds by iron. For example, cyanamide solution acidified with sulphuric acid is warmed at 80° and a paste containing 83% of ferrosiferrous oxide is added with shaking. The transformation to carbamide is complete in one hour. In acid solution no dicyandiamide is formed; neither, in dilute solution, does the cyanamide combine with the sulphuric acid. A smaller amount of catalyst is needed than where ferric oxide or ferric hydroxide is used. G. W. R.

Quantitative Reduction by Hydriodic Acid of Halogenated Malonyl Derivatives. II. The s.-Tetra-substituted Amides of Bromo- and Chloro-malonic Acid. RALPH WINTON WEST (T., 1922, 121, 2196—2202).

The Oxime of Mesoxamide (isoNitrosomalonomide) and some Allied Compounds. IV. The Ethers of isoNitrosomalonomide, isoNitrosomalondimethylamide, and isoNitrosomalondibenzylamide. ARTHUR GEOFFREY RENDALL and MARTHA ANNIE WHITELEY (T., 1922, 121, 2110—2119).

Iron as Photochemical Catalyst. I. The Decomposition of Potassium Ferrocyanide in Daylight. OSKAR BAUDISCH and LAWRENCE W. BASS (*Ber.*, 1922, 55, [B], 2698—2706).—A pale yellow, alkaline solution of potassium ferrocyanide in water speedily becomes lemon-yellow in colour when exposed to direct sunlight in the complete absence of oxygen, but reverts to its original tint when placed in the dark. After some time, colourless crystals of ferrous hydroxide separate in very small amount; these do not redissolve when the mixture is removed from the light. The change in colour is not therefore due to the formation of a peroxo-compound as supposed previously (A., 1921, ii, 337). In the presence of air, the initial intensely yellow coloration is succeeded by a brown turbidity and ultimate separation of ferric hydroxide. The first part of the change in the absence of air is accompanied by a reversible development of alkalinity in the solution and at this stage the presence of active oxygen (which is formed later) cannot be detected. The two processes are considered to occur in accordance with the schemes (I)
$$\left[\text{Fe}^{\text{NC}}_{(\text{NC})_5} \right] \text{K}_3 \xrightarrow{+\text{H}_2\text{O} + \text{light}} \left[\text{Fe}^{\text{NC}\cdot\text{H}}_{(\text{NC})_5} \right] \text{K}\cdot\text{OH}$$
 and (II)
$$\left[\text{Fe}^{\text{NCH}}_{(\text{NC})_5} \right] \text{K}\cdot\text{OH} \xrightarrow{\text{H}_2\text{O}} \left[\text{Fe}^{\text{OH}_2}_{(\text{NC})_5} \right] \text{K}_3 + \text{HCN} + \text{KOH}.$$
 Confirmation of this hypothesis is found in the observation that an intensely blue colour is developed when nearly colourless, oxygen-free solutions of potassium ferrocyanide and nitrosobenzene are exposed in a vacuum to sunlight, $[\text{Fe}(\text{NC})_6]\text{K}_4 +$

$\text{PhNO} \xrightarrow{\text{light}} \left[\text{Fe} \begin{smallmatrix} \text{Ph} \cdot \text{NO} \\ (\text{CN})_5 \end{smallmatrix} \right] \text{K}_3 + \text{KCN}$. The primary production of a pentacyano-compound is also established by the formation of potassium pentacyanoperoxoferroate, $\left[\text{Fe} \begin{smallmatrix} \text{O}_2 \\ (\text{NC})_5 \end{smallmatrix} \right] \text{K}_3$. The subsequent photochemical decomposition of the pentacyano-compound has not been studied in detail, but appears to proceed in a somewhat complex manner since sodium pentacyanoaquoferroate in almost complete absence of oxygen is rapidly and completely converted by light energy into ionised substances. Freshly prepared aqueous solutions of sodium pentacyanoaquoferroate are alkaline in reaction and contain active oxygen shortly after their exposure to the air, even in the absence of light.

The experiments just described have caused the author to modify his views somewhat as to the nature of ferrous hydroxide peroxide which is now formulated, $\left[\text{Fe} \begin{smallmatrix} \text{O}_2\text{H} \\ (\text{OH})_5 \end{smallmatrix} \right] \begin{smallmatrix} \text{OH} \\ (\text{OH})_2 \end{smallmatrix}$; the group, O_2H , co-ordinately united to the iron ion is able to decompose into O_2 and H , that is, active molecular oxygen and atomic hydrogen, thus explaining its simultaneous behaviour as oxidising and reducing agent.

H. W.

Mechanism of Reaction of Aliphatic Diazo-compounds.

E. OLIVERI-MANDALÀ (*Gazzetta*, 1922, 52, ii, 103—111).—The author discusses the formation of heterocyclic rings by the addition of diazo-derivatives of aliphatic hydrocarbons to unsaturated compounds, and the reaction of these diazo-derivatives with compounds of even slight acid properties, $\text{RH} + \text{CH}_2\text{N}_2 = \text{CH}_3\text{R} + \text{N}_2$. These two reactions are regarded as essentially similar in character, and the conclusion is drawn that diazo-hydrocarbons are capable of causing intramolecular transformations as a result of processes of addition and elimination occurring at unsaturated linkings. It is, therefore, not considered possible to draw accurate conclusions concerning the structures of compounds from those of the alkyl derivatives obtained on etherification by means of diazo-derivatives of aliphatic hydrocarbons.

T. H. P.

Organic Compounds of Arsenic. VIII. Action of Cyanogen Bromide on Tertiary Arsines. WILHELM STEINKOPF, HANS DONAT, and PAUL JAEGER (*Ber.*, 1922, 55, [B], 2597—2614; cf. this vol., i, 118, and previous abstracts).—In contrast to tertiary amines, tertiary arsines, even when they contain two or three phenyl groups, combine with cyanogen bromide to form arsine bromocyanides which are readily hydrolysed but otherwise are relatively stable and suffer fission only at an elevated temperature. Triphenylarsine bromocyanide is decomposed thereby mainly into its components. All bromocyanides of aliphatic or aliphatic-aromatic substituted arsines lose alkyl bromide and give cacodyl cyanides. Loss of methyl precedes that of ethyl, *n*-propyl, or phenyl, that of ethyl takes place before *isobutyl* and phenyl, whereas elimination of ethyl and *n*-propyl occurs with about equal

readiness. The firmness of the attachment of hydrocarbon residues to arsenic and to carbon is therefore not the same, at any rate as far as the unsymmetrical pinacones are concerned (cf. Meerwein, A., 1920, i, 2). *cyclo*Pentamethylarsine derivatives yield bromocyanides which decompose in a complex manner, without, however, giving evidence of the rupture of the arsenic ring such as is evidenced by *N*-phenylpiperidine; the *cyclopentamethylene*-arsenic ring is therefore more stable towards cyanogen bromide than the piperidine ring. The greater stability of the bromocyanides of the arsines as compared with the amines depends on the more metallic and positive character of the arsenic atom. The introduction of strongly negative groups into the molecule of the arsine (trinitrotriphenylarsine) deprives the latter of its ability to unite with cyanogen bromide.

Diphenylethylarsine, AsPh_2Et , b. p. 162—163°/10 mm., prepared by the action of magnesium ethyl bromide on diphenylchloroarsine in ethereal solution, is converted by cyanogen bromide in the presence of light petroleum into *diphenylethylarsine bromocyanide*, $\text{AsPh}_2\text{EtBr}\cdot\text{CN}$, m. p. 75°, which is decomposed when heated into ethyl bromide and *diphenylcyanoarsine*, b. p. 207—209°/23 mm., m. p. 31·5°. *Diphenylethylarsine hydroxybromide*, m. p. 97·5°, is prepared from diphenylethylarsine and cyanogen bromide in ethereal solution; the corresponding *picrate*, $\text{AsPh}_2\text{Et}(\text{OH})\cdot\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_3$, crystallises in lemon-yellow leaflets, m. p. 116°.

Ethyl-di-n-propylarsine, a highly refractive liquid, b. p. 60—64°/14 mm., prepared from ethyldichloroarsine and magnesium *n*-propyl bromide in ethereal solution, gives *ethyl-di-n-propylarsine bromocyanide*, a granular substance which is unusually sensitive towards moisture. It is decomposed by heat into a mixture of ethyl bromide (about 25%) and propyl bromide (about 75%) and of *ethyl-n-propylcyanoarsine* and *di-n-propylcyanoarsine* (a little of the original material remains undecomposed and is identified as *methylethyldi-n-propylarsonium iodide*, m. p. 175°). *Ethyl-di-n-propylarsine hydroxybromide* is too hygroscopic to permit of its isolation, but its formation (in the manner described for the corresponding diphenylethyl compound) is established by the isolation of the corresponding *picrate*, a yellow, crystalline powder, m. p. 85·5°.

Ethyl-diisobutylarsine, from ethyldichloroarsine and magnesium isobutyl bromide, is a colourless, highly refractive liquid, b. p. 86°/16 mm., which is transformed in the usual manner into *ethyl-diisobutylarsine bromocyanide*, m. p. 69°, and *ethyl-diisobutylarsine hydroxy-bromide*, which could not be caused to crystallise (the corresponding *hydroxy-picrate* crystallises in slender, yellow needles, m. p. 82°). The bromocyanide is decomposed by heat into ethyl bromide and *diisobutylcyanoarsine*, b. p. 116°/16 mm. *Phenyl-methylethylarsine*, b. p. 93—99°/11 mm., prepared from phenyl-methylchloroarsine and magnesium ethyl bromide, gives *phenyl-methylethylarsine bromocyanide*, which could not be caused to

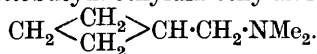
solidify, and *phenylmethylethylarsine hydroxy-bromide*, a colourless, microcrystalline mass, m. p. 83° (*hydroxy-picrate*, a pale yellow, crystalline powder, m. p. 113.5°). Fission of the cyanide gives rise to methyl bromide and *phenylethylcyanoarsine*, a colourless liquid, b. p. $148-150^{\circ}/23$ mm. *Phenylmethyl-n-propylarsine*, a colourless liquid, b. p. $105-106^{\circ}/12$ mm., prepared from phenylmethylchloroarsine and magnesium *n*-propyl bromide, gives a non-crystalline *bromocyanide*, and *phenylmethyl-n-propylarsine hydroxy-bromide*, m. p. 146° (corresponding *hydroxy-picrate*, brilliant yellow needles, m. p. 84°). The bromocyanide is decomposed by heat into methyl bromide and *phenyl-n-propylcyanoarsine*, b. p. $150-155^{\circ}/20$ mm.

Phenylbenzylmethylarsine, b. p. $174-177^{\circ}$, is prepared from phenylmethylchloroarsine and magnesium benzyl bromide. The corresponding bromocyanide could not be isolated in a homogeneous condition, but its existence is established by converting it into *phenylbenzylmethylarsine hydroxy-bromide*, a microcrystalline powder, m. p. 147° (*hydroxy-picrate*, yellow needles, m. p. 119°).

Ethylcyclopentamethylenearsine, $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2\cdot\text{CH}_2 \\ \text{CH}_2\cdot\text{CH}_2\end{smallmatrix}\rangle\text{AsEt}$, b. p. $62-64^{\circ}/12.5$ mm., is obtained in poor yield by the addition of an ethereal solution of ethyldichloroarsine to a well-stirred ethereal solution of the Grignard reagent from $\alpha\epsilon$ -dibromopentane. It is readily converted by methyl and ethyl iodide into *methylethylcyclopentamethylenearsonium iodide*, a somewhat unstable solid, m. p. 276° , and *diethylcyclopentamethylenearsonium iodide*, respectively. *Ethylcyclopentamethylenearsine bromocyanide* is extremely sensitive to moisture; *ethylcyclopentamethylenearsine hydroxy-bromide* has m. p. 71° . The decomposition of the bromocyanide by heat proceeds in a somewhat complicated manner, giving as identifiable products ethylcyclopentamethylenearsine (identified as the methiodide, m. p. 276°), cyanogen bromide, and ethyl bromide.

Trinitrotriphenylarsine does not appear to react with an excess of cyanogen bromide at 55° . H. W.

Methylenecyclobutane and Dimethylcyclobutylmethylamine. N. J. DEMJANOV and MARIE DOJARENKO (*Ber.*, 1922, 55, [B], 2727-2730).—Unsuccessful attempts are recorded to prepare methylenecyclobutane, $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{C}\cdot\text{CH}_2$, by the action of heat on cyclobutylmethylamine nitrite, of oxalic acid on cyclobutylmethyl alcohol, or by the distillation of cyclobutylmethylamine phosphate; in every case isomerisation to cyclopentene occurred. The desired compound has, however, been obtained by the application of Hofmann's reaction to cyclobutylmethyltrimethylammonium hydroxide, $\text{CH}_2\langle\begin{smallmatrix}\text{CH}_2 \\ \text{CH}_2\end{smallmatrix}\rangle\text{CH}\cdot\text{CH}_2\cdot\text{NMe}_3\cdot\text{OH}$; the yield of the hydrocarbon is small, since the base is mainly decomposed into cyclobutylmethyltrimethylamine,



Methylenecyclobutane has b. p. $40.6-41.6^{\circ}/32$ mm., d_4^{20} 0.7585, d_4^{10} 0.7487, d_4^{15} 0.7425, n_D^{10} 1.42626, n_D^{15} 1.42353; its identity with Gustavson's "vinyltrimethylene" is established by its physical properties and comparison of the nitrosites from either source.

cycloButylmethyl~~dimethyl~~amine has b. p. $125.4-126^{\circ}/740$ mm., d_4^{20} 0.8143, d_4^{10} 0.8056, d_4^{15} 0.8019, n_D^{10} 1.4356, n_D^{15} 1.43408. The corresponding *hydrochloride*, long prisms; *platinichloride*, long, lustrous prisms; *aurichloride*, large, yellow crystals; *picrate*, long, yellow prisms, m. p. (indefinite) 130° , and *methiodide*, large, pale yellow crystals, are described. H. W.

The Structure of Benzene. MAURICE L. HUGGINS (*Science*, 1922, **55**, 679—680).—A theory of conjugation similar to that of Erlenmeyer (*Annalen*, 1901, **316**, 43, 71, 75) has been developed, and found to be subject to one objection only, namely, that ortho- and meta-disubstitution products should give stereoisomerides. In this model, the six carbon tetrahedra have their bases all in the same plane, the hydrogen atoms and the points of the tetrahedra to which they are bonded being alternately above and below this plane. There are six electrons grouped round the centre of each hexagon, and two at each of the hexagon corners and on the centre lines between each hydrogen atom and the carbon atom to which it is bonded. The structure of graphite, as determined by X-ray analysis (Debye and Scherrer, *Physikal. Z.*, 1916, **17**, 277; A., 1917, ii, 437; Hull, *Physical Rev.*, 1917, **10**, 661; Anon, *Engineering*, 1917, **104**, 594), is exactly that which would be obtained if it were built up of layers of benzene hexagons of the type described, the carbon-hydrogen bonds of the benzene molecules being replaced by carbon-carbon bonds between the layers. In the case of a considerable number of aromatic compounds in which large distortions would not be expected, the dimensions of the hexagon are very close to the corresponding dimensions in graphite. A. A. E.

Monochlorotrinitrobenzenes. A. F. HOLLEMAN (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 223—224).—Of the six possible isomeric monochlorotrinitrobenzenes, picryl chloride and 1-chloro-3 : 4 : 6-trinitrobenzene alone have hitherto been prepared. The author describes the preparation of three of the missing isomerides. 1-Chloro-3 : 4 : 5-trinitrobenzene is prepared by substituting the nitro-groups of 4-chloro-3 : 5-dinitroaniline by amino-groups by Körner and Contardi's method. The product crystallises in large, yellow crystals, m. p. 168° , in a 70% yield. On treating 1-chloro-2 : 3-dinitrobenzene with a mixture of fuming nitric acid and 50% oleum at $160-170^{\circ}$ for five hours and pouring the product into water, an oil is obtained which after some time partly crystallises. The crystals are separated by centrifuging and recrystallised from alcohol, and shown to be 1-chloro-2 : 3 : 5-trinitrobenzene, m. p. 106° , by conversion into 2-chloro-4 : 6-dinitroaniline, m. p. 159° , which is well known. On keeping the mother-liquor from the nitration above, other crystals separate after a long time and

these are found to be 1-chloro-2 : 3 : 4-trinitrobenzene, m. p. 69°. A better method of preparing 1-chloro-3 : 4 : 6-trinitrobenzene than that described by Nietzki is described, which consists in passing ammonia into an alcoholic solution of 1 : 3-dichloro-4 : 6-dinitrobenzene until a test portion has the melting point of 3-chloro-4 : 6-dinitroaniline (174°). The amino-group is then replaced by the nitro-group by Körner and Contardi's method. J. F. S.

Oxidation of Side-chains with Potassium Permanganate.

II. LUCIUS A. BIGELOW (*J. Amer. Chem. Soc.*, 1922, **44**, 2010—2019).—In a previous communication (A., 1920, i, 20) the behaviour of the three nitrotoluenes towards potassium permanganate has been described; the work has now been extended to the three bromotoluenes.

The oxidations are effected in a copper vessel provided with a reflux condenser and an efficient stirrer. The bromotoluene is heated with the requisite amount of sodium hydroxide solution almost to boiling, the potassium permanganate is added in one portion and gentle ebullition and vigorous agitation are maintained until the pink colour of the permanganate disappears.

Nearly all the influences which have been brought to bear on the oxidations are found to have a considerable effect on the reactions, but the result in every case is merely to alter the proportion of bromotoluene attacked by the permanganate, the sum of the bromobenzoic acid and unchanged bromotoluene remaining essentially constant. The same observation has been recorded with the nitrotoluenes. This emphasises the conclusions that the quantity of organic matter entirely destroyed during the reaction is practically independent of variations in procedure, and that two entirely independent changes occur within the reacting mixture, (*a*) the oxidation of the side-chain to carboxyl, and (*b*) the decomposition of the permanganate into oxides of manganese and free oxygen; differing conditions merely accelerate the one or the other of these changes, causing varying amounts of material to be attacked before all the permanganate has been destroyed.

An increasing concentration of alkali in the oxidation mixture, beyond a certain very low concentration, retards the oxidation of all three bromotoluenes, but, in the case of the meta-isomeride this effect is not observed until the alkaline strength of the solution becomes very considerable. The absence of accelerating action of the alkali hydroxide is attributed to the impossibility of any of the bromotoluenes passing into a quinoid form (cf. A., 1920, i, 20).

The effect of using an excess of potassium permanganate above that required theoretically for the oxidation of the bromotoluene is peculiar. In general, the reaction is favoured, except perhaps when the oxidising agent is present in great excess. In the cases of the ortho- and meta-derivatives the effect is not quite uniform, the oxidation being favoured, retarded, and favoured again as the excess of permanganate is increased. It does not appear at present possible to explain these peculiarities.

As in the case of the nitrotoluenes, increasing dilution of the

reaction mixture favours the oxidation of the bromotoluenes. This is doubtless due to the fact that alkaline permanganate solutions have a decreasing tendency to dissociate into free oxygen and manganate as they become more dilute.

The rate of reaction is approximately the same in the oxidation of the three bromotoluenes, although slightly greater with the para-compound than with the other isomerides. It is less than with the nitrotoluenes. It is not greatly affected by changes in the alkalinity of the reaction mixture. *p*-Bromotoluene gives the highest yield of the corresponding acid; the meta-isomeride gives the next highest yield, and the ortho-derivative the lowest.

Improved methods are described in detail for the preparation of *o*-bromotoluene from *o*-toluidine, of *m*-bromotoluene from *m*-bromo-*p*-toluidine, and of *p*-bromotoluene from *p*-toluidine.

H. W.

Preparation of Mono-substituted Sulphonamides. FARBEN-FABRIKEN VORM. FRIEDRICH BAYER & CO. (D.R.-P. 346810; from *Chem. Zentr.*, 1922, ii, 1136—1137).—Sulphonamides are treated with alkylating or arylalkylating reagents in the presence of carbonates. Mono-substituted derivatives of the composition $R\cdot SO_2\cdot NHR'$ are obtained without the formation of disubstitution products. *p*-Toluene-*p*-sulphonethylamide is obtained by heating toluene-*p*-sulphonamide with sodium ethyl sulphate and sodium carbonate at 170—200°. *p*-Toluene-*p*-sulphonbenzylamide, m. p. 115—117°, is similarly prepared by the action of benzyl chloride on toluene-*p*-sulphonamide in the presence of sodium carbonate or calcium carbonate.

G. W. R.

Investigations and Ring Closures in the Methylnaphthalene Series. FRITZ MAYER AND ADOLF SIEGLITZ (*Ber.*, 1922, 55, [B], 2940).—An addendum to a previous communication (this vol., i, 740).

Naphthalene-1 : 4-dicarboxylic acid has been described previously by Scholl and Neumann (this vol., i, 261); it has m. p. 309° instead of 288° as previously given. 4-Benzoyl-1-methylnaphthalene can also be prepared from α -methylnaphthalene and benzoyl chloride; it melts at 74—75° (instead of 174—175°). 4-Methylperibenzanthrone has m. p. 193—194° (instead of 115°). The boiling point of 1-benzoyl-2-methylnaphthalene is 140—145°/15 mm. (instead of 240—245°).

H. W.

2 : 6-Dimethylnaphthalene. FRITZ MAYER AND ERIKA ALKEN (*Ber.*, 1922, 55, [B], 2278—2285).—2 : 6-Dimethylnaphthalene is reduced by sodium and boiling amyl alcohol to 2 : 6-dimethyl- $\Delta^{2:3}$ -dihydronaphthalene, b. p. 125—126°/15 mm.; the constitution of the compound is deduced from the observation that it yields a liquid dibromide which is smoothly decomposed when distilled into hydrogen bromide and 2 : 6-dimethylnaphthalene. 1-Nitro-2 : 6-dimethylnaphthalene, yellow leaflets, m. p. 68°, is prepared by the action of nitric acid (*d* 1.51) on a solution of the hydrocarbon in glacial acetic acid at 70°. 1-Amino-2 : 6-dimethyl-

naphthalene crystallises in colourless needles, m. p. 91° ; the corresponding *acetyl* derivative crystallises in lustrous needles, m. p. 211° , whereas the *benzoyl* derivative forms brown leaflets, m. p. 219 – 220° . Nitration of the mononitro-compound dissolved in concentrated sulphuric acid gives a *dinitro*-derivative, colourless needles, m. p. 186° , whereas in glacial acetic acid an isomeric *dinitro*-compound, slender, yellow needles, m. p. 179° , is obtained (the 1:4- or 1:5-position of the nitro-groups has not been elucidated for either compound). The latter compound is reduced by stannous chloride and hydrochloric acid to the corresponding *diamine*, dark red crystals, m. p. 158 – 159° (the *diacetyl* derivative is described). *Trinitro-2:6-dimethylnaphthalene*, slender, pale yellow needles, m. p. 243° , is isolated from the mother-liquors obtained by nitrating the mononitro-compound in glacial acetic acid solution.

The presence of a nitro-group in the ortho-position to the methyl radicle enables 1-nitro-2:6-dimethylnaphthalene to condense with ethyl oxalate in the presence of alcoholic sodium ethoxide to form 1-nitro-6-methylnaphthyl-2-pyruvic acid, $\text{NO}_2 \cdot \text{C}_{10}\text{H}_5\text{Me} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$, pale brown needles, m. p. 195° (*methyl* ester, coarse brown needles, m. p. 119° ; *oxime*, yellow needles, m. p. 176°). The substituted pyruvic acid is oxidised by hydrogen peroxide in the presence of sodium hydroxide to 1-nitro-6-methylnaphthyl-2-acetic acid, yellow crystals, m. p. 201° (*methyl* ester, m. p. 89°) and by potassium permanganate in alkaline solution to 1-nitro-6-methylnaphthalene-2-carboxylic acid, lustrous needles, m. p. 238 – 239° . The latter acid is reduced by ferrous sulphate to 1-amino-6-methylnaphthalene-2-carboxylic acid, pale yellow needles, m. p. 205 – 207° . Nitrous acid converts 1-nitro-6-methylnaphthylpyruvic acid into 1-nitro-6-methylnaphthyl-2-acetonitrile, pale yellow needles, m. p. 162° ; apparently the nitrous acid is reduced to hydroxylamine, which then gives the oxime of the pyruvic acid derivative, the latter being decomposed into the nitrile, carbon dioxide, and water.

7-Methyl- α -naphthindole-2-carboxylic acid, $\text{C}_{10}\text{H}_5\text{Me} \cdot \begin{smallmatrix} \text{NH} \\ \text{CH} \end{smallmatrix} \geq \text{C} \cdot \text{CO}_2\text{H}$, colourless needles, m. p. 211° , is prepared by the reduction of 1-nitro-6-methylnaphthylpyruvic acid by ferrous sulphate and ammonia, and is purified conveniently through the *barium* salt; when heated at 220° , it yields 7-methyl- α -naphthindole, brown crystals, m. p. 143° . Decomposition of 1-nitro-6-methylnaphthylpyruvic acid by sodium hydroxide leads to the production of 1-nitro-6-methylnaphthyl-2-acetaldehyde, a yellow compound, m. p. about 212 – 213° , which is isolated in small amount by decomposing its bisulphite compound with cold dilute sulphuric acid; the corresponding *phenylhydrazone* crystallises in pale yellow leaflets, m. p. 156° . If decomposition of the bisulphite compound is effected with hot dilute sulphuric acid, 7-methyl- α -naphthhisatin, slender red needles, m. p. 265° (*phenylhydrazone*, red needles, m. p. 275°) is immediately obtained. The reduction of 1-nitro-6-methylnaphthyl-2-acetic acid with ferrous sulphate gives 7-methyl- α -naphthoxindole, dark brown crystals, m. p. above 280° .

H. W.

Higher Terpene Compounds. VI. The two Methylisopropynaphthalenes from Cadalene. L. RUZICKA and M. MINGAZZINI (*Helv. Chim. Acta*, 1922, **5**, 710—715).—The naphthoic acid, $C_{15}H_{16}O_2$, obtained by the oxidation of cadalene with chromic acid (this vol., i, 561) is now shown to be 6-methyl-4-isopropyl-1-naphthoic acid, since the methylisopropynaphthalene obtained on heating it with lime is different from the synthetic 1-methyl-4-isopropynaphthalene, which would have been formed had the acid had the only other possible structure, namely, 1-methyl-4-isopropyl-6-naphthoic acid. For the synthesis of 1-methyl-4-isopropynaphthalene, 1-methyl-2- β -bromoethyl-4-isopropylbenzene was condensed with ethyl malonate, giving *ethyl β -2-cymylethylmalonate*, $C_6H_3MePr^{\beta}\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2$, a viscous, colourless oil, b. p. 200—210°/12 mm. This was converted into γ -2-cymylbutyric acid, $C_6H_3MePr^{\beta}\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO_2H$, b. p. 195—200°/12 mm., and from this, by the action of thionyl chloride, the *chloride*, b. p. 165°/12 mm., was prepared, which, with aluminium chloride, gave 5-keto-1-methyl-4-isopropyltetrahydronaphthalene, b. p. 160—170°/12 mm.; *semicarbazone*, m. p. 178—180°. The keto-compound was reduced with zinc and hydrochloric acid to 1-methyl-4-isopropyl-5:6:7:8-tetrahydronaphthalene, b. p. 135—140°/12 mm. This was heated with sulphur to dehydrogenate it to 1-methyl-4-isopropynaphthalene, a nearly colourless oil, b. p. 135—145°/12 mm., *picrate*, orange-yellow needles, m. p. 99—100°. The hydrocarbon from the above naphthoic acid, that is, 6-methyl-4-isopropynaphthalene, gave a *picrate*, m. p. 101—102°, and a *styphnate*, m. p. 163—164°. It is shown that eudalin is not identical with the synthetic 1-methyl-4-isopropynaphthalene or with the 6-methyl-4-isopropyl compound from the naphthoic acid. Eudalin is probably not an *apocadalene*, as has been supposed. E. H. R.

Nitration of Hydrocarbons in Basic or Neutral Medium. M. BATTEGAY and PH. BRANDT (*Bull. Soc. chim.*, 1922, [iv], **31**, 910—915; cf. Wagner, A., 1886, 708; Verley, A., 1901, i, 143; Meisenheimer and Connerade, A., 1904, i, 391).—Anthracene and naphthalene may be nitrated by means of anhydrous pyridinium nitrate in presence of excess of pyridine. The products obtained are 9-nitroanthracene and α -nitronaphthalene; in the former case the yield represents 70% of the hydrocarbon used, in the latter, 40%. Other products of the reactions are anthraquinone and nitroanthrone from anthracene and 1-nitro-2:3-phthalic acid from naphthalene. The formation of nitroanthracene is explained by the authors on the hypothesis that nitrodihydroanthranol is first formed as an additive product and is then transformed into nitroanthracene with loss of water. H. J. E.

Action of Light on 9-Nitroanthracene. M. BATTEGAY, PH. BRANDT and J. MORITZ (*Bull. Soc. chim.*, 1922, [iv], **31**, 915—917; cf. preceding abstract).—9-Nitroanthracene is yellow in dilute alcoholic solution. On exposure to sunlight, the liquid becomes strongly fluorescent and smells of acetaldehyde. When the solution is sufficiently concentrated, nitrous acid is evolved and crystals of

anthraquinone are deposited. On shaking the solution in contact with air, the fluorescence disappears; when again exposed to sunlight it reappears, but more rapidly than at first. The fluorescence is due to photochemical reduction of anthraquinone, and is exhibited by alcoholic solutions of that substance; the reduction product is readily oxidised in air. H. J. E.

Studies in the Anthracene Series. III. EDWARD DE BARRY BARNETT, JAMES WILFRED COOK, and HERBERT HENRY GRAINGER (T., 1922, 121, 2059—2069).

The Solubility of Phenanthrene in Various Organic Solvents. HERBERT HENSTOCK (T., 1922, 121, 2124—2128).

Action of Polyhalogenated Compounds of Methane and Ethane on Magnesyl [Magnesium Alkyl] Compounds. II. R. BINAGHI (*Gazzetta*, 1922, 52, ii, 132—138; cf. this vol., i, 313).—Both chloroform and bromoform react readily with magnesium phenyl bromide giving triphenylmethane, alone in the former case, and mixed with tetraphenylethane in the latter. The first phase of the reaction probably consists in the formation of the compound CHPh_2X , which then yields either triphenylmethane or tetraphenylethane or, with bromoform, the two together: $\text{CHPh}_2\text{Br} + \text{MgPhBr} = \text{MgBr}_2 + \text{CHPh}_3$, and $2\text{CHPh}_2\text{Br} + \text{MgPhBr} = \text{MgBr}_2 + \text{C}_6\text{H}_5\text{Br} + \text{CHPh}_2\cdot\text{CHPh}_2$. With all three trihalogenated derivatives of methane, bromobenzene also is formed, so that, even with chloroform, the formation of triphenylmethane is not represented by the equation $3\text{MgPhBr} + \text{CHCl}_3 = 3\text{MgClBr} + \text{CHPh}_3$.

The action of bromoform on magnesium ethyl bromide is analogous to that of iodoform, the products being acetylene, ethane, methane, ethyl bromide, dibromomethane, and a small proportion of triethylmethane; a distinct odour resembling that of moulds is observed, especially after the final treatment of the products with water. The various reactions involved are probably $3\text{MgEtBr} + 2\text{CHBr}_3 = 3\text{MgBr}_2 + 3\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_2$; $\text{C}_2\text{H}_2 + 2\text{MgEtBr} = 2\text{C}_2\text{H}_6 + \text{MgBr}\cdot\text{C}\equiv\text{C}\cdot\text{MgBr}$; the latter $+ 2\text{H}_2\text{O} = 2\text{MgBr}\cdot\text{OH} + \text{C}_2\text{H}_2$; $\text{CHBr}_3 + \text{MgEtBr} = \text{C}_2\text{H}_5\text{Br} + \text{CHBr}_2\cdot\text{MgBr}$; the latter $+ \text{H}_2\text{O} = \text{MgBr}\cdot\text{OH} + \text{CH}_2\text{Br}_2$; $\text{CHBr}(\text{MgBr})_2 + 2\text{H}_2\text{O} = 2\text{MgBr}\cdot\text{OH} + \text{CH}_3\text{Br}$, and $\text{CH}(\text{MgBr})_3 + 3\text{H}_2\text{O} = 3\text{MgBr}\cdot\text{OH} + \text{CH}_4$.

Quite different is the interaction of chloroform and magnesium ethyl bromide, which yields methane, ethylene, and a small proportion of ethylene dibromide, but no acetylene, and gives a further evolution of gas when the products are treated with water. The mechanism of the reaction may be explained by the equations $\text{CHCl}_3 + 3\text{MgEtBr} = \text{CH}(\cdot\text{Cl}\cdot\text{MgEtBr})_3$, and $\text{CHCl}_3 + 3\text{MgEtBr} = 3\text{MgClBr} + 3\text{C}_2\text{H}_4 + \text{CH}_4$. T. H. P.

Free Pentaphenylethyl. The Nature of the Carbon Linking. W. SCHLENK and HERMANN MARK (*Ber.*, 1922, 55, [B], 2285—2299).—The preparation of free pentaphenylethyl is described. The usual method of preparing this type of free radicle could not be adopted primarily in this instance, owing to the impossibility

of converting pentaphenylethanol into pentaphenylethyl chloride and subsequently bringing the latter into reaction by a suitable method; the process adopted consists, therefore, essentially in the preparation of octaphenylpropane and decaphenylbutane, and taking advantage of the dissociability of these compounds into pentaphenylethyl and triphenylmethyl and pentaphenylethyl, respectively. The success of the operations is greatly facilitated by the unexpected completeness of the dissociation of the fully phenylated hydrocarbons into the radicles. *Pentaphenylethyl*, $\text{CPh}_3 \cdot \text{CPh}_2$, forms golden-yellow crystals with a metallic glance, and is particularly noteworthy, since it exists in solution practically entirely in the unimolecular condition. It may be regarded as triphenylmethyl in which one phenyl group is replaced by a triphenylmethyl residue. Since the free fourth carbon valency of triphenylmethyl is markedly weaker than the ordinary carbon valency, it follows that, if the principle of the equality of action and reaction be accepted, it can only make a relatively small affinity demand on the central carbon atom of the diphenylmethyl group, and that, in consequence, a relatively larger measure of affinity must remain for the two phenyl groups and the free valency. It would therefore be expected that the free valency of pentaphenylethyl would be relatively stronger than that of triphenylmethyl. The balance of the experimental evidence is directly against this view, so that the authors draw the conclusion that an equal demand is not necessarily made on the two carbon atoms of a C-C linking with respect to energy of combination.

An ethereal solution of sodium triphenylmethyl is treated with a similar solution of dichlorodiphenylmethane [benzophenone chloride] in an atmosphere of nitrogen. The solution is filtered from sodium chloride, somewhat concentrated, and cooled, whereon a mixture of coarsely crystalline pentaphenylethyl and hexaphenylethane separates. The supernatant liquid containing suspended hexaphenylethane is decanted and the residual pentaphenylethyl is purified by repeated washing with cold absolute ether. In a somewhat similar manner, pentaphenylethyl is obtained by the action of triphenylmethyl chloride on disodium tetraphenylethane in the presence of anhydrous ether; the yield in this instance is poor, since the main reaction occurs in accordance with the scheme: $\text{CPh}_2\text{Na} \cdot \text{CPh}_2\text{Na} + 2\text{Ph}_3\text{CCl} \rightarrow 2\text{NaCl} + \text{CPh}_2 \cdot \text{CPh}_2 + 2\text{CPh}_3$. Pentaphenylethyl combines readily with chlorine to form *chloropentaphenylethane*, which is hydrolysed with unusual ease and readily decomposed by rise in temperature into pentaphenylethyl and chlorine; it gives pentaphenylethyl when its ethereal solution is treated with copper-bronze. The successive action of sodium amalgam and water on pentaphenylethyl leads to the production of pentaphenylethane, m. p. 173° , $\text{CPh}_3 \cdot \text{CPh}_2 \cdots \xrightarrow{+\text{Na}} \text{CPh}_3 \cdot \text{CPh}_2\text{Na} \xrightarrow{\text{H}\cdot\text{OH}} \text{NaOH} + \text{CPh}_3 \cdot \text{CHPh}_2$. H. W.

Analogues of Pentaphenylethyl. W. SCHLENK and HERMANN MARK (*Ber.*, 1922, **55**, [B], 2299—2302).—In the triphenylmethyl series, it has been shown that the position of the dissocia-

tion equilibrium is largely dependent on the nature of the aryl groups, and that the tendency towards dissociation is greatly increased by the substitution of the biphenyl for the phenyl group. In the pentaphenylethyl series, this does not appear to be the case, since triphenylbiphenylethyl, like the parent radicle (preceding abstract), exists entirely in the unimolecular condition in solution. Possibly with the pentaphenyl derivative the tendency towards dissociation is so powerful that it is unaffected by comparatively slight alterations in structure.

Triphenylbiphenyleneethyl, comparatively large, violet prisms, is prepared by the gradual addition of an ethereal solution of fluorenone chloride to a solution of sodium triphenylmethyl in an atmosphere of nitrogen; in consequence of its relatively sparing solubility in ether, the separation of the new radicle from simultaneously formed triphenylmethyl is readily effected. It is converted by treatment with chlorine dissolved in chloroform into *triphenylbiphenylene-ethyl chloride*, from which the radicle is regenerated by agitation with copper powder. The chloride is hydrolysed with great readiness. It is dissociated in sunlight at the atmospheric temperature into its components which reunite when preserved in the absence of light.

H. W.

Aromatic Chloroamines. II. STEFAN GOLDSCHMIDT and LUDWIG STROHMENGER (*Ber.*, 1922, **55**, [B], 2450—2470).—The preparation of the very unstable di- ω -chloroaniline has been described previously (Goldschmidt, A., 1913, i, 1173). The observations have now been extended to a number of its derivatives. The presence of negative substituents increases the stability of the molecule, which reaches its maximum in the case of di- ω -chloropentachloroaniline which may be preserved unchanged for weeks at the atmospheric temperature if moisture is completely excluded. Positive substituents, on the other hand, diminish the stability of the molecule. The chemical behaviour of the compounds is completely in accord with the hypothesis that a radicle, $R\cdot N\cdot$, is primarily formed. In every instance, polymerides of this radicle are ultimately isolated, either solely as azo-compounds or as mixtures of these with *N*-arylquinonedi-imides, according to the choice of the amine. The same products are obtained by the action of oxidising agents on aniline and its homologues (cf. Goldschmidt, A., 1920, i, 226) when such oxidation is possible, thus giving renewed support to the hypothesis that both types of reaction take place through the same intermediate product, the radicle $R\cdot N\cdot$.

An improved process for obtaining an ethereal solution of hypochlorous acid (cf. Wohl, A., 1907, i, 194) is described.

*Di- ω -chloro-*p*-nitroaniline*, $NO_2\cdot C_6H_4\cdot NCl_2$, is prepared by the action of hypochlorous acid on *p*-nitroaniline in ethereal solution at 20° (the necessary manipulation and apparatus are described in detail). It forms reddish-yellow prisms which can be preserved unchanged during several days at -80°, but decompose rapidly at the atmospheric temperature, ultimately exploding and leaving

a residue containing 4:4'-dinitroazobenzene. Its melting point, determined in a pre-heated bath, is about 50°. It is decomposed by ethereal hydrogen chloride solution into 2:6-dichloro-*p*-nitroaniline, m. p. 189—190°, and by aqueous alcoholic potassium iodide solution into 4:4'-dinitroazobenzene, m. p. 222° after softening at 219°, which is also obtained by the action of a solution of ammonia in ether and of an alcoholic solution of sodium ethoxide. The auto-decomposition of di-*o*-chloro-*p*-nitroaniline, dissolved in ether, light petroleum, acetic anhydride, or ethyl benzoate, gives varying proportions of 4:4'-dinitroazobenzene and 2:6-dichloro-*p*-nitroaniline.

Di-o-chloro-o-nitroaniline, pale yellow to brown prisms, m. p. (in pre-heated bath) 48—50° (complete decomp.) is prepared in the same manner as the para-isomeride. It can be preserved unchanged at a low temperature, but decomposes with ultimate explosion at the atmospheric temperature. In ethereal solution, it decomposes slowly at the ordinary temperature with production of 4:6-dichloro-*o*-nitroaniline, whereas in boiling carbon tetrachloride it yields chlorine, hydrogen chloride, and 2:2'-dinitroazobenzene, m. p. 209—210° after softening at 207°. It is converted by ethereal hydrogen chloride in the absence of an excess of hypochlorous acid into 4-chloro-*o*-nitroaniline, m. p. 115°, and a brown liquid which has not been further examined, whereas if hypochlorous acid is present in excess it gives 4:6-dichloro-*o*-nitroaniline, m. p. 101—102°; sodium thiosulphate solution transforms it into 2:2'-dinitroazobenzene.

Di-o-chloro-m-nitroaniline is prepared in the same manner as the ortho- and para-isomerides, to which it exhibits close similarity; it is converted by alcoholic sodium ethoxide solution or copper powder into 3:3'-dinitroazobenzene, m. p. 149—150°.

Di-o-chloro- α - ψ -cumidine [1-dichloroamino-2:3:5-trimethylbenzene] is prepared from hypochlorous acid and α - ψ -cumidine in ethereal solution, but is too unstable to permit isolation as a solid. It is converted by the successive action of a large excess of potassium iodide solution and zinc dust and glacial acetic acid into *chloroaminodicumylamine*, colourless needles, m. p. 167—168° (which is partly transformed by distillation with steam into 4(?) -chloro-2:3:5-trimethylaniline), colourless needles, m. p. 110.5—111° and 4:4' (?) -dichloro-2:3:5:2':3':5'-hexamethylazobenzene, lustrous, red needles, m. p. 189—190°. Chloroaminodicumylamine, dissolved in light petroleum, is transformed by lead peroxide into *chlorocumylcumyloquinonedi-imide*, $C_6HMe_3Cl \cdot N:C_6HMe_3 \cdot NH$, dark red, oblique prisms, m. p. 113—116°, the constitution of which is elucidated from its conversion into 4(?) -chloro-2:3:5-trimethylbenzene and cumoquinol.

Di-o-chloro-m-toluidine resembles the compound just described in that it can only be isolated in solution. It is converted by aqueous alcoholic potassium iodide solution and subsequent treatment with zinc dust into *aminoditolylamine*, prisms, m. p. 121°; 6-chloro-3-aminotoluene, colourless crystals, m. p. 83.5—84°; and 4:4' (?) -dichloro-3:3'-dimethylazobenzene, lustrous, yellow needles,

m. p. 162—163°. *m-Tolyltoluquinonedi-imide* could not be isolated in the crystalline condition by the action of lead peroxide in the presence of sodium sulphate on an ethereal solution of aminoditolylamine.

Detailed directions are given for the conversion of 2 : 6-dichloro-*p*-nitroaniline into 5-nitro-*m*-dichlorobenzene, for the reduction of the latter to 3 : 5-dichloroaniline and the chlorination of the base to 2 : 3 : 4 : 5 : 6-pentachloroaniline, m. p. 232°. The pentachloro-compound is transformed by hypochlorous acid in ethereal solution into *di-ω-chloropentachloroaniline*, pale yellow, transparent, thin prisms, m. p. 111° (decomp.). This substance behaves towards neutral or acid potassium iodide solution in the same manner as the chloroamines described previously. In boiling toluene solution, it is decomposed into *decachloroazobenzene*, dark red, lustrous plates or flesh-coloured needles, m. p. 317—318° after softening at 316°.

H. W.

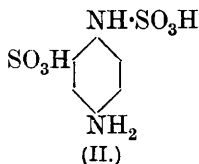
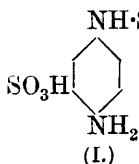
The Action of Sodium Hydrogen Sulphite on the Nitroanilines. HUGO WEIL and PAUL WASSERMANN (*Ber.*, 1922, 55, [B], 2533—2542; cf. Weil and Moser, this vol., i, 443).—An extension of previous work to the nitroanilines and related compounds.

p-Nitroacetanilide is converted by a boiling aqueous solution of sodium hydrogen sulphite (40%) into *sodium p-acetylaminophenylsulphamate*, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO}_3\text{Na} \cdot \text{H}_2\text{O}$; the corresponding *benzidine* salt, $\text{C}_{28}\text{H}_{30}\text{O}_2\text{N}_6(\text{SO}_3)_2 \cdot \text{H}_2\text{O}$, *α-naphthylamine* salt ($+\text{H}_2\text{O}$), and *β-naphthylamine* salt ($+\text{H}_2\text{O}$) are described. *p*-Acetylaminophenylsulphamic acid is converted by boiling aqueous sodium hydroxide into *p-aminophenylsulphamic acid*, $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{NH} \cdot \text{SO}_3\text{H}$, colourless crystals, whereas boiling dilute mineral acids transform it into acetyl-*p*-phenylenediamine. Sodium *p*-aminophenylsulphamate condenses with chloro-2 : 4-dinitrobenzene to give the salt, $\text{C}_{12}\text{H}_8\text{O}_4\text{N}_4 \cdot \text{SO}_3\text{Na}$, a red, crystalline substance; the corresponding *barium* salt is sparingly soluble in water. *p*-Aminophenylsulphamic acid can be diazotised, and the diazonium compound couples with *β*-naphthol to give an *azo-dye* which retains the *N*-sulphonic group.

p-Nitro-*o*-acetotoluidide and *p*-nitro-*o*-acetanisidide are reduced by sodium hydrogen sulphite, but the products are respectively too soluble and too unstable to permit their isolation in the homogeneous condition.

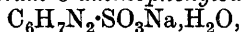
p-Nitrobenzanilide, which is most conveniently prepared from *p*-nitroaniline and benzoyl chloride in the presence of pyridine, is reduced similarly to, but much more slowly than, the corresponding acetyl derivative, forming *sodium p-benzoylamino-phenylsulphamate*, $\text{C}_{13}\text{H}_{11}\text{ON}_2 \cdot \text{SO}_3\text{Na} \cdot 2\text{H}_2\text{O}$, which is relatively sparingly soluble in water. *Sodium p-benzoylamino-*o*-tolylsulphamate* is prepared in a similar manner. Benzylated nitroanilines cannot be reduced with sodium hydrogen sulphite. *p*-Nitroaniline is gradually dissolved by a boiling solution of sodium hydrogen sulphite, but a sulphamic acid cannot be isolated, although its presence can be detected. If, however, the solution is greatly concentrated and acidified with dilute hydrochloric acid, it yields

the *monosodium* salt of a sulphamsulphonic acid (annexed formula



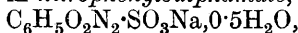
I or II) (the corresponding β -naphthylamine salt is described) which loses a sulphonic group under the influence of hydrochloric acid and forms *p*-phenylenediaminesulphonic acid. Although it contains a

primary amino-group, it does not react with benzoyl chloride or chloro-2:4-dinitrobenzene, possibly because of the presence of the sulphonic group in the ortho-position to the amino-group (formula I). In harmony with these observations, the free amino-group is not affected by nitrous acid; the compound can be diazotised and the diazonium compound couples with β -naphthol to form a dye, but the amino-group which takes part in the change is that which is formed by the loss of a sulphonic group from the compound. *p*-Nitro-*o*-toluidine is converted similarly into *sodium amino-o-tolyl-p-sulphamsulphonate*, $\text{SO}_3\text{H}\cdot\text{C}_7\text{H}_8\text{N}_2\cdot\text{SO}_3\text{Na}\cdot 0\cdot5\text{H}_2\text{O}$. *o*-Nitroaniline, on the other hand, is transformed into *sodium o-aminophenylsulphamate*,



colourless, lustrous crystals. The products of the reduction of *m*-nitroaniline with sodium hydrogen sulphite are too soluble to permit their isolation, but they can be diazotised in solution and subsequently coupled with β -naphthol; the azo-dye thus formed is acidic in character and retains this property after being boiled with mineral acid, although it loses sulphuric acid under these conditions. It appears, therefore, that a sulphosulphamic acid is formed initially.

m-Dinitrobenzene is reduced by sodium hydrogen sulphite to a mixture of *sodium m-nitrophenylsulphamate*,



and *sodium m-phenylenedisulphamate*, $\text{C}_6\text{H}_6\text{N}_2(\text{SO}_3\text{Na})_2\cdot 3\cdot5\text{H}_2\text{O}$.

H. W.

Nitro-derivatives of *m*-Nitrodimethylaniline. AQUILA FORSTER and WILLIAM COULSON (T., 1922, 121, 1988—1997).

Bases obtained in the Decomposition of the Azides of Thiocarbamic Acids. E. OLIVERI-MANDALÀ (*Gazzetta*, 1922, 52, ii, 98—103; cf. A., 1921, i, 900).—By heating azides of thiocarbamic acids with concentrated hydrochloric acid, the author has previously (A., 1914, i, 1144) obtained in the free state some of the bases described by Freund and Schwarz (A., 1897, i, 125) as thiocyanamides, $\text{NHR}\cdot\text{CS}\cdot\text{N}_3 \rightarrow \text{NHR}\cdot\text{CSN}$. As regards both their genesis and their constitution, these bases exhibit close analogy to Wieland's nitrile oxides (A., 1907, i, 527; 1909, i, 216, 217, 923). This analogy extends also to the anomalous cryoscopic behaviour, compounds of both classes exhibiting in solution molecular weights considerably higher than the calculated values, owing probably to polymerisation. The bases in question differ, however, from the nitrile oxides, which may also undergo isomeric

change to the corresponding esters of *isocyanic acid*, in that, when heated with water or a dilute mineral acid or an organic solvent, they readily lose the sulphur atom, giving polymerides of the corresponding derivatives of cyanamide, $3\text{NHR}\cdot\text{CNS} \rightarrow (\text{NHR}\cdot\text{CN})_3$; on the other hand, the nitrile oxides lose the oxygen atom by reduction, yielding nitriles, $\text{R}\cdot\text{CNO} + \text{H}_2 = \text{H}_2\text{O} + \text{R}\cdot\text{CN}$.

The constitution of these bases is most probably represented by the formula $\text{NHR}\cdot\text{C}\equiv\text{N}\cdot\text{S}$, and it is proposed to name the compound $\text{NHPh}\cdot\text{C}\equiv\text{N}\cdot\text{S}$, anilinesulphonitrile, rather than phenylthiocyanamide.

o-Toluidinesulphonitrile, $\text{C}_6\text{H}_4\text{Me}\cdot\text{NH}\cdot\text{C}\equiv\text{N}\cdot\text{S}$, obtained by prolonged boiling of the corresponding azide (A., 1921, i, 900) with concentrated hydrochloric acid, forms crystals, m. p. $138\text{--}140^\circ$, and shows abnormally high molecular weight in freezing acetic acid. The *hydrochloride* and *platinichloride* were analysed.

p-Toluidinesulphonitrile, similarly prepared, was obtained crystalline, and the *hydrochloride* and *platinichloride* were prepared.

Anilinesulphonitrile, $\text{C}_6\text{H}_5\text{N}_2$ (cf. A., 1914, i, 1144) has m. p. $122\text{--}123^\circ$ and exhibits high molecular weight in acetic acid. The *hydrobromide* and *platinichloride* were prepared.

Ethylaminesulphonitrile, $\text{NHEt}\cdot\text{C}\equiv\text{N}\cdot\text{S}$, was not prepared in the free state owing to the readiness with which it decomposes, but is obtained as *hydrochloride* when the azide of carbamic acid is boiled with concentrated hydrochloric acid; the *platinichloride* was also prepared. The azide of thiocarbamic acid, $\text{NHEt}\cdot\text{CS}\cdot\text{N}_3$, obtained by the interaction of ethylthiocarbimide and azoimide in ethereal solution, is identical with the compound prepared by Freund and Schwarz (*loc. cit.*) by the action of nitrous acid on ethylthiosemicarbazide and termed triazosulphole, $\text{NHEt}\cdot\text{C} \begin{smallmatrix} \text{N}\cdot\text{N} \\ \parallel \\ \text{S}\cdot\text{N} \end{smallmatrix}$;

with mercuric oxide, it yields, not the corresponding azide of carbamic acid, but the additive compound, $\text{C}_3\text{H}_6\text{N}_4\text{S}\cdot\text{HgO}$, which crystallises in needles.

T. H. P.

The Condensation of Aromatic *o*-Aminsulphonic Acids with *isoCyanic Acid*. JOHN RICHARD SCOTT and JULIUS BEREND COHEN (T., 1922, 121, 2034—2051).

Electrolytic Reactions of Naphthalene and its Derivatives.
III. Electrolytic Oxidation of α -Naphthylamine and *ar*-Tetrahydro- α -naphthylamine. KASHICHI ONO (*Mem. Coll. Sci. Kyoto*, 1922, 5, 345—357; cf. A., 1921, i, 334, 726).—The electrolytic oxidation of α -naphthylamine has been examined in a divided cell in which a small sheet lead cathode is immersed in sulphuric acid (20%) and the anode liquid is a solution of α -naphthylamine in acetone and dilute sulphuric acid. Platinum, graphite, and lead peroxide, respectively, are used as anode materials, the last-named giving the best results. Under these conditions, α -naphthylamine is converted into a mixture of naphthylamine-violet and α -naphthoquinone. Its behaviour thus differs from that of aniline, which, at a platinum electrode, is transformed solely into aniline-black,

but the apparent stability of the latter may be due entirely to its solubility in the anode liquid. The current yield diminishes with increasing current density and attains its maximum at approximately 1 ampere per 100 sq. cm. Elevation of the electrolytic temperature does not necessarily favour the yield. A suitable concentration of sulphuric acid is 10–30%, the best results being observed with a 10% solution. Potassium chromate, chrome alum, potassium chlorate, and ferric sulphate act effectively as oxygen carriers. The possibility of the formation of 4-amino- α -naphthol as an intermediate product of the oxidation of α -naphthylamine is discussed, but its production could not be established experimentally.

The electrolytic oxidation of *ar*-tetrahydro- α -naphthylamine has been examined under closely similar conditions; it is converted mainly into *ar*-tetrahydro- α -naphthaquinone. Platinum, lead peroxide, and graphite are used as anode material, and of these lead peroxide gives the best results. The most suitable conditions are a current density of about 1 amp./100 sq. cm., a temperature between 18° and 23°, and a concentration of sulphuric acid between 10% and 30%. Chrome alum, potassium chromate, potassium chlorate, and potassium ferrocyanide are efficient oxygen carriers.

H. W.

Preparation of Symmetrical Tetra-substituted Carbamides.

ARTHUR PERCIVAL TANBERG and HERBERT WINKEL (E. J. DU PONT DE NEMOURS & Co.) (Brit. Pat. 144681; from *Chem. Zentr.*, 1922, ii, 1136).—Secondary aromatic amines, dissolved in indifferent solvents such as benzene, xylene, solvent naphtha, or carbon tetrachloride, are heated at 70° and treated with the necessary amount of carbonyl chloride. *s*-Diphenyldimethylcarbamide is thus prepared from methylaniline according to the equation $4\text{NHMePh} + \text{COCl}_2 = \text{CO}(\text{NMePh})_2 + 2\text{NH}_2\text{MePhCl}$. G. W. R.

The Chlorohydrin and Oxide of Methylene-cyclobutane and the Transformation of the Former into cyclopentanone.

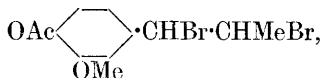
N. J. DEMJANOV and MARIE DOJARENKO (*Ber.*, 1922, 55, [B], 2730–2737).—Methylene-cyclobutane (cf. this vol., i, 996) is converted by hypochlorous acid into the corresponding *chlorohydrin*, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{C}(\text{OH})\cdot\text{CH}_2\text{Cl}$ or $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{CCl}\cdot\text{CH}_2\cdot\text{OH}$, b. p. 64.5°/20 mm., 75°/33 mm., 83°/47 mm., 158°/747 mm., d_4^{20} 1.1657, d_4^{15} 1.1502, d_4^{20} 1.1448, n_D^{20} 1.4657. The corresponding *phenylurethane* crystallises in needles, m. p. 112.5–113°. When heated under a reflux condenser with water and lead oxide, the chlorohydrin is converted into *cyclopentanone*, which is identified as the oxime and semicarbazone; the same reaction takes place very slowly at the atmospheric temperature. Glutaric and succinic acids are produced by the action of nitric acid (d 1.2) on the chlorohydrin. Concentrated aqueous potassium hydroxide solution converts the chlorohydrin into the *oxide*, $\text{CH}_2\langle\begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix}\rangle\text{C}\langle\begin{smallmatrix} \text{CH}_2 \\ \text{O} \end{smallmatrix}\rangle$, b. p.

89—92°/754 mm., the constitution of which is established by its isomerisation (by means of zinc chloride) to *cyclobutaldehyde*.

The *dichloride*, $\text{CH}_2 \begin{smallmatrix} \text{CH}_2 \\ \text{CH}_2 \end{smallmatrix} \text{CCl} \cdot \text{CH}_2 \text{Cl}$, b. p. 67—69°/36 mm., d_4^{20} 1.1928, d_4^{25} 1.1772, n_D^{25} 1.4756, is obtained as by-product during the preparation of the chlorohydrin. H. W.

The Solubility of the Chlorophenols. NEVIL VINCENT SIDGWICK and SYDNEY LEONARD TURNER (T., 1922, **121**, 2256—2263).

Derivatives of *isoEugenol*. G. RASTELLI (*Gazzetta*, 1922, **52**, ii, 129—130).—*Dibromoacetylisoegenol*,



forms white crystals, m. p. 125°, and darkens rapidly in the light. *Dibromobenzoylisoegenol*, $\text{C}_{17}\text{H}_{16}\text{O}_3\text{Br}_2$, crystallises in lustrous, white scales, m. p. 113°, stable towards light. *Di-iodoacetylisoegenol* (?) forms dirty white crystals, and *di-iodobenzoylisoegenol*, $\text{C}_{17}\text{H}_{16}\text{O}_3\text{I}_2$, white, silky needles, m. p. 85—86°. T. H. P.

The Interchange of Alcohol Radicles in Esters. II. AKIRA SHIMOMURA and JULIUS BEREND COHEN (T., 1922, **121**, 2051—2059).

Influence of Substitution in the Components on Equilibria in Binary Solutions. XXXVI. The Equilibria of Dihydroxynaphthalenes with Amines. ROBERT KREMANN, FRANZ HEMMELMAYR, and HEINRICH RIEMER (*Monatsh.*, 1922, **43**, 164—208).—The system 1:4-dihydroxynaphthalene-β-naphthylamine gives a *compound* (1 mol. : 1 mol.), m. p. 143°, which forms a eutectic with 1:4-dihydroxynaphthalene at 125° containing 36%, and one with β-naphthylamine at 96° containing 76%, of β-naphthylamine. 1:5-Dihydroxynaphthalene and β-naphthylamine give a *compound* (1 mol. : 1 mol.), m. p. 229.5°, which forms a eutectic with 1:5-dihydroxynaphthalene at 212° containing 35%, and one with β-naphthylamine at 107° containing 95%, of β-naphthylamine. 1:6-Dihydroxynaphthalene and β-naphthylamine give a *compound* (2 mol. : 3 mol.), m. p. 110.5°, which forms a eutectic with 1:6-dihydroxynaphthalene at 92° containing 42%, and one with β-naphthylamine at 96° containing 65%, of β-naphthylamine. 1:8-Dihydroxynaphthalene and β-naphthylamine give a *compound* (1 mol. : 1 mol.), m. p. 124°, which forms a eutectic with 1:8-dihydroxynaphthalene at 75° containing 38%, and one with β-naphthylamine at 76° containing 55%, of β-naphthylamine. 2:3-Dihydroxynaphthalene and β-naphthylamine give a *compound* (1 mol. : 1 mol.), m. p. 168°, which forms a eutectic with 2:3-dihydroxynaphthalene at 145° containing 24%, and one with β-naphthylamine at 106.5° containing 97%, of β-naphthylamine. 2:6-Dihydroxynaphthalene and β-naphthylamine give a *compound*

(1 mol. : 2 mol.), m. p. 171.5° , which forms a eutectic with 2 : 6-dihydroxynaphthalene at 165° containing 41%, and one with β -naphthylamine at 109° containing 98%, of β -naphthylamine. 2 : 7-Dihydroxynaphthalene and β -naphthylamine give a *compound* (1 mol. : 1 mol.), m. p. 163° , which forms a eutectic with 2 : 7-dihydroxynaphthalene at 153° containing 36%, and one with β -naphthylamine at 108° containing 98.5%, of β -naphthylamine.

1 : 5-Dihydroxynaphthalene and α -naphthylamine give a eutectic at 44° containing 95% of α -naphthylamine. 2 : 6-Dihydroxynaphthalene and α -naphthylamine give a eutectic at 46° containing 98% of α -naphthylamine. 2 : 7-Dihydroxynaphthalene and α -naphthylamine give a eutectic at 35° containing 91% of α -naphthylamine. 1 : 4-Dihydroxynaphthalene and α -naphthylamine give a *compound* (1 mol. : 1 mol.), m. p. 143° , which forms a eutectic with 1 : 4-dihydroxynaphthalene at 129° containing 39%, and one with α -naphthylamine at 44° containing 94%, of α -naphthylamine. 1 : 6-Dihydroxynaphthalene and α -naphthylamine give a *compound* (2 mols. : 3 mols.), m. p. 84.5° , which forms a eutectic with 1 : 6-dihydroxynaphthylamine at 76° containing 53%, and one with α -naphthylamine at 43° containing 92.5%, of α -naphthylamine. 1 : 8-Dihydroxynaphthalene and α -naphthylamine give a *compound* (1 mol. : 1 mol.), m. p. 76.5° , which forms a eutectic with 1 : 8-dihydroxynaphthalene at 74° containing 45%, and one with α -naphthylamine at 41° containing 84%, of α -naphthylamine. 2 : 3-Dihydroxynaphthalene and α -naphthylamine give a *compound* (2 mols. : 3 mols.), m. p. 103° , which forms a eutectic with 2 : 3-dihydroxynaphthalene at 97° containing 54.5%, and one with α -naphthylamine at 35° containing 87%, of α -naphthylamine.

1 : 6-Dihydroxynaphthalene and *p*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 170° , which forms a eutectic with 1 : 6-dihydroxynaphthalene at 121° containing 15%, and one with *p*-phenylenediamine at 125° containing 95%, of *p*-phenylenediamine. 1 : 8-Dihydroxynaphthalene and *p*-phenylenediamine form a *compound* (2 mols. : 1 mol.), m. p. 118° , which gives a eutectic with 1 : 8-dihydroxynaphthalene at 109° containing 21%, and one with *p*-phenylenediamine at 106° containing 37%, of *p*-phenylenediamine. 2 : 3-Dihydroxynaphthalene and *p*-phenylenediamine form a *compound* (2 mols. : 1 mol.), m. p. 164° , which gives a eutectic with 2 : 3-dihydroxynaphthalene at 141° containing 4%, and one with *p*-phenylenediamine at 118° containing 70%, of *p*-phenylenediamine. 2 : 6-Dihydroxynaphthalene and *p*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 212° , which gives a eutectic with 2 : 6-dihydroxynaphthalene at 195° containing 10%, and one with *p*-phenylenediamine at 140° containing 95%, of *p*-phenylenediamine. 2 : 7-Dihydroxynaphthalene and *p*-phenylenediamine give a *compound* (2 mols. : 1 mol.), m. p. 180° , which forms a eutectic with 2 : 7-dihydroxynaphthalene at 171° containing 10.5%, and one with *p*-phenylenediamine at 129° containing 81%, of *p*-phenylenediamine.

1 : 4-Dihydroxynaphthalene and *m*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 124° , which forms a eutectic with

m-phenylenediamine at 55° containing 92.5% of *m*-phenylenediamine. 1 : 6-Dihydroxynaphthalene and *m*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 125°, which forms a eutectic with 1 : 6-dihydroxynaphthalene at 87° containing 22%, and one with *m*-phenylenediamine at 49° containing 89%, of *m*-phenylenediamine. 1 : 8-Dihydroxynaphthalene and *m*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 101°, which forms a eutectic with 1 : 8-dihydroxynaphthalene at 75° containing 32%, and one with *m*-phenylenediamine at 58° containing 92%, of *m*-phenylenediamine. 2 : 3-Dihydroxynaphthalene and *m*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 149°, which forms a eutectic with 2 : 3-dihydroxynaphthalene at 122° containing 24%, and one with *m*-phenylenediamine at 53° containing 94%, of *m*-phenylenediamine. 2 : 6-Dihydroxynaphthalene and *m*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 171°, which forms a eutectic with 2 : 6-dihydroxynaphthalene at 125° containing 35%, and one with *m*-phenylenediamine at 61° containing 98%, of *m*-phenylenediamine. 2 : 7-Dihydroxynaphthalene and *m*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 139°, which forms a eutectic with 2 : 7-dihydroxynaphthalene at 126° containing 33%, and one with *m*-phenylenediamine at 53° containing 98%, of *m*-phenylenediamine.

The system 1 : 4-dihydroxynaphthalene-*o*-phenylenediamine has a eutectic at 87° containing 83% of *o*-phenylenediamine. The system 2 : 3-dihydroxynaphthalene-*o*-phenylenediamine has a eutectic at 96° containing 93% of *o*-phenylenediamine. The formation of a compound in these cases was not proved. 1 : 6-Dihydroxynaphthalene and *o*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 95°, which forms a eutectic with 1 : 6-dihydroxynaphthalene at 76° containing 32%, and one with *o*-phenylenediamine at 62° containing 61%, of *o*-phenylenediamine. 1 : 8-Dihydroxynaphthalene and *o*-phenylenediamine give a *compound* (1 mol. : 1 mol.), m. p. 151°, which forms a eutectic with 1 : 8-dihydroxynaphthalene at 117° containing 7%, and one with *o*-phenylenediamine at 93° containing 85%, of *o*-phenylenediamine. 2 : 6-Dihydroxynaphthalene and *o*-phenylenediamine give a *compound* (2 mols. : 3 mols.), m. p. 150°, which forms a eutectic with 2 : 6-dihydroxynaphthalene at 124° containing 30%, and one with *o*-phenylenediamine at 99° containing 92%, of *o*-phenylenediamine. 2 : 7-Dihydroxynaphthalene and *o*-phenylenediamine give a *compound* (2 mols. : 3 mols.), m. p. 140°, which forms a eutectic with 2 : 7-dihydroxynaphthalene at 101° containing 38%, and one with *o*-phenylenediamine at 96° containing 91%, of *o*-phenylenediamine.

1 : 4-Dihydroxynaphthalene and benzamide give a eutectic at 91° containing 61.5% of benzamide. 1 : 5-Dihydroxynaphthalene and benzamide form a eutectic at 106° containing 72% of benzamide. 1 : 1-Dihydroxynaphthalene and benzamide form a eutectic at 90° containing 45% of benzamide. 1 : 8-Dihydroxynaphthalene and benzamide form a eutectic at 46° containing 46% of benzamide. 2 : 6-Dihydroxynaphthalene and benzamide form a eutectic at 87° containing 48% of benzamide. 2 : 7-Dihydroxynaphthalene and

benzamide form a eutectic at 78° containing 52% of benzamide. 2:3-Dihydroxynaphthalene and benzamide give a *compound* (1 mol.: 3 mols.), m. p. 113°, which gives a eutectic with 2:3-dihydroxynaphthalene at 80° containing 48%, and one with benzamide at 106° containing 75%, of benzamide. C. K. I.

Synthesis of 1:12-Dihydroxyperylene and Perylene. ALOIS ZINCKE and RUPERT DENG (Monatsh., 1922, 43, 125—128).—Most of the work detailed in this paper has been described previously (this vol., i, 132). 1:12-Dibenzoyloxyperylene forms brownish-yellow, amorphous flocks, and decomposes at about 224°. C. K. I.

The Valency Problem of Sulphur. VII. *o*-Nitrophenyldithiochloride. HANS LECHER and KURT SIMON (Ber., 1922, 55, [B], 2423—2432).—In a recent communication, the analogy between dithiochlorides, $\text{Ar}\cdot\text{S}_2\cdot\text{Cl}$, and diazonium chlorides, $\text{Ar}\cdot\text{N}_2\cdot\text{Cl}$, has been indicated (A., 1920, i, 860). Further examination of *o*-nitrophenyl dithiochloride shows that the similarity is purely formal and that the dithiochloride does not exhibit the typical properties of diazonium compounds. *o*-Nitrophenyldithiochloride is not a salt, since its solutions in ethylene chloride are non-conductors of electricity; it belongs to the relatively small class of sulphides in which bivalent sulphur functions as a positive element and in which its linkings are not heteropolar and ionisable.

The preparation of *o*-nitrophenyl mercaptan, m. p. 57—58°, from *oo'*-dinitrodiphenyl disulphide and dextrose, is described in detail.

o-Nitrophenyl dithiochloride, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}\cdot\text{S}\cdot\text{Cl}$, is stable at the atmospheric temperature; when heated by itself, it suffers incipient decomposition at about 100°, evolves sulphur chloride at about 150°, and explodes above 200°. It appears to be hydrolysed by water in accordance with the equation $2\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2\text{Cl} + \text{H}_2\text{O} \rightarrow (\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2)_2\text{O} + 2\text{HCl}$, but attempts to isolate the oxide in a homogeneous condition were not successful. Aqueous potassium hydroxide decomposes it according to the scheme $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2\text{Cl} + 2\text{KOH} \rightarrow \text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SK} + (\text{HO}\cdot\text{S}\cdot\text{OH}) + \text{KCl}$. It reacts with dimethylaniline dissolved in anhydrous ether to form 4-dimethylaminophenyl 2'-nitrophenyl disulphide, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2\cdot\text{C}_6\text{H}_4\cdot\text{NO}_2$, orange-coloured plates, m. p. 115.5—117° (corr.).

2:2'-Dinitrodiphenyl trisulphide, yellow needles, m. p. 174.5—176° (corr.) when rapidly heated and placed in a pre-heated bath, is prepared by mixing ethereal solutions of *o*-nitrophenyl dithiochloride and *o*-nitrophenyl mercaptan. It could not be obtained satisfactorily from the mercaptan and sulphur dichloride or from *o*-nitrophenyl thiochloride and hydrogen sulphide. It is hydrolysed by concentrated aqueous potassium hydroxide at 70—80° in accordance with the equation $(\text{NO}_2\cdot\text{C}_6\text{H}_4)_2\text{S}_3 + 2\text{KOH} = 2\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{SK} + (\text{HO}\cdot\text{S}\cdot\text{OH})$. *o*-Nitrophenyl dithiochloride reacts with piperidine, but the expected mixed disulphide, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{S}_2\cdot\text{C}_5\text{H}_{10}$, could not be isolated in a well-defined condition. H. W.

Vinylcyclopropane, certain Derivatives of Methylcyclopropylcarbinol and the Isomerisation of the cycloPropane Ring. N. J. DEMJANOV and MARIE DOJARENKO (*Ber.*, 1922, 55,

[B], 2718—2727).—Acetylcyclopropanoxime, $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CMe} \cdot \text{N} \cdot \text{OH}$,

is reduced to the corresponding amine, which is transformed by methyl iodide into trimethyl-2-cyclopropylethylammonium iodide. The hydroxide corresponding with the latter compound decomposes

when distilled mainly into vinylcyclopropane, $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CH} \cdot \text{CH}_2$,

a colourless, mobile liquid, b. p. 40—40.2°/755 mm., d_4^{20} 0.741, d_4^{10} 0.731, d_4^{15} 0.726, d_4^{18} 0.723, n_D^{20} 1.4205, n_D^{15} 1.4172. α -cycloPropyl-

ethyldimethylamine, $\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CHMe} \cdot \text{NMe}_2$, is produced in very

small amount during the action and is characterised in the form of its *picrate*, yellow needles, m. p. 187—188°, and *aurichloride*, thin, yellow, rectangular leaflets. Vinylcyclopropane reacts vigorously with bromine to give the corresponding *dibromide*, b. p. 86—88°/21—22 mm., d_4^{20} 1.842, d_4^{10} 1.825, d_4^{15} 1.818, n_D^{20} 1.54447, which reacts only very slowly with bromine. The hydrocarbon is oxidised by potassium permanganate at 0—5° to formic acid, cyclopropanecarboxylic acid and cyclopropylethylene glycol,

$\begin{smallmatrix} \text{CH}_2 \\ | \\ \text{CH}_2 \end{smallmatrix} > \text{CH} \cdot \text{CH}(\text{OH}) \cdot \text{CH}_2 \cdot \text{OH}$, b. p. 213—215°/750 mm., d_4^{20} 1.0823, d_4^{20} 1.0677, n_D^{20} 1.4637.

Methylcyclopropylcarbinol is transformed by iodine and red phosphorus into the *iodide*, $\text{C}_5\text{H}_9\text{I}$, a colourless liquid which becomes brown when preserved, b. p. 57.5—58.5°/19—20 mm., 69—70°/36 mm., d_4^{20} 1.597, d_4^{15} 1.575, d_4^{10} 1.5675, n_D^{20} 1.5244, n_D^{15} 1.5221; a specimen prepared by the action of hydrogen iodide on the carbinol at 0° had b. p. 68°/35 mm., d_4^{20} 1.6083, d_4^{15} 1.587, d_4^{10} 1.579, R 37.34. The iodide is converted by alcoholic potassium hydroxide solution into piperylene, $\text{CHMe} \cdot \text{CH} \cdot \text{CH} \cdot \text{CH}_2$, b. p. 41.8—42.2°/748 mm., d_4^{20} 0.697, d_4^{10} 0.688, d_4^{15} 0.6827, n_D^{20} 1.4366, n_D^{15} 1.43398, which is transformed by bromine into $\alpha\beta\gamma\delta$ -tetrabromo-*n*-pentane, long prisms, m. p. 116°. It appears, therefore, that the iodide, $\text{C}_5\text{H}_9\text{I}$, must have the constitution $\text{CH}_2 \cdot \text{CH} \cdot \text{CH}_2 \cdot \text{CHI} \cdot \text{CH}_3$ or $\text{CH}_3 \cdot \text{CH} \cdot \text{CH} \cdot \text{CHI} \cdot \text{CH}_3$ (probably the former), and that the cyclopropyl ring must have suffered fission during the action.

The action of dehydrating agents (acetic anhydride, oxalic acid, and phosphoric oxide) on the carbinol has been examined in the hope of obtaining vinylcyclopropane in this manner. A definite result is obtained only with acetic anhydride which gives the corresponding *acetate*, b. p. 138—139°/747 mm., d_4^{20} 0.949, d_4^{10} 0.939, d_4^{15} 0.931, n_D^{20} 1.4200, n_D^{15} 1.4182. H. W.

Ketens. XL. Ketenacetals. H. STAUDINGER and G. RATHSAM (*Helv. Chim. Acta*, 1922, 5, 645—655).—The preparation and examination of phenylketenacetal have shown that this is much more stable than the corresponding keten. Attempts were first

made to obtain the acetals of ordinary keten and of methylketen by heating the ortho-esters of acetic and propionic acids with phosphoric oxide, according to the scheme $\text{CH}_3\cdot\text{C}(\text{OEt})_2 \rightarrow \text{CH}_2\cdot\text{C}(\text{OEt})_2 + \text{EtOH}$, but without success. On the other hand, the ortho-ester of phenylacetic acid gave a good yield of phenylketenacetal when it was distilled several times at 12–15 mm. pressure. *Phenylketenacetal*, $\text{CHPh}\cdot\text{C}(\text{OEt})_2$, boils at $136^\circ/12$ mm. Compared with phenylketen, it is quite stable, and only polymerises very slowly at 130° . It is not oxidised by air at the ordinary temperature, but is very sensitive to water, giving ethyl phenylacetate; with bromine it gives ethyl phenylbromoacetate. It combines with 2 mols. of diphenylketen to form a compound, probably a cyclohexane derivative; $\text{C}_{40}\text{H}_{36}\text{O}_4$, white crystals, m. p. 138° . By hydrolysis, this gives an acid, which was not further investigated.

By the action of dry sodium methoxide on *as*-diphenyldichloroethylene, diphenylketenacetal was not obtained, but a complex reaction ensued with production of diphenylmethane, tolane, and methyl alcohol. Attempts to prepare the ortho-ester of diphenylacetic acid by the action of alcohol on ethyl diphenylimidoacetate were unsuccessful. *Ethyl diphenylimidoacetate*, $\text{CHPh}_2\cdot\text{C}(\text{NH})\cdot\text{OEt}$, was prepared by passing hydrogen chloride at -80° into a mixture of light petroleum, diphenylacetonitrile and the calculated quantity of alcohol in an autoclave and allowing the mixture to remain at the ordinary temperature for a long time. Its *hydrochloride* has m. p. 128 – 130° , decomposing into diphenylacetamide and ethyl chloride.

By the action of diphenylketen on orthoformic ester at 60° , the *acetal* of *ethyl diphenylformylacetate*, $\text{CO}_2\text{Et}\cdot\text{CPh}_2\cdot\text{CH}(\text{OEt})_2$, is formed, m. p. 58° , a remarkably stable substance. It is not decomposed by alcoholic potassium hydroxide, but with warm concentrated hydrochloric acid it breaks up, giving diphenylacetic acid, ethyl chloride, and formic acid.

E. H. R.

Ketens. XLI. Methylenecarbonic Acid Derivatives [*Ketenacetals, etc.*]. H. STAUDINGER and P. MEYER (*Helv. Chim. Acta*, 1922, **5**, 656–678).—From the analogies in the constitutions $\text{O}\cdot\text{C}(\text{OEt})_2$ and $\text{CR}_2\cdot\text{C}(\text{OEt})_2$, the ketenacetals (previous abstract) may be regarded as the normal esters of methylene-carbonic acid. Their derivatives, such as $\text{CR}_2\cdot\text{C}(\text{ONa})\cdot\text{OEt}$, are enolic forms of derivatives of acid esters. These are already known in the form of derivatives of ethyl malonate. In the present paper are described attempts to obtain derivatives of the types $\text{CR}_2\cdot\text{C}(\text{OM}')\cdot\text{OEt}$ and $\text{CR}_2\cdot\text{C}(\text{OM}')_2$, where M' is an alkali metal, most of the experiments being made with ethyl diphenylacetate. *Potassoxyethoxy-diphenylketen*, $\text{CPh}_2\cdot\text{C}(\text{OK})\cdot\text{OEt}$, was obtained best by treating ethyl diphenylacetate with potassamide in liquid ammonia. An additive product was first obtained which by heating in a vacuum at 100 – 120° lost ammonia. It was also prepared by treating the ester with potassium suspended in toluene, but was not isolated by this method. The salt is spontaneously oxidised by oxygen,

without, however, forming a stable peroxide. The oxidised salt is decomposed by water, giving benzophenone and benzilic acid. When alkylated with methyl iodide, the ester salt gives ethyl $\alpha\alpha$ -diphenylpropionate. Diphenylketen reacts with it to form tetraphenylacetone and tetraphenylallene, the production of which is difficult to explain.

The carboxylic acids show little tendency to form enol derivatives. Thus it was found impossible by heating sodium diphenylacetate or sodium *isobutyrate* with sodium methoxide to obtain the normal sodium salt derivative of diphenylketendiol. Sodium diphenylacetate showed some tendency to enolise under these conditions to form a yellow salt, but the best result was obtained by heating potassium diphenylacetate with potassamide in liquid ammonia, when dipotassoxydiphenylketen, $\text{CPh}_2\text{:C(OK)}_2$, was obtained as a yellow precipitate. The yellow salt could not be crystallised. It was also obtained by the action of potassium on potassium diphenylacetate in liquid ammonia, and a similar salt was obtained from diphenyleneacetic acid, $\text{C}_6\text{H}_4\text{>CH}\cdot\text{CO}_2\text{H}$, but not from salts

of acetic, *isobutyric*, succinic, or malonic acid. It is noteworthy that whilst ethyl malonate enolises more readily than ethyl diphenylacetate, in the case of the potassium salts the tendency to enolise is reversed. Dipotassoxydiphenylketen undergoes autoxidation in oxygen, forming an explosive peroxide. The peroxide, a colourless solid, is formed by absorption of two atoms of oxygen and appears to have a high molecular weight. When gently heated, it decomposes more or less explosively into benzophenone and potassium carbonate. When the potassium compound, suspended in toluene, is oxidised carefully with air, a monoxide is formed, probably having the structure $\text{O}<\text{CPh}_2$, which when

treated with acids or alkalis forms benzilic acid. Alkylation of dipotassoxydiphenylketen with methyl iodide gives potassium $\alpha\alpha$ -diphenylpropionate, whilst the more active methyl sulphate gives the corresponding methyl ester. These products of alkylation afford proof that when enolic compounds are alkylated the alkyl group becomes primarily attached to the carbon atom. If combination first occurred at the oxygen atom, a potassium enol derivative of the ester would be formed and a *C*-alkylated derivative would not be obtained.

The greater reactivity of the salts of ketendiol, which are coloured and autoxidisable, compared with the esters which are not, is paralleled by the greater reactivity of the salts of the polyhydroxy-benzenes such as pyrocatechol and pyrogallol as compared with their ethers.

E. H. R.

Alkali Salts of Benzil and the Benzilic Acid Transformation. H. STAUDINGER and A. BINKERT (*Helv. Chim. Acta*, 1922, 5, 703—710).—In a previous paper (preceding abstract) the difference between the reactivity, for instance the autoxidisability, of the polyhydroxybenzenes in the form of their alkyl derivatives and

of their sodium salts, was compared with the difference between the salts and esters derived from ketenacetals. The investigation is now extended to the salts of stilbenediol, $\text{OH}\cdot\text{CPh}\cdot\text{CPh}\cdot\text{OH}$, which is isomeric with diphenylketendiol, $\text{Ph}_2\text{C}\cdot\text{C}(\text{OH})_2$. The potassium salts of stilbenediol are formed to some extent when benzoin is treated with potassamide in liquid ammonia, or by the reduction of benzil by potassium in liquid ammonia, but they are best obtained by reducing benzil with potassium in boiling benzene. The dipotassium salt is red and the monopotassium salt violet. The red salt is decomposed by water, giving benzoin; with acetic anhydride, it gives β -stilbene diacetate, probably with a little of the α -form, and with benzoyl chloride the corresponding *dibenzoate* in two probably stereoisomeric forms, m. p. 159° and 185 — 187° . The *dimethyl ether*, probably the α -form, has m. p. 127° . The monopotassium salt is to be regarded as a compound of the quinhydrone type, formed between one mol. of benzil and one of dipotassium salt, as in the annexed formula. Its deep colour $\text{Ph}\cdot\text{COK} \dots \text{O}\cdot\text{C}\cdot\text{Ph}$ supports this opinion, and also the fact that $\text{Ph}\cdot\text{COK} \dots \text{O}\cdot\text{C}\cdot\text{Ph}$ with acetic anhydride and benzoyl chloride it gives a mixture of benzil and of stilbenediol derivative. The dipotassium salt is autoxidisable, like the corresponding salt of diphenylketendiols; in the cold, potassium benzoate is formed, but in the warm a mixture of benzoic acid and benzoic acid. The former probably results from a peroxide, $\text{O}\cdot\text{CPh}\cdot\text{OK}$, the latter from a monoxide, $\text{O}\cdot\text{CPh}\cdot\text{OK}$. A suggested explanation of the benzoic acid transformation is as follows. The action of alkali on benzil leads first to an additive product, a pinacone, $\text{OK}\cdot\text{CPh}(\text{OH})\cdot\text{CPh}(\text{OH})\cdot\text{OK}$. This may lose water to form the above oxide, which then undergoes transformation, or the pinacone may change over directly, the transformation being a special case of the pinacone-pinacoline change. E. H. R.

isoCampholic Acid. H. RUPE and P. BRIELLMANN (*Helv. Chim. Acta*, 1922, 5, 767—777).—Experiments were made to investigate more fully the *isocampholic acid* first prepared by Guerbet (A., 1895, i, 61) and if possible to determine its constitution. The material was obtained from the campholic acid prepared by heating camphor with potassium hydroxide at 280° in an iron autoclave, and was finally purified by converting it into the acid chloride and thence into the amide. The *chloride*, $\text{C}_{10}\text{H}_{17}\text{OCl}$, is a mobile liquid, b. p. $103^\circ/11$ mm.; the *amide* forms lustrous, white scales, m. p. 112° . The *isocampholic acid* prepared by hydrolysing the amide forms a pale yellow, mobile oil, b. p. $141^\circ/9$ mm., d_4^{20} 0.9789, $[\alpha]_D^{20} +30.36^\circ$, $[\alpha]_D +26.26^\circ$ in benzene, $n=1.46061$. Ethyl *isocampholate* is a liquid with a peppermint-like odour, b. p. $103^\circ/12$ mm., d_4^{20} 0.9426, $[\alpha]_D^{20} +26.64^\circ$, $n=1.44572$. The *anilide* crystallises in fine, white needles or prisms, m. p. 119.5° , and the *p-toluidide* in needles, m. p. 133 — 134° . *isoCampholic acid* is formed slowly when campholic acid is heated with potassium hydroxide at 280° . By nitric acid it is oxidised to camphoric

nn^*

acid. By bromination with bromine and phosphorus, *isocampholic* acid was converted into a *bromoisocampholic bromide*, a white solid which reacted with alcohol, giving ethyl *bromoisocampholate*, a white, mobile oil with an intense peppermint-like odour, b. p. 125.5°/8 mm. When boiled with methyl alcoholic potassium hydroxide, the *bromoisocampholic* ester was converted into an *unsaturated acid*, an odourless oil, b. p. 146—147°/8 mm., d_4^{20} 1.0374, $[\alpha]_D +15.88^\circ$. It forms a *silver* salt, fine, white needles, $C_{10}H_{15}O_2Ag$. The constitution of this acid was not elucidated. It is shown that *isocampholic* acid cannot be identical with dihydrocampholenic acid, as supposed by Mahle and Tiemann (A., 1900, i, 507) or with the dihydrocampholenic acid described by van Kregten (A., 1916, i, 480). It is suggested that it may have the constitution $CMe_2 \cdot CMe_2 > CH \cdot CO_2H$, being formed by intramolecular change $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} \text{---} CH_2$ from campholic acid.

E. H. R.

***p*-Dithiobenzoic Acid.** SAMUEL SMILES and DOUGLAS CREESE HARRISON (T., 1922, 121, 2022—2026).

The Constitution of Vacciniin. HEINZ OHLE (*Biochem. Z.*, 1922, 131, 611—613).—Monoacetoneglucose was benzoylated in pyridine solution by benzoyl chloride in chloroform and gave ζ -benzoylmonoacetoneglucose identical with the acetone condensation product of vacciniin (A., 1918, i, 226). Monoacetoneglucose is converted by shaking with anhydrous copper sulphate in dry acetone into diacetoneglucose. This reaction fails with ζ -benzoylmonoacetoneglucose and thus determines the ζ -position for the benzoyl group in vacciniin.

H. K.

The Chlorination and Bromination of the Toluic Acids and the Preparation of the Phthalaldehydic Acids. WILLIAM DAVIES and WILLIAM HENRY PERKIN, jun. (T., 1922, 121, 2202—2215).

Photo-reactions of the *trans*- and *cis*-Cinnamic Acids. HANS STOBBE and FRANZ KARL STEINBERGER (*Ber.*, 1922, 55, [B], 2225—2245; cf. de Jong, this vol., i, 339).—The authors' views on the polymerisation of the cinnamic acids under the influence of light coincide with those of de Jong in that α -truxillic acid is considered to be formed solely by the polymerisation of two molecules of *trans*-cinnamic acid, but differ with regard to the origin of β -truxinic acid. From the results of his experiments on the polymerisation of mixtures of *trans*- and *cis*-cinnamic acids, de Jong has drawn the conclusion that a molecule of β -truxinic acid is formed from a molecule of *cis*- and a molecule of *trans*-cinnamic acid. The author does not consider that the experimental evidence is conclusive, and is of the opinion that the whole process is represented accurately by the scheme β -truxinic acid \leftarrow *cis*-cinnamic acid (solid) \rightleftharpoons *trans*-cinnamic acid (solid) \rightarrow α -truxillic acid, according to which β -truxinic acid is derived solely from *cis*-cinnamic acid. Experimental evidence in favour of this view is now recorded.

Exposure of molten *allo*-cinnamic acid to the light of a quartz-mercury vapour lamp causes extensive isomerisation to *trans*-cinnamic acid, but does not result in the formation of truxillic or truxinic acids, its behaviour under these conditions resembling that which is observed in benzene solution (Stoermer, A., 1910, i, 114). The action is caused mainly by the rays of wave length, 270—320 $\mu\mu$, although those of shorter and greater length are active to a less extent.

The behaviour of pure *allo*- and *trans*-cinnamic acids and of mixtures of them when exposed to the light of the Uviol lamp and to sunlight, respectively, has been examined in detail. The isomerisation of the *cis*- to the *trans*-acid takes place in much the same manner with either source of light, but sunlight is far more effective than artificial light in causing polymerisation. This is due to the dissimilarity of the lights. The Uviol rays of long wave-length induce polymerisation, whereas those of short wave-length retard polymerisation and actually have a depolymerising effect on the truxinic and truxillic acids. The exposure of *cis*-cinnamic acid to sunlight leads invariably and generally preponderatingly to the production of β -truxinic acid; prolonged exposure causes isomerisation to the *trans*-acid and subsequent polymerisation to α -truxillic acid. *trans*-Cinnamic acid, on the other hand, is polymerised almost exclusively to α -truxillic acid. After protracted illumination, the formation of relatively small amounts of β -truxinic acid, in addition to much resinous matter, is observed, but the presence of *cis*-cinnamic acid could not be established. The addition of *trans*- to *cis*-cinnamic acid does not result in the increased production of β -truxinic acid. (The structure assigned to β -truxinic acid by de Jong (*loc. cit.*) is thus invalidated, but it is not yet possible to decide between the alternatives proposed by Stoermer and Scholtz [A., 1921, i, 180].)

trans-Cinnamic acid is polymerised to α -truxillic acid and autoxidised to benzaldehyde if its aqueous solution is exposed to light, particularly in the presence of a little hydrochloric acid. Under similar conditions, *cis*-cinnamic acid (m. p. 68°) gives β -truxinic acid and benzaldehyde; the yield of acid diminishes after protracted illumination particularly in the presence of hydrochloric acid, owing to pronounced autoxidation. Experiments with a mixture of the *cis*- and *trans*-acids show that the production of β -truxinic acid is independent of the presence of admixed *trans*-acid. It is remarkable that the *trans*-cinnamic acid formed by isomerisation is less readily polymerised than the acid introduced in powder form; the phenomenon is explained by a progressive change in the absorptive capacity of the illuminated crystals.

The conversion of prismatic, metastable β -*trans*-cinnamic acid by light into β -truxinic acid has been recorded by de Jong (*loc. cit.*). It is now shown that the latter acid is produced in relatively better yield when the β -cinnamic acid is exposed to light shortly after its recrystallisation than after the lapse of such an interval that its partial conversion into α -cinnamic acid has commenced and that β -cinnamic acid freshly precipitated from solutions of its

sodium salt gives exclusively β -truxinic acid, which is free from α -truxillic acid. A possible explanation of these observations is found in the suggestion that the highly reactive β -cinnamic acid is more readily isomerised than α -cinnamic acid to *allocinnamic* acid which is subsequently polymerised normally to β -truxinic acid. The authors do not consider that the difference in the behaviour towards light of α - and β -cinnamic acids necessarily proves their chemical isomerism; since the observations have been uniformly made with crystalline material and the power of absorbing light varies in anisotropic material according to the direction of the axis, it is possible that the two acids are to be regarded as two forms of a dimorphous cinnamic acid.

The influence of temperature on the photochemical polymerisation of *allocinnamic* acid has been examined by de Jong (*loc. cit.*), who, however, does not appear to have taken into consideration the importance of the melting of the acid at temperatures above 60° .

A convenient method for the preparation of *allocinnamic* acid by the partial hydrogenation of sodium phenylpropiolate in the presence of palladised barium sulphate is described in detail. A modified process for the estimation of *cis*- and *trans*-cinnamic acids, α -truxinic and β -truxillic acids in mixtures containing the four substances is given (cf. de Jong, A., 1913, i, 384; Stoermer, A., 1919, i, 444).
H. W.

Preparation of *d*-Pimaric Acid of m. p. 212° . EDMUND KNECHT and EVA HIBBERT (*J. Soc. Dyers and Col.*, 1922, **38**, 221—222).—*l*-Pimaric acid, of m. p. 161° and $\alpha_D -80^\circ$, when exposed to the air for prolonged periods, or when subjected to alkaline oxidation, is partly converted into the *d*-pimaric acid, $C_{20}H_{30}O_2$, m. p. 212° and $\alpha_D +62.5^\circ$, described by Laurent, Vesterberg, and others. The reaction is conveniently carried out by keeping overnight a mixture of a dilute solution of the sodium salt of *l*-pimaric acid (25 grams) and 400 c.c. of sodium hypochlorite solution (75 grams available chlorine per litre). The crystalline precipitate which forms is dissolved in boiling water and decomposed with sulphuric acid. By recrystallising the liberated acid from alcohol, it is obtained in a pure condition in a yield of about 10%. *d*-Pimaric acid, m. p. 161° , $\alpha_D +80^\circ$, behaves in a similar way to the *l*-acid.
G. F. M.

Keto-enolic Equilibria and Claisen's Rule. W. DIECKMANN (*Ber.*, 1922, **55**, [B], 2470—2491).—As the result of an extended study of a large variety of desmotropic substances, the author draws the conclusion that Claisen's rule has only a very limited applicability and that the tendency towards enolisation of a substance and its acidity are influenced in a complex manner by other constitutive influences which are not yet distinctly defined. Meyer's bromine titration method has been found to be very generally applicable and the relationship $K=EL$ (in which E is the constant of enolisation, K the equilibrium constant, and L the enolising action of the solvent) has been confirmed in the great majority of cases (cf. K. H. Meyer, A., 1912, i, 940).

It has been considered previously by Meyer that the enolising power of the carbomethoxy- is inferior to that of the carbethoxy-group, although there is no difference in their acidity. The enolic constants of methyl and ethyl acetoacetates are now found to be identical as are those of the corresponding benzoylacetates. The differences in enol content of the equilibrium esters is explicable if they are regarded as solutions of the enolic ester in the ketonic ester, and it is remembered that the ketonic ethyl ester has a higher enolising power than the corresponding methyl compound. This hypothesis is supported by the observation that ethyl acetate has a higher desmotropic constant than methyl acetate and that these constants are related to one another in the same ratio as the equilibrium constants of ethyl and methyl acetoacetates.

According to Meyer's observations (A., 1914, ii, 351), the behaviour of unsubstituted diacylmethanes is in accordance with Claisen's rule. This is not the case with the monoalkyldiacylmethanes, $R \cdot CO \cdot CHMe \cdot COR'$. In equilibrium in alcoholic solution, methylacetylacetone contains about 34% of enol, methylbenzoylacetone 7%, and methyldibenzoylacetone only about 0.3% of enol. The enolic constant diminishes from methylacetylacetone ($E = ca. 3.9$) to methylbenzoylacetone ($E = 0.06$) and further to methyldibenzoylmethane ($E = ca. 0.02$). A similar deviation from Claisen's rule is observed among triacylmethanes, the enolic constant of tribenzoylmethane ($E = ca. 10$) being very appreciably lower than that of dibenzoylacetylmethane ($E = ca. 78$).

Cyclic β -ketonic carboxylic esters do not conform to Claisen's rule. Such esters of the penta- and hexa-methylene series are distinguished from their aliphatic analogues, the monoalkyl-acetoacetic esters, by greater acidity, as demonstrated by their solubility in alkali, and power of forming copper salts when treated with copper acetate. The acidity is considerably more pronounced in the *cyclopentane* than in the *cyclohexane* series. It is now shown that the more strongly acidic ethyl *cyclopentane*-2-one-1-carboxylate contains only 4.5% of enol in its equilibrium mixture, and that this value only slightly exceeds that of its aliphatic analogue, ethyl ethylacetoacetate (3%), whereas ethyl *cyclohexane*-2-one-1-carboxylate contains 76% of enol. This remarkable difference persists in its equilibrium mixtures in solution. The enolic constant of ethyl *cyclopentane*-2-one-1-carboxylate ($E = ca. 0.5$) is only slightly greater than that of ethyl ethylacetoacetate ($E = 0.23$) and very much less than that of ethyl *cyclohexane*-2-one-1-carboxylate ($E = ca. 12$). The tendency towards enolisation appears to be conditioned in these cases by constitutive influences other than acidity, and is presumably connected with the condition of strain in the *cyclopentane* and *cyclohexane* rings. To gain further insight into these relationships, other ring systems have been studied. Ethyl *cycloheptane*-2-one-1-carboxylate has $E = ca. 1.2$ and similar acidity to the *cyclohexanone* ester, whereas ethyl camphorcarboxylate, which contains a five- and a six-membered ring, has a remarkably lower enolic constant ($E = 0.04$) and very slight acidity.

In contrast to the tendency towards enolisation of ethyl β -cyclohexanonecarboxylate, it is remarkable that ethyl cyclopentane-2 : 3-dione-1 : 4-dicarboxylate and its 5-phenyl derivative are stable in the dienolic form in the solid state and in solution; this is also true for ethyl cyclopentane-2 : 3-dione-1-carboxylate and its 5-phenyl compound. The marked increase in tendency towards enolisation is explained in accordance with Claisen's rule by the great increase in acidity due to the presence of the keto-group in the α -position.

The great dependence of tendency towards enolisation and acidity on cyclic structure and constitutive influences is illustrated by the behaviour of benzo-derivatives of cyclopentanonecarboxylic esters. Ethyl α -hydrindone- β -carboxylate, $\text{C}_6\text{H}_4\langle\frac{\text{CO}}{\text{CH}_2}\rangle\text{CH}\cdot\text{CO}_2\text{Et}$, has the enolic constant $E=\text{ca. } 2.4$, and is a relatively weak acid which cannot be titrated with alkali in aqueous-alcoholic solution, whereas ethyl β -hydrindone- α -carboxylate, $\text{C}_6\text{H}_4\langle\frac{\text{CH}\cdot(\text{CO}_2\text{Et})}{\text{CH}_2}\rangle\text{CO}$, has a high enolic constant and such marked acidity that it can be titrated with alkali in aqueous-alcoholic solution as a monobasic acid. The acyclic analogues of the esters exhibit greatly diminished acidity and considerably smaller constants of enolisation. Ethyl benzylbenzoylacetate has $E=\text{ca. } 0.3$, whereas ethyl $\alpha\gamma$ -diphenylacetoacetate has $E=3.6$.

Meyer indirect and direct bromine titration methods are smoothly applicable to unsubstituted 1 : 3-dicarbonyl compounds, $\text{R}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{R}'$. The monoalkyl derivatives of these compounds cannot in many cases be so treated. The indirect method is unsuitable, since the bromo-derivatives do not react smoothly and quantitatively with hydriodic acid; the direct method is difficult, owing to the uncertainty in recognition of the end-point, particularly in dilute solution and in the presence of small amounts of material. Under these conditions, it is frequently advisable to modify the process by adding a known excess of bromine followed by potassium iodide and immediately titrating the liberated iodine.

The following substances have been prepared incidentally. Methyl dibenzoylmethane, $\text{COPh}\cdot\text{CHMe}\cdot\text{COPh}$, from dibenzoylmethane, sodium ethoxide, and methyl iodide in absolute ethyl alcoholic solution, m. p. about 85° (cf. Beyme, *Diss.*, Leipzig, 1900), and the corresponding enolic form, colourless leaflets, m. p. 110° ; ethyl cyclopentane-2 : 3-dione-1-carboxylatediphenylhydrazone, yellow crystals, m. p. 138° ; ethyl 5-phenylcyclopentane-2 : 3-dione-1-carboxylatediphenylhydrazone, yellow crystals, m. p. 181° ; ethyl methylquinoxalinocyclopentane-2 : 3-dione-1-carboxylate (from the parent ester and *o*-tolylenediamine), yellow crystals, m. p. 123° ; ethyl 2-hydrindone-3-carboxylate (enolic form), $\text{C}_6\text{H}_4\langle\frac{\text{C}(\text{CO}_2\text{Et})}{\text{CH}_2}\rangle\text{C}\cdot\text{OH}$, colourless crystals, m. p. $68-69^\circ$. H. W.

Ethyl Esters of p - β -Hydroxyethylaminobenzoic Acid and of p -Bis- β -hydroxyethylaminobenzoic Acid. J. ALTWEGG and J. LANDRIVON (U.S. Pat. 1418900).—Ethyl p - β -hydroxyethylamino-

benzoate, colourless crystals, m. p. 63—64°, b. p. 213—214°/4 mm., is obtained by distillation under reduced pressure after heating a mixture of equimolecular proportions of ethyl *p*-aminobenzoate and ethylene oxide at 50° for several hours. *Ethyl p-bis-β-hydroxy-ethylaminobenzoate*, white lamellæ, m. p. 94°, b. p. 246°/3—4 mm., is similarly obtained from 2 mols. of ethylene oxide with the addition of small quantities of water and alcohol. The compounds are adapted for use as local anæsthetics. CHEMICAL ABSTRACTS.

The Reduction of Substituted Salicylic Acids. HUGO WEIL, MAX TRAUN, and SIGISMOND MARCEL (*Ber.*, 1922, **55**, [B], 2664—2674; cf. A., 1908, i, 800; this vol., i, 139).—Reduction of 2 : 3-, 2 : 5-, and 2 : 4-hydroxymethylbenzoic acids by sodium amalgam in the presence of boric acid and neutral sodium sulphite solution gives the corresponding aldehydes in a yield of about 33%. 5-Chlorosalicylic acid, m. p. 167·5°, prepared from 5-aminosalicylic acid hydrochloride, is similarly reduced to 5-chlorosalicylaldehyde, m. p. 99·5° (yield 20%); 5-bromosalicylic acid gives 5-bromosalicylaldehyde, m. p. 104—105° (yield 12·5%), and 3 : 5-dibromosalicylic acid yields 3 : 5-dibromosalicylaldehyde, m. p. 85° (yield 5%). Quinol- and pyrogallol-carboxylic acids cannot be reduced in this manner, whereas resorcylic acid gives resorcyaldehyde, large, yellow crystals, m. p. 134—135°. 5-Aminosalicylic acid hydrochloride, prepared by the reduction of 5-nitrosalicylic acid with zinc dust and dilute hydrochloric acid, suffers loss of the amino-group when reduced and appears to be converted into *hexahydrosalicylaldehyde*, which cannot be isolated. With phenylhydrazine, it gives a very unstable compound, straw-yellow leaflets, m. p. 151° (which is examined more fully in the form of its more stable *hydrochloride*, a crystalline substance, m. p. 137°); it appears to be an osazone-like substance formed presumably owing to the presence of a hydroxyl group in the ortho-position to the aldehydic group on the reduced nucleus. Stable, oxygen-free derivatives of the aldehyde are obtained with *p*-bromo- and *p*-nitro-phenylhydrazines, but neither compound appears to be perfectly homogeneous.

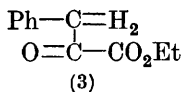
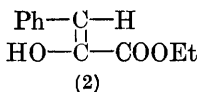
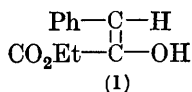
[With SIGISMOND MARCEL.]—Further examination of the reduction of 5-aminosalicylic acid has shown that 5-aminosalicylaldehyde (see later) may be produced in yield which may amount to 16%. For its isolation, the reduction is effected in the usual manner and the solution is boiled under a reflux condenser with sulphuric acid until the sulphur dioxide is removed. The solution is treated with sodium acetate until it is no longer acid towards Congo-red, and preserved during twenty-four hours in an atmosphere of carbon dioxide. 5-Aminosalicylaldehyde separates as a red precipitate which is precipitated by phenylhydrazine as the compound $C_{19}H_{24}N_4$, almost colourless, unstable crystals, m. p. 155°; the corresponding *di-p-bromophenylhydrazone* forms almost colourless crystals, m. p. 204°. The residual solution after the separation of 5-aminosalicylaldehyde is continuously extracted with ether, whereby pimelaldehyde, $[CH_2]_5(CHO)_2$ (Braun and Danziger, A.,

1913, i, 243) [identified as the *disemicarbazone*, a colourless, crystalline powder, m. p. 244° (decomp.)], is obtained.

For comparative purposes, 5-aminosalicylaldehyde is prepared in the following manner. Salicylaldehyde is dissolved in dilute aqueous sodium hydroxide solution and mixed with a diazotised solution of sulphanilic acid, when 5-*benzeneazosalicylaldehyde-4'-sulphonic acid* is produced. This is dissolved in water and reduced at 60—70° by hydrogen sulphide in the presence of sodium carbonate; 5-aminosalicylaldehyde separates completely in the course of two or three days. It is analysed in the form of its red *hydrochloride*, $C_7H_7O_2N.HCl$. It is further characterised by conversion into its *phenylhydrazone* [which exists in two modifications, m. p. 263° (decomp.), and pale yellow flocks, m. p. 164—165° (decomp.), respectively], and *semicarbazone*, m. p. above 300° (decomp.).

H. W.

Ethyl Phenylpyruvate. H. GAULT and R. WEICK (*Bull. Soc. chim.*, 1922, [iv], 31, 867—897; cf. Bougault and Hemmerlé, A., 1915, i, 78).—A third isomeride of ethyl phenylpyruvate was obtained as a white solid by the action of a solution of sodium acetate or copper acetate for forty-eight hours at 0° on the liquid isomeride previously described. The three forms— α , white needles, m. p. 52°; β , mobile, yellow liquid, b. p. 152°/15 mm., and γ , white solid, m. p. 79°—were studied with regard to their mutual transformations, and it was found that the α - and γ -esters are converted into the β -form by slow distillation under reduced pressure, whilst treatment with a saturated solution of sodium carbonate transforms both β - and γ -esters into the α -form. Treatment with acetate (see above) changes the β - into the γ -isomeride, but no direct transformation from α to γ was effected. An examination of the three substances with the view of determining their constitutions leads to the conclusion that, in addition to the keto-enolic isomerism, the enolic form exhibits stereoisomerism and the formulæ assigned are



(1) and (2) represent the α - and β -esters, the γ -ester being of the ketonic type.

H. J. E.

The Solubility of the Aldehydobenzoic Acids. NEVIL VINCENT SIDGWICK and HERBERT CLAYTON (T., 1922, 121, 2263—2267).

Cinnamoylformic Acids. GUSTAV HELLER, HILDE LAUTH, and ARNOLD BUCHWALDT (*Ber.*, 1922, 55, [B], 2679).—*m*- and *p*-Nitrocinnamoylformic acids have been described by Ciusa (A., 1919, i, 402). They were, however, obtained by condensation in an alkaline medium, whereas the authors (this vol., i, 348) worked in acid solution, in which the different ability of the three nitro-aldehydes to undergo condensation is manifest.

H. W.

The Friedel-Crafts' Reaction with Phthalic Anhydride.

T. C. McMULLEN (*J. Amer. Chem. Soc.*, 1922, **44**, 2055—2060; cf. Heller, A., 1908, i, 994; 1912, i, 357; McMullen, this vol., i, 140; Stephens, this vol., i, 141; Rubidge and Qua, A., 1914, i, 539; Lawrence and Oddy, this vol., i, 453).—Phthalic anhydride and aluminium chloride dissolve in benzene to form a clear solution from which a viscous precipitate separates subsequently with the evolution of hydrogen chloride. The precipitate yields *o*-benzoylbenzoic acid when hydrolysed.

The clear solution of phthalic anhydride and aluminium chloride in benzene is transformed when heated with naphthalene into a mixture of benzoylbenzoic acid (60%), naphthoylbenzoic acid (35%), and phenylnaphthylphthalide (5%). If the "clear solution" is treated with ether, a heavy, pale brown liquid is precipitated which yields exclusively *o*-benzoylbenzoic acid on treatment with dilute hydrochloric acid and does not give naphthoylbenzoic acid when heated with naphthalene. The "insoluble intermediate compound," which appears to have the composition $C_{14}H_9O_3Al_2Cl_5$, is prepared conveniently by slowly heating aluminium chloride, benzene, and phthalic anhydride to 50°; it is transformed by acetic anhydride and toluene into a little benzoylbenzoic acid and much phenyl-*p*-tolylphthalide, m. p. 106°, by acetic anhydride and naphthalene into a mixture of phenyl- β -naphthylphthalide, m. p. 153—154°, and phenyl- α -naphthylphthalide, m. p. 227—228°, and by anthracene into a mixture of *o*-benzoylbenzoic acid and two substances, yellowish-white crystals, m. p. 171—173°, and brownish-white crystals, m. p. 280—283°, which are probably phenylanthrylphthalides, but could not be identified more completely (a non-crystalline gum is also produced in considerable quantity). The intermediate compound from toluene reacts slowly with benzene and acetic anhydride, yielding *p*-toluoylbenzoic acid together with a relatively small amount of phenyl-*p*-tolylphthalide. The intermediate compound from naphthalene reacts sluggishly under similar conditions, but it is not possible to separate any phthalide from the viscous product of the reaction.

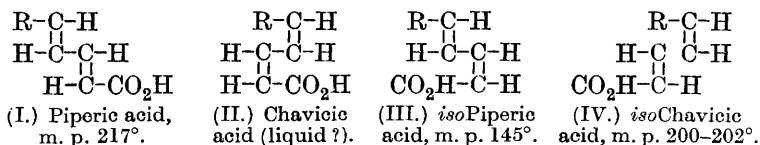
α -Naphthoylbenzoic acid, m. p. 176°, is prepared according to the method of Heller and Schülke (A., 1908, i, 994); considerable amounts of β -naphthoylbenzoic acid (cf. Pickles and Weizman, P., 1904, **20**, 201), needles, m. p. 165°, are simultaneously produced. The α -acid is converted by acetic anhydride into the corresponding *acetyl* compound, m. p. 141°, which is transformed by benzene and aluminium chloride into phenyl- α -naphthylphthalide (see above). Similarly, the *acetyl* derivative of β -naphthoylbenzoic acid, m. p. 140°, is converted into phenyl- β -naphthylphthalide.

Phenyl- α -naphthylphthalide is reduced by zinc dust in the presence of potassium hydroxide solution to 2-phenyl- α -naphthylmethylbenzoic acid, m. p. 189°, the *potassium*, *silver*, and *barium* salts of which are described. The latter salt is transformed when heated with barium hydroxide into diphenyl- α -naphthylmethane, m. p. 152° (cf. Acree, A., 1904, i, 315). Similarly, phenyl- β -naph-

thylphthalide is reduced to *phenyl-2-β-naphthylmethylbenzoic acid*, m. p. 150° (m. p. 76—77° when containing benzene of crystallisation); the *silver* salt was analysed. The *barium* salt is converted by barium hydroxide at about 225° into *diphenyl-β-naphthylmethane*, m. p. 73—74°.

H. W.

Natural and Artificial Pepper-substances. II. The Chavicine of Pepper-resin, the Primarily Active Constituent of Black Pepper. ERWIN OTT and FRITZ EICHLER [with OTTO LÜDEMANN and HEINRICH HEIMANN] (*Ber.*, 1922, **55**, [B], 2653—2663; cf. Ott and Zimmermann, this vol., i, 137).—The active constituent of black pepper has been isolated previously by Buchheim, who designated it chavicine and, in an incompletely purified material, identified the presence of piperidine and a resin acid, chavivic acid, which was not further identified. Re-examination of purified pepper-resin has shown that it very closely resembles piperine, and has established its nature as a piperidide. It is hydrolysed by alkali hydroxide with extreme difficulty, and the acid which is formed differs so widely from chavivic acid in its properties that the conclusion is drawn that it has suffered isomerisation during the change. In its general behaviour, the new *isochavivic* acid is very closely allied to piperic acid, from which it differs somewhat in colour and melting point, but is mainly distinguished by its completely amorphous nature. For the four acids of this series, the possible formulæ are shown in the scheme, in which R represents the piperonyl radicle :



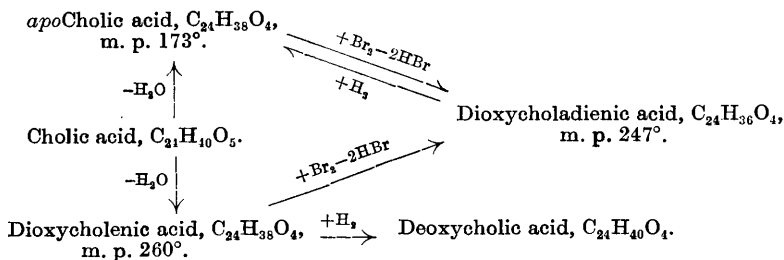
The allocation of formula I to piperic acid is justified by a review of the literature on this compound; the syntheses of *isopiperic* acid is recorded in the present communication, and its method of preparation leaves no doubt as to its configuration. The high melting point and general resemblance of *isochavivic* to piperic acid prove it to be a *trans*-acid, thus leaving formula II for chavivic acid.

Finely divided *Piper nigrum Singapore* is extracted with boiling rectified spirit and the solvent removed from the extract, leaving a solid, sticky residue which is extracted with ether until the solution is no longer coloured. The residue consists essentially of piperine. The ethereal solution is agitated with potassium hydroxide (10%) and washed with water; after removal of the ether, the residue is subjected to a very protracted distillation with steam to remove essential oils. The non-volatile portion is repeatedly treated with ether, and the solutions are cooled, thus causing the separation of piperine. The ethereal solution is evaporated, the residue extracted with light petroleum, and the undissolved matter decolorised by animal charcoal in alcoholic solution, after

complete removal of the solvent, whereby pepper-resin is obtained as a dark brown, transparent, very viscous mass; the material thus isolated is not quite homogeneous since in addition to chavicine it contains not inconsiderable amounts of wax and possibly also of chlorophyll. The hydrolysis of pepper-resin with alcoholic sodium hydroxide solution leads to the formation of piperidine and *isochavicine acid*, a yellow, amorphous substance, m. p. 200—202°. It is readily reduced by hydrogen in alcoholic solution and in the presence of palladised animal charcoal to tetrahydropiperic acid.

[With HEINRICH HEIMANN.]—*isoPiperic acid*, microscopic crystals, m. p. 145°, is prepared in poor yield by heating piperonylenemalonic acid at about 190° in the presence of quinoline. H. W.

Unsaturated Bile Acids. III. The Relationships of *apocholic Acid*, *Dioxycholenic Acid* [m. p. 260°], and *Cholic Acid* to *Deoxycholic Acid*. F. BOEDECKER and H. VOLK (*Ber.*, 1922, 55, [B], 2302—2309; cf. A., 1920, i, 848; 1921, i, 865).—Further investigation of the unsaturated bile acids has shown that they are inter-related as indicated in the scheme :



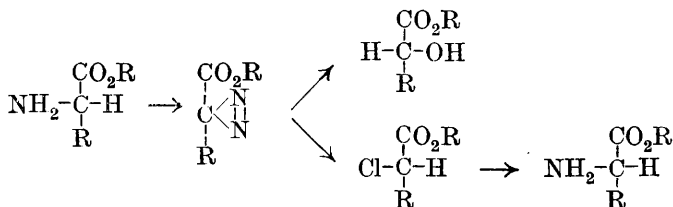
Dioxycholadienic acid, short rods, m. p. 245—247° (slight decomp.), $[\alpha]_D^{25} +20.3^\circ$ in absolute ethyl alcoholic solution, is prepared by the gradual addition of bromine to a solution of the additive compound of *apocholic* and glacial acetic acids in methyl alcohol at -10° and subsequent treatment of the product with water; it is obtained in somewhat better yield and by an analogous process from *dioxycholenic acid*, m. p. 260°. Its *alkali* salts are soluble in water. The *magnesium* and *barium* salts are obtained as oily precipitates which become crystalline when warmed. The *silver* salt crystallises in small, slender needles. The *methyl* ester, prepared by means of diazomethane, has m. p. 85° after softening at 79°. *Dioxycholadienic acid* absorbs one molecular proportion of hydrogen in glacial acetic acid in the presence of palladium black, the product formed appearing to be identical with *apocholic acid* as judged from the similarity of the acids themselves, their additive compounds with glacial acetic acid, xylene, and camphor, respectively, and their methyl esters; a divergence is noted, however, in the specific rotations, the additive compounds of glacial acetic acid, and the reduction products of *dioxycholadienic acid* from *apocholic* and *dioxycholenic acids* having $[\alpha]_D^{25} +55.9^\circ$ and $[\alpha]_D^{25} +52.04^\circ$ in alcoholic solution, whereas *apocholic acid* has $[\alpha]_D^{25} +45.35^\circ$ under similar conditions. The *dioxycholadienic*

acid prepared from this acid by addition of bromine and subsequent elimination of hydrogen bromide is identical with that prepared from *apocholic* acid except as regards specific rotation.

Dioxycholenic acid, m. p. 260° , is reduced by hydrogen in glacial acetic acid solution in the presence of palladium black to deoxycholic acid.

H. W.

Ethyl Benzylidenechitosamate and Ethyl Diazobenzylideneglucuronate (Mannonate). P. A. LEVENE (*J. Biol. Chem.*, 1922, **53**, 449—461).—When the diazo-group in ethyl diazobenzylideneglucosamate (A., 1915, i, 786) is hydrolysed or replaced by hydrogen chloride or bromide, a single substance, and not a pair of epimerides, results in each case. In the former process, however, the direction of the rotation of the product is opposite to that of chitosamic acid, whereas it is the same in the products from the two latter processes. Further, conversion of the chloro-derivative into chitosamic acid (α -aminomannonic acid) takes place without change in the direction of the rotation and without the formation of epimerides. Assuming that, in these compounds, the configuration of the α -carbon atom determines the sign of the rotation of the acid, it appears that chitosamic acid undergoes the Walden inversion when deaminised through the diazo-compound (as it does when directly deaminised), whilst the diazo-compound can be reconverted through the chloro-derivative into the amino-acid without inversion. This is shown in the following scheme :



Ethyl benzylidenechitosamate [glucosamate] hydrochloride has m. p. 200° (uncorr.) and $[\alpha]_D^{20} -30^{\circ}$. By treatment with sodium hydroxide it is converted partly into *ethyl benzylidenechitosamate*, $\text{C}_{15}\text{H}_{21}\text{O}_6\text{N}$, m. p. 120° (corr.), $[\alpha]_D^{20} -50^{\circ}$ (in methyl alcoholic solution), and partly into *benzylidenechitosamic acid*, $\text{C}_{13}\text{H}_{17}\text{O}_6\text{N}$, m. p. 230° (uncorr.), $[\alpha]_D^{20} -28^{\circ}$ in aqueous solution. When boiled in acetone solution, ethyl benzylidenechitosamate yields *ethyl benzylideneacetonechitosamate*, $\text{C}_{18}\text{H}_{25}\text{O}_6\text{N}$, m. p. 128° , $[\alpha]_D^{20} -70^{\circ}$, which is readily reconverted into the hydrochloride of the former substance by treatment with ethereal hydrogen chloride in methyl alcoholic solution. Ethyl diazobenzylideneglucosamate has $[\alpha]_D^{20} -50^{\circ}$, and when hydrolysed yields different products according to the conditions. When the reaction is carried out in organic solvents containing only a small proportion of water, ethyl $\alpha\beta$ -anhydroglucuronate is apparently produced, for the product yields mesotartaric acid on oxidation with nitric acid. Hydrolysis with dilute acetic acid, however, appears to yield ethyl gluconate or ethyl $\alpha\delta$ -anhydroglucuronate, since in this case either saccharic or

anhydrosaccharic acid is formed on oxidation. Treatment of the diazo-compound with hydrobromic acid in ethereal solution gives *ethyl β-bromobenzylidenemannonate*, $C_{15}H_{19}O_6Br$, m. p. 119° (corr.), $[\alpha]_D^{20} -33^\circ$, which is converted by treatment with ammonia into either *ethyl benzylidene-αβ-anhydromannonate*, $C_{15}H_{18}O_6$, $[\alpha]_D^{20} -73.3^\circ$, or the corresponding *amide*, $C_{13}H_{15}O_5N$, m. p. 230° , $[\alpha]_D^{20} +65^\circ$ according to the conditions. Reduction of the last-mentioned ester with hydrogen in the presence of colloidal palladium gives *ethyl benzylidenedeoxygluconate* (mannonate), $C_{15}H_{20}O_6$, m. p. 126° (corr.), $[\alpha]_D^{20} -26^\circ$. *Ethyl α-chlorobenzylidenegluconate*, $C_{15}H_{19}O_6Cl$, m. p. 127° , $[\alpha]_D^{20} -20^\circ$, and the corresponding *amide*, $C_{13}H_{16}O_5NCl$, m. p. 197° (corr.), $[\alpha]_D^{20} -23^\circ$, have also been prepared; the former is converted into chitosamic acid by treatment with ammonia and subsequent hydrolysis.

E. S.

Benzaldehyde-Copper and the Heterogeneous Rate of Formation of this Substance. AUGUST L. BERNOULLI and FRITZ SCHAAF (*Helv. Chim. Acta*, 1922, **5**, 721—731).—When a dilute solution of benzaldehyde in a solvent such as toluene, *m*-xylene, benzene, chlorobenzene, ethyl acetate, etc., is in contact with metallic copper, the metal dissolves forming an intense green solution. The rate of solution depends on the solvent, the benzaldehyde concentration, the temperature, and the surface area of copper exposed. The “specific solution velocity,” v (the weight of copper dissolved per minute divided by the square root of the surface area of the copper in $cm.^2$), is a constant for a given solvent at a given concentration and temperature. The values of v for a series of different solvents at similar concentrations of benzaldehyde follow the same order as the value of the fluidity of the solvent. With toluene as solvent, the maximum rate of solution is reached with 16% benzaldehyde, when $v \times 10^7 = 254.2$ at 50° , whilst in benzene the maximum, $v \times 10^7 = 92.54$, is at a benzaldehyde concentration of 14% by volume. The most favourable concentration appears to be determined by the fluidity of the solution. In a 10% solution of benzaldehyde in toluene the value of $v \times 10^7$ increases from 21.4 at 25° to 758.8 at 105° . Pure benzaldehyde has no solvent action. Of substituted benzaldehydes, *p*-tolualdehyde and *p*-chlorobenzaldehyde behave similarly to benzaldehyde in toluene solution, whilst *p*-nitrobenzaldehyde has no solvent action on copper. The copper compound of benzaldehyde crystallises from toluene solution in green crystals having the composition $(C_6H_5 \cdot CHO)_2Cu$. The crystals are remarkably stable, being unattacked by water, alkalis, or dilute hydrochloric acid. With dilute nitric acid, benzoic acid and copper nitrate are formed. The crystals are also formed when benzylidene chloride is heated with copper in presence of a little sodium carbonate solution. The constitution of the substance is at present uncertain. Cupric oxide and sulphide also dissolve in benzaldehyde and toluene, forming a green solution. Of other metals, lead behaves in the same way as copper, forming a yellowish-brown solution, zinc gives a greenish-brown, silver a brownish-black, magnesium a

yellowish-brown, and cobalt a brown solution. Nickel, iron, and aluminium do not dissolve.

E. H. R.

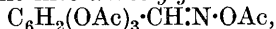
Gallaldehyde and its Derivatives. KARL W. ROSENMUND and E. PFANNKUCH (*Ber.*, 1922, 55, [B], 2357—2372).—The synthetic preparation of pure gallaldehyde has been achieved, and a number of its derivatives have been prepared. Considerable experimental difficulties are encountered owing to the sensitiveness of the aldehyde towards chemical reagents and to the physical characteristics of its derivatives. Attempts to circumvent these drawbacks by using the acylated aldehydes were prevented by the lack of activity of these substances.

Triacetyl-gallaldehyde, m. p. 107—108°, is prepared in good yield by the catalytic reduction of triacetyl-galloyl chloride according to the method of Rosenmund and Zetzsche (*A.*, 1918, i, 300), the purity of the materials being a very essential condition for success. The entrance of the acetyl groups inhibits almost completely the activity of the aldehyde complex; the only derivative obtainable is the *p*-nitrophenylhydrazone, yellow, rhombic plates or long needles, m. p. 207—208° (slight decomp.) when rapidly heated. It is hydrolysed by a boiling alcoholic solution of potassium acetate to gallaldehyde. Tribenzoyl-gallaldehyde, from gallaldehyde and benzoyl chloride by the Schotten-Baumann method, could only be obtained as a viscous, yellowish-brown mass which is identified as the *p*-nitrophenylhydrazone, indistinct, yellow crystals, m. p. 232—233° (decomp.) when placed in a bath pre-heated to 200°.

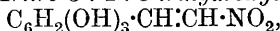
According to previous investigators, gallaldehyde is a stronger acid than acetic acid. This is not confirmed by observations on the electrical conductivity of its aqueous solutions, but the substance appears to be twice as strongly acid as pyrogallol.

Triacetyl-gallaldehyde diacetate, $C_6H_2(OAc)_3 \cdot CH(OAc)_2$, leaflets, m. p. 166°, is prepared by the action of acetic anhydride on gallaldehyde in the presence of pyridine.

Gallaldoxime, $C_6H_2(OH)_3 \cdot CH:N \cdot OH \cdot H_2O$, crystallises in rectangular plates, decomp. (anhydrous), 195—200° after darkening at about 160°. It is converted by cautious treatment with acetic anhydride and pyridine into triacetyl-gallaldoxime acetate,



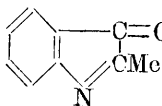
m. p. 126—127°. ω -Nitro-3 : 4 : 5-trihydroxystyrene,



reddish-yellow needles, decomp. 180—185° after incipient decomposition at about 160°, is prepared by the action of nitromethane on gallaldehyde in the presence of methylamine, and is transformed by acetic anhydride and pyridine into ω -nitro-3 : 4 : 5-triacetoxystyrene, colourless needles, m. p. 183° after previous darkening (ω -nitro-*p*-acetoxystyrene, long, pale yellow needles, m. p. 163°, and ω -nitro-3 : 4-diacetoxystyrene, pale yellow needles, m. p. 127°, are prepared similarly). Reduction of gallaldoxime by hydrogen in the presence of palladised barium sulphate gives mainly digallylamine, $NH \cdot [CH_2 \cdot C_6H_2(OH)_3]_2$, which could not be isolated in the pure condition; the corresponding hydrochloride, m. p. 208—210°,

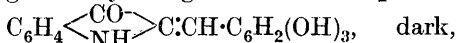
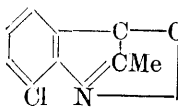
and *picrate*, long, yellow needles, incipient decomp. $150\text{--}153^\circ$, are described. Triacetyl-gallaldoxime acetate, on the other hand, is reduced under similar conditions to triacetyl-gallylamine, which is isolated in the form of its *hydrochloride*, needles, m. p. $196\text{--}197^\circ$ (decomp.). The latter is hydrolysed by dilute aqueous hydrochloric acid to *gallylamine hydrochloride*, m. p. $225\text{--}226^\circ$ (decomp.), from which, however, free gallylamine could not be isolated.

Gallaldehyde reacts with methylketol in the presence of a saturated solution of hydrogen chloride in alcohol to form 3 : 4 : 5-*trihydroxyphenyl-2'-methyl-3'-indolydenemethane* (annexed formula), the *hydrochloride* of which forms yellowish-red needles,



decomp. about 170° after

darkening at 140° . The salt is converted into the corresponding *dye* (annexed formula) by chloranil. When condensed with indoxylie acid, gallaldehyde gives the *compound*,



brownish-red leaflets, m. p. $110\text{--}115^\circ$ (decomp.) when rapidly heated.

Triacetyl-gallaldehyde is not reduced by hydrogen in the presence of palladium or spongy platinum; under similar conditions, gallaldehyde readily absorbs hydrogen, giving a more or less brown, amorphous mass which could not be purified, and, as judged from the molecular weight of its *acetate*, a pale yellow, amorphous powder, m. p. about $183\text{--}185^\circ$, is formed by the association of at least six molecules of the simple aldehyde.

Gallaldehydecyanohydrin, brownish-yellow, crystalline nodules, decomp. about $150\text{--}160^\circ$ when very rapidly heated, is prepared by the addition of anhydrous hydrocyanic acid and a drop of concentrated potassium cyanide solution to gallaldehyde covered with alcohol. It is converted by acetic anhydride and pyridine into *tetra-acetyl-gallaldehydecyanohydrin*, $\text{C}_6\text{H}_2(\text{OAc})_3 \cdot \text{CH}(\text{OAc}) \cdot \text{CN}$, colourless crystals, m. p. 135° .

Triacetylprotocatechualdehydecyanohydrin,
 $\text{C}_6\text{H}_3(\text{OAc})_2 \cdot \text{CH}(\text{OAc}) \cdot \text{CN}$,

has m. p. 112° .

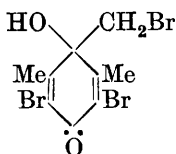
H. W.

2-Hydroxy-4 : 6-dimethylbenzaldehyde, Hemellitenol, and *iso-ψ*-Cumenol. K. VON AUWERS and K. SAURWEIN (*Ber.*, 1922, **55**, [B], 2372—2389).—In continuation of their investigations on the oxidation of meta-substituted *o*-aminophenols (Auwers, Borsche, and Weller, A., 1921, i, 571), the authors have prepared hemellitenol [3 : 4 : 5-trimethylphenol] and *iso-ψ*-cumenol [3 : 5 : 6-trimethylphenol]. Since these compounds have been difficultly accessible previously and consequently but little examined, they have been subjected to examination in several different directions.

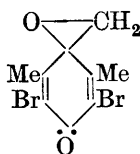
The initial material is *s.m*-xylenol which is converted by hydrocyanic acid and aluminium chloride according to Gattermann's method into a mixture of 2-hydroxy-4 : 6-dimethylbenzaldehyde

and 4-hydroxy-2 : 6-dimethylbenzaldehyde. The production of the *o*-hydroxyaldehyde appears to be contrary to Gattermann's rule, but is possibly attributable to the presence of moisture, since, on one occasion, the accidental presence of a relatively large quantity of water increased the yield of the substance from 8—12% to about 25%. In agreement with the observations of Steinich (A., 1916, i, 36), 2-hydroxy-4 : 6-dimethylbenzaldehyde has m. p. 48—49°. Its *semicarbazone*, a colourless powder, m. p. about 240°, according to the rate of heating; *phenylhydrazone*, colourless, lustrous needles, m. p. 126·5—127°; *anil*, yellow, silky needles, m. p. 88·5—89°; *oxime*, slender needles, m. p. 125—126°, and *methyl ether*, long, slender, colourless needles, m. p. 48—49°, are described. The oxidation of the aldehyde to the corresponding acid could not be effected, whereas its methyl ether is slowly transformed by potassium permanganate in the presence of sodium hydroxide into 2-methoxy-4 : 6-dimethylbenzoic acid, colourless, lustrous platelets, m. p. 167·5—168°. 2-Acetoxy-4 : 6-dimethylbenzonitrile, colourless needles, m. p. 49—50°, is prepared by the action of sodium acetate and acetic anhydride on the oxime of the hydroxyaldehyde; it is hydrolysed by alcoholic potassium hydroxide to 2-hydroxy-4 : 6-dimethylbenzonitrile, slender, colourless needles, m. p. 177—178°. 5-Benzeneazo-2-hydroxy-4 : 6-dimethylbenzaldehyde, matt, brown leaflets, m. p. 97·5—98° (m. p. 122° was observed on an isolated occasion), is prepared from the aldehyde and benzenediazonium chloride in alkaline solution; its *sodium* salt is sparingly soluble in water.

Hemellitenol [3 : 4 : 5-trimethylphenol], long, colourless needles, m. p. 107°, is prepared in 40% yield by the reduction of 4-hydroxy-2 : 6-dimethylbenzaldehyde by amalgamated zinc and hydrochloric acid according to Clemmensen's process. It is transformed by bromine into 2 : 6-dibromo-3 : 4 : 5-trimethylphenol, small leaflets, m. p. 142·5—143°, which is converted with difficulty by bromine at 100° into 2 : 6-dibromo-3 : 5-dimethyl-4-bromomethylphenol, m. p. 138·5—139·5°. The action of hot, concentrated nitric acid on the phenol bromide leads to the production of the *ψ*-quinol

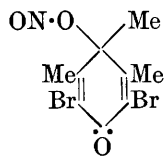


(I.)

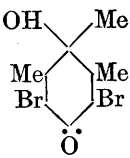


(II.)

monoclinic leaflets, m. p. 108°, which is transformed by boiling glacial acetic acid into dibromohemellityl-*ψ*-quinol (IV), long, slender, lustrous needles, m. p. 214—215°. Hemellitenol is remarkably stable towards cold concentrated nitric acid, by which it is converted at a higher temperature into *dinitrohemellitylquinol*, m. p. 146—147° (decomp.), which is trans-



(III.)



(IV.)

(annexed formula, I), colourless, matted needles, m. p. 213°, which is converted by sodium hydroxide into the *oxide* (annexed formula, II), leaflets, m. p. indefinite, 156—160° (decomp.). Dibromohemellitenol is converted by cold, concentrated nitric acid into *dibromohemellitylquinol* (III), large

formed by glacial acetic acid at 50° into *dinitrohemellityl- ψ -quinol*, slender, colourless needles, m. p. 213° . Hemellitenol is transformed by an aqueous solution of formaldehyde in the presence of slaked lime at 50° into 3 : 4 : 5-trimethyl-2 : 6-dihydroxymethylphenol, small, colourless needles, m. p. 148° , which when the action is prolonged passes into a substance, m. p. above 360° , which has not been investigated closely; a similar change is observed in the presence of sodium hydroxide. A solution of the dihydroxy-alcohol in glacial acetic acid is converted by hydrogen bromide into 3 : 4 : 5-trimethyl-2 : 6-dibromomethylphenol, short, colourless needles, m. p. 164 – 165° , which could not be reduced to penta-methylphenol by zinc and hydrochloric acid, the dihydroxy-alcohol being obtained. Hemellitenol couples with benzenediazonium chloride in the presence of sodium hydroxide solutions of varying concentrations to yield 6-benzeneazo-3 : 4 : 5-trimethylphenol, slender, brownish-red needles, m. p. 126.5 – 127° .

3 : 5 : 6-Trimethylphenol, m. p. 93 – 94° , is prepared conveniently and in 40% yield by the reduction of 2-hydroxy-4 : 6-dimethylbenzaldehyde with amalgamated zinc and hydrochloric acid. It is converted by concentrated nitric acid in the presence of glacial acetic acid into 2-nitro-3 : 5 : 6-trimethylphenol, pale yellow leaflets, m. p. 78 – 79° . It couples with an equivalent amount of benzenediazonium chloride in the presence of sodium hydroxide to give a mixture of 4-benzeneazo-3 : 5 : 6-trimethylphenol, lustrous, flattened, red needles, m. p. 154.5 – 156.5° , and 2 : 4-bisbenzeneazo-3 : 5 : 6-trimethylphenol, small, brown crystals, m. p. 130.5 – 131.5° ; increasing concentration of alkali hydroxide favours the production of the di-derivative.

H. W.

The Isomerism of the Oximes. X. Cinnam- and Nitrocinnam-aldoximes. OSCAR LISLE BRADY and CLIFFORD DANE THOMAS (T., 1922, **121**, 2098–2110).

The Interaction of Aldehydes or Ketones and Thiocarbamides in the Presence of Acids. II. JOHN TAYLOR (T., 1922, **121**, 2267–2272).

The Friedel-Crafts' Reaction. HEINRICH WIELAND and LUDWIG BETTAG (*Ber.*, 1922, **55**, [B], 2246–2255).—A further examination of the possibility that substitution in the benzene series is preceded by a primary additive process at a double bond, and that the mechanism of reaction is similar in the aromatic and aliphatic series (cf. Wieland and Sakellarios, A., 1920, i, 280; Wieland and Rahn, A., 1921, i, 782). The ability of substances to react with acetyl chloride and similar compounds in the presence of aluminium chloride has usually been ascribed to the presence in them of a mobile hydrogen atom, but indications of the production of a primary additive compound have been recorded by Darzens (A., 1910, i, 856) in the case of acetyl chloride and cyclohexene, and by Böeseken (A., 1913, i, 330) in that of tetrachloroethylene and chloroform. The isolation of the primary chloro-ketone from cyclohexene and acetyl chloride in the pure condition

is now described, and, further, it is shown that this substance is transformed into the unsaturated ketone under the normal conditions of the Friedel-Crafts' reaction. The difference in the behaviour of aliphatic and aromatic compounds during this synthesis is purely qualitative. The highly reactive aliphatic double bond allows addition to occur under conditions such that the primary additive compound is to some extent stable, whereas with the less reactive aromatic double bond addition is only possible in circumstances which cause the additive compound to be unstable. The catalytic function of aluminium chloride is attributed to its ability to weaken the bond between carbon and chlorine, and thus to facilitate the combination of the two addenda.

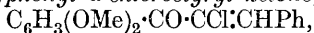
In the case of the synthesis of hydrocarbons according to Friedel and Crafts, it has not been found possible to adduce such definite experimental evidence. The cause lies in the slower velocity of the action of alkyl haloids, and the consequent predominance of the formation of resinous polymerides from the olefines under the influence of aluminium chloride; in addition, the newly-formed alkyl haloids have a marked tendency towards further reaction with the olefine. It has therefore not been possible to cause *n*-propyl chloride to react in the desired manner with ethylene, amylene, or cyclohexene, although it could be shown that products containing chlorine are produced, thus probably pointing to a primary additive change.

Aluminium chloride is added gradually to a solution of cyclohexene and acetyl chloride in carbon disulphide at -18° ; reaction takes place almost without evolution of hydrogen chloride and results in the formation of 2-chlorocyclohexyl methyl ketone and tetrahydroacetophenone, which cannot be separated from one another by fractional distillation. The unsaturated compound is decomposed by oxidising the mixture with potassium permanganate in the presence of acetone, and the chloro-ketone is isolated as a pale yellow, somewhat unstable liquid, b. p. $60-63^{\circ}$ (slight decomp.)/1 mm., through the semicarbazone, colourless leaflets, m. p. 163° (decomp.). It is transformed by further treatment with aluminium chloride in the presence of carbon disulphide into tetrahydroacetophenone. In a similar manner, cyclohexene and benzoyl chloride yield 2-chlorocyclohexyl phenyl ketone, a pale yellow, viscous liquid, b. p. $120-122^{\circ}$ (slight decomp.)/1 mm., which is further transformed by aluminium chloride and carbon disulphide into tetrahydrobenzophenone [semicarbazone, pale yellow prisms, m. p. 213° (decomp.)], in minimal yield (the direct preparation of tetrahydrobenzophenone from cyclohexene and benzoyl chloride also gives very poor yields). Acetyl chloride and β -methyl- Δ^2 -butene give chloro-sec.isoamyl methyl ketone, $\text{CMe}_2\text{Cl}\cdot\text{CHMe}\cdot\text{COMe}$, a pale yellow, very unstable liquid with an odour resembling that of camphor. H. W.

The Condensation of α -Halogeno-ketones with Aldehydes.
K. HUGO BAUER and FRITZ WERNER (*Ber.*, 1922, **55**, [B], 2494—2500).—It has been shown by Widman (*A.*, 1916, i, 406) that ω -bromo- or ω -chloro-acetophenone condenses with benzaldehyde

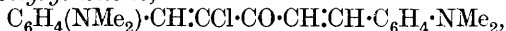
in the presence of sodium ethoxide with the formation of benzoyl-phenylethylene oxide. Condensation of these substances can also be brought about by hydrogen chloride or hydrogen bromide in the presence of glacial acetic acid; in all cases, $\alpha\beta$ -unsaturated α -halogeno-ketones appear to be the initial products, but the change may proceed further and result, by addition of hydrogen haloid, in the formation of $\alpha\beta$ -dihalogeno-ketones.

Phenyl styryl ketone dibromide, $\text{COPh}\cdot\text{CHBr}\cdot\text{CHBrPh}$, small, colourless crystals, m. p. $158-159^\circ$, is prepared by the action of hydrogen bromide on a solution of ω -bromoacetophenone and benzaldehyde in glacial acetic acid at the atmospheric temperature. Phenyl 3':4'-methylenedioxystyryl ketone dibromide, colourless leaflets, m. p. 152° , is obtained similarly from ω -bromoacetophenone and piperonal or by the addition of bromine to methylenedioxy-chalkone in carbon tetrachloride solution. 3:4-Dimethoxyphenyl styryl ketone dichloride, colourless crystals, m. p. $133-135^\circ$, is derived from ω -chloroacetoveratrone and benzaldehyde in the presence of hydrogen chloride, whereas the ketone and *p*-dimethylaminobenzaldehyde give 3:4-dimethoxyphenyl α -chloro-4'-dimethylaminostyryl ketone, intensely yellow leaflets, m. p. $129-130^\circ$. α -Bromoacetoveratrone, benzaldehyde, and hydrogen chloride form 3:4-dimethoxyphenyl α -chlorostyryl ketone,

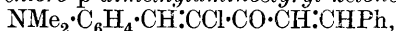


large, transparent cubes, m. p. $108-109^\circ$.

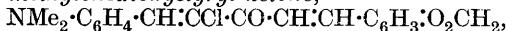
p-Dimethylaminobenzaldehyde condenses with chloroacetone in glacial acetic acid solution in the presence of hydrogen chloride to give a mixture of α -chloro-4-dimethylaminostyryl methyl ketone, $\text{NMe}_2\cdot\text{C}_6\text{H}_4\cdot\text{CH}\cdot\text{CCl}\cdot\text{COMe}$, yellow leaflets, m. p. 115° (semicarbazone, a colourless, crystalline powder, m. p. $202-203^\circ$, phenylhydrazone, slender, pale yellow needles, m. p. $206-208^\circ$) and α -chloro-di-*p*-dimethylaminostyryl ketone,



m. p. 225° ; the latter may also be obtained by the action of sodium hydroxide on chloro-*p*-dimethylaminostyryl methyl ketone and *p*-dimethylaminobenzaldehyde dissolved in alcohol. Chloro-*p*-dimethylaminostyryl methyl ketone and benzaldehyde condense in aqueous alcoholic solution in the presence of sodium hydroxide to form styryl α -chloro-*p*-dimethylaminostyryl ketone,



dark, tile-red leaflets, m. p. $150-151^\circ$. α -Chloro- α -*p*-dimethylaminostyryl methylenedioxystyryl ketone,



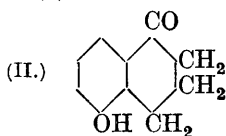
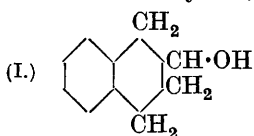
orange-coloured leaflets, m. p. 186.5° , is obtained similarly from chloro-*p*-dimethylaminostyryl methyl ketone and piperonal.

H. W.

Position of the Double Linking in Piperitone. II. A. R. PENFOLD (*Perf. Essent. Oil Rec.*, 1922, 13, 322-323; cf. this vol., i, 259).—From the products of the action of neutral potassium permanganate on piperitone, in addition to diosphenol, the following acids were isolated: α -hydroxy- α -methyl- α -isopropyladipic

acid, m. p. 143-5°, γ -acetyl- α -isopropylbutyric acid, identified by means of its semicarbazone, m. p. 158°, and α -isopropylglutaric acid, m. p. 94-95°. The formation of these substances confirms the constitution of piperitone as Δ^1 -menthen-3-one, previously put forward. In view of the conflicting statements as to the m. p. of the oxime and semicarbazones of piperitone, these derivatives were again prepared; the oxime melts at 117-118° as stated by Simonsen (T., 1921, **119**, 1644), the m. p. given by Read and Smith (T., 1921, **119**, 779) being incorrect. Three semicarbazones were isolated, dl- α -semicarbazone, m. p. 225-226°, dl- β -semicarbazone, m. p. 175-176°, and the racemic semicarbazone, m. p. 188-189°. The best method for preparing piperitone hydroxylamino-oxime is to dissolve equal weights of the ketone, hydroxylamine hydrochloride, and potassium hydroxide in aqueous alcohol, and after keeping for some hours the whole solidifies to a crystalline mass of the oxime in almost quantitative yield. G. F. M.

Preparation of α -Keto-substituted Hydrogenated Naphthalenes. GEORG SCHROETER and TETRALIN G. M. B. H. (D.R.-P. 352720; from *Chem. Zentr.*, 1922, iv, 158).— α -Naphthol and iso- or hetero-nuclear substituted α -naphthols, melted or in solution, are treated with hydrogen under pressure in amount corresponding with less than two molecules, in the presence of metallic catalysts. For example, colourless α -naphthol is mixed with tetrahydronaphthalene and a catalyst consisting of reduced nickel deposited on kieselguhr, and treated with hydrogen at 120-180° under a pressure of 10-20 atmospheres. After absorption of hydrogen corresponding with 1.5 molecules, the reaction is ended and the filtered liquid fractionated under reduced pressure. At 14 mm. pressure, the tetrahydronaphthalene distils over at 100°. α -Keto-tetrahydronaphthalene has b. p. 134-135°/14 mm. The distillate at higher temperatures is a mixture of α -naphthol and ar-tetrahydro- α -naphthol, which is again submitted to reduction. β -Naphthol similarly treated gives no ketone, but a little ar-tetrahydro- β -naphthol and ac-tetrahydro- β -naphthol (I).



1:5-Dihydroxynaphthalene yields similarly, by reduction, 1-keto-5-hydroxytetrahydronaphthalene (II), colourless crystals, m. p. 156-157°. It forms a semicarbazone, m. p. 224°; an acetyl derivative; a methyl ether, and a phenylurethane. 1:8-Dihydroxynaphthalene gives, by reduction, 1-keto-8-hydroxytetrahydronaphthalene. 1-Hydroxy-5-acetylaminonaphthalene gives 1-keto-5-acetylaminotetrahydronaphthalene. G. W. R.

The Mechanism of the Formation of Benzoylbenzoin by Treatment of Benzoylmandelonitrile with an Alcoholic Solution of Sodium Ethoxide. HERBERT GREENE and ROBERT ROBINSON (T., 1922, **121**, 2182-2196).

Dioximes. III. G. PONZIO (*Gazzetta*, 1922, **52**, ii, 145—160; cf. this vol., i, 627).—By the action of hydroxylamine on oximinobenzoylacetone, Ceresole (A., 1884, 1167) obtained a compound, m. p. 178°, which he regarded as one of the two possible α -dioximes of phenylmethyltriketone and is described in Beilstein's "Handbuch" (Vol. III, p. 270) as butyltrionephenidioxime, $\text{NOH}:\text{CMe}:\text{CBz}:\text{NOH}$. The author finds, however, that the product of this reaction is a mixture of two benzoylmethylglyoximes which are not mere spacial isomerides. The action of nitrogen tetroxide on one of these oximes (termed the α -compound) yields α -oximino- β - ψ -nitrole- γ -ketophenylbutane, so that the two oximino-groups in this oxime are not equivalent to one another; with the second isomeride (β), however, nitrogen tetroxide gives a peroxide, furoxan, the two oximino-groups being hence equivalent, since each loses its hydrogen atom. From the chemical behaviour of the two compounds the conclusion is drawn that the α -form is an equilibrated mixture of the two tautomeric modifications, β -nitroso- α -oximino- γ -ketophenylbutane, $\text{NOH}:\text{CMe}:\text{CHBz}:\text{NO}$, and $\alpha\beta$ -dioximino- γ -ketophenylbutane, $\text{NOH}:\text{CMe}:\text{CBz}:\text{NOH}$, and that the β -form consists of the latter tautomeride alone. The β -form may be regarded as the stable form of the $\alpha\beta$ -dioxime of phenylmethyltriketone, since it results when the α -form is heated with various solvents or with a base. It is evident, therefore, that not all α -dioximes behave as if they contain the group $-\text{C}(\text{NOH})\cdot\text{C}(\text{NOH})-$, and that the isomerism of the different forms of an α -dioxime may depend on the possession of different structures by one of the two oximino-groups.

Since oximinobenzoylacetone contains an oximino-group in the same position as one of those in the α -isomeride of benzoylmethylglyoxime, it may be represented by the equilibrium $\text{NOH}:\text{CAcBz} \rightleftharpoons \text{NO}\cdot\text{CHAcBz}$, the hydrogen atom of the oximino-group being mobile. On this basis, the formation, by the action of hydroxylamine, of two glyoximes, one an equilibrated mixture, is readily explainable.

Like all α -dioximes regarded by Tschugaev as *syn*-forms, $\alpha\beta$ -dioximino- γ -ketophenylbutane acts in aqueous solution on nickel, copper, cobalt, and iron (this vol., i, 17), forming with the first three metals complex salts derived from two molecules of the glyoxime by replacement of two atoms of hydrogen, one from each molecule, by an atom of the metal. The equilibrated mixture termed the α -modification does not attack these metals, but it yields a cupric salt derived from one molecule of the dioxime by replacement of two hydrogen atoms by an atom of copper. The only other known salt of this type is that obtained by Atack (T., 1913, **103**, 1317) from γ -benzildioxime and given by him the formula $\text{Ni} \begin{smallmatrix} \text{NO}:\text{CPh} \\ \text{NO}:\text{CPh} \end{smallmatrix}$, but the author regards as more probable for his

copper salt the structure $\text{O} \begin{smallmatrix} \text{N}=\text{CMe} \\ | \\ \text{Cu}\cdot\text{CBz}\cdot\text{NO} \end{smallmatrix}$.

The action of hydroxylamine on the α - and β -forms of benzoylmethylglyoxime yields two distinct phenylmethyltriketone trioximes; isomerism in the trioximes has not previously been

observed, and no explanation is now offered of the existence of these two modifications. Both the trioximes act, in aqueous solution, on nickel, forming two different complex salts, each derived from two molecules of trioxime by replacement of two oximinic hydrogen atoms by an atom of the bivalent metal. Neither of the two dioximes and neither of the two trioximes is obtainable directly from phenylmethyltriketone.

α-Benzoylmethylglyoxime, $\text{NOH}:\text{CMe}:\text{CBz}:\text{NOH}$, crystallises in white, rectangular laminae, often united to pennate aggregates, m. p. 135° (decomp., turning green), and dissolves in alkali hydroxide or ammonia solution without coloration, and in cold, concentrated sulphuric acid, giving an orange-brown coloration turned deep brown by addition of phenol. In aqueous solution at $80\text{--}90^\circ$, it readily loses water, yielding benzoylmethylfurazan, $\text{O} < \begin{smallmatrix} \text{N}:\text{CMe} \\ \text{N}:\text{CBz} \end{smallmatrix}$. Its copper salt, $\text{C}_{10}\text{H}_8\text{O}_3\text{N}_2\text{Cu}$, forms a somewhat

unstable, olive-green powder, and when heated slowly has m. p. about 195° (decomp.), whilst when heated rapidly it explodes at about 185° . The diacetyl compound, $\text{OAc}:\text{N}:\text{CMe}:\text{CBz}:\text{NOAc}$, crystallises in flattened, white prisms, m. p. 113° , and yields benzoylmethylfurazan when heated with water.

α-Oximino-β-ψ-nitrole-γ-ketophenylbutane, $\text{NOH}:\text{CMe}:\text{CBz}:\text{N}_2\text{O}_3$, forms white prisms, m. p. 111° (decomp.), and dissolves in concentrated sulphuric acid to a colourless solution which becomes emerald green when heated gently with phenol. Even dilute solutions of bases readily hydrolyse it, rupture of the carbon atom chain taking place between the ψ-nitrole and carbonyl groups; thus, with ammonia solution, it yields aminomethylglyoxime, $\text{NOH}:\text{CMe}:\text{C}(\text{NH}_2):\text{NOH}$, and benzamide.

β-Benzoylmethylglyoxime, $\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_2$, crystallises in white laminae or prisms, m. p. $193\text{--}194^\circ$ (decomp.), and dissolves in alkali hydroxide or ammonia solution with a golden-yellow coloration and in concentrated sulphuric acid without coloration. The nickel salt, $(\text{C}_{10}\text{H}_9\text{O}_3\text{N}_2)_2\text{Ni}$, crystallises in flat, blood-red needles, m. p. 258° , decomposing at 260° , and is readily decomposed by mineral acids, but is stable towards acetic acid. The copper salt, $(\text{C}_{10}\text{H}_9\text{O}_3\text{N}_2)_2\text{Cu}$, forms a pale coffee-coloured, compact, microcrystalline powder, m. p. 201° (decomp.). The cobaltous salt is obtained as a brownish-violet, microcrystalline powder, which remains unmelted at 300° and readily forms colloidal solutions with various organic solvents and possibly also with alkali hydroxide solutions. The diacetyl derivative, $\text{OAc}:\text{N}:\text{CMe}:\text{CBz}:\text{NOAc}$, forms white prisms, m. p. 68° , and the dibenzoyl derivative, $\text{C}_{24}\text{H}_{18}\text{O}_5\text{N}_2$, white prisms, m. p. $220\text{--}221^\circ$ (decomp.).

Benzoylmethylfurozan, $\text{CH}_3\cdot\text{C}_2\text{N}_2\text{O}_2\cdot\text{COPh}$, crystallises in long, white needles, m. p. 70° , and is converted into the β-benzoylmethylglyoxime when reduced by means of zinc dust and acetic acid.

Phenylmethyltriketone-α-trioxime, $\text{NOH}:\text{CMe}:\text{C}(\text{NOH})\cdot\text{CPh}:\text{NOH}$, forms white, prismatic needles, m. p. 204° (decomp.), and dissolves without coloration in alkali hydroxide or ammonia solution or

concentrated sulphuric acid. The *nickel* salt, $(C_{10}H_{10}O_3N_3)_2Ni$, an orange-yellow powder, decomposes unmelted at about 220° . The *triacetyl* derivative, $C_{16}H_{17}O_6N_3$, forms prisms, m. p. 111° .

Phenylmethyltriketone- β -trioxime forms white needles, m. p. 196° (decomp.), if heated rapidly, or a somewhat lower temperature if heated slowly. The *nickel* salt crystallises in lustrous, orange-red laminae, m. p. 236° (decomp.), or a lower temperature if heated slowly. The *triacetyl* compound forms large prisms, m. p. 107° .

The *cobaltous* salt of *dimethylglyoxime*, $(NOH:CMc:CMc:N\cdot O)_2Co$, obtained by the action of aqueous dimethylglyoxime solution on strips of cobalt, forms a coffee-coloured powder with a violet lustre, and begins to undergo change, without melting, at about 200° .

T. H. P.

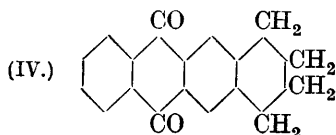
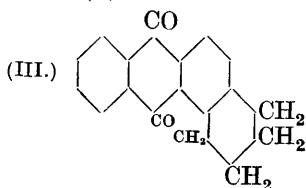
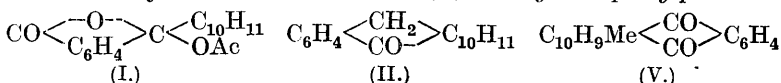
The Labile Nature of the Halogen Atom in Organic Compounds. V. The Action of Hydrazine on the Halogen Derivatives of some Esters and substituted *cyclo*Hexanes.

EDMUND LANGLEY HIRST and ALEXANDER KILLEN MACBETH (T., 1922, 121, 2169—2178).

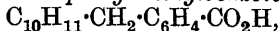
Preparation of Anthraquinone. CHARLES R. DOWNS (U.S. Pat. 1374721; from *Chem. Zentr.*, 1922, ii, 1055).—For the preparation of anthraquinone, anthracene in the state of vapour is passed, mixed with a gas containing oxygen, over vanadium oxide as catalyst, at about 375° . The temperature is maintained constant by introduction of mercury vapour into the reaction zone.

G. W. R.

Preparation of Hydrogenated Anthraquinones. TETRALIN G. M. B. H. (D.R.-P. 346673; from *Chem. Zentr.*, 1922, ii, 1079—1080).—Tetrahydronaphthalene or substituted tetrahydronaphthalenes are treated when gently heated with anhydrides of aromatic *o*-dicarboxylic acids, especially phthalic anhydride, in the presence of aluminium chloride and with addition of benzene and similar diluents. The γ -ketocarboxylic acids formed are changed into hydrogenated anthraquinones by condensing reagents, particularly fuming sulphuric acid. Tetrahydronaphthalene and phthalic anhydride give, at 60 — 70° in the presence of benzene and aluminium chloride, β -*tetrahydronaphthoyl-o-benzoic acid*; it forms crystals, m. p. 153 — 155° . It gives with acetic anhydride a crystalline *acetyl-lactone* (I), m. p. 135° . The *methyl* ester has m. p. 73 — 74° . By reduction of the acid, β -*tetrahydronaphthylphthalide*



(II) and a *o*- β -*tetrahydronaphthylmethylbenzoic acid*,



are obtained. By the action of fuming sulphuric acid on *tetrahydronaphthoyl-o*-benzoic acid, a mixture of α -*tetrahydronaphthanthraquinone* (III), m. p. 135°, and β -*tetrahydronaphthanthraquinone* (IV), m. p. 211°, is obtained. The compounds are separated by fractional crystallisation. Both form yellow needles. They yield corresponding anthraquinols on reduction and readily give substituted derivatives with halogens, sulphuric acid, and nitric acid. 2-Methyl*tetrahydronaphthalene*, obtained by the catalytic hydrogenation of 2-methylnaphthalene, is a colourless oil, b. p. 219—220°. It gives, on condensation with phthalic anhydride, 3-methyl-2-*tetrahydronaphthoyl-o*-benzoic acid, $\text{C}_{10}\text{H}_{10}\text{Me}\cdot\text{CO}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$, needles, m. p. 160°. By the action of fuming sulphuric acid, 3-methyl*tetrahydro-2:1-naphthanthraquinone* (V) is obtained; it forms yellow needles, m. p. 119°. G. W. R.

Tetranitroanthrachryson. GUSTAV HELLER and PAUL LINDNER (*Ber.*, 1922, 55, [B], 2674—2679; cf. Heller and Skraup, A., 1913, i, 1207).—A more extended examination of the substance (cf. D.R.-P. 73605).

Tetranitroanthrachryson [2:4:6:8-tetranitro-1:3:5:7-tetrahydroxyanthraquinone] is prepared by the action of nitric acid (*d* 1.26) and concentrated sulphuric acid on a solution of anthrachryson in the latter acid; it crystallises in orange-coloured leaflets, which darken at 200° and explode at about 285°. It is remarkable that the entrance of the four nitro-groups occurs simultaneously so that unchanged original material remains if too little nitric acid is used. Its salts with the alkalis and ammonia are described. It is readily attacked by boiling aqueous ammonia, but the change appears to be so complicated that it is impossible to isolate a uniform material. Reduction does not occur smoothly, since the replacement of an amino-group by hydrogen occurs simultaneously with the complete conversion of the nitro- into the amino-group. The action of stannous chloride appears to lead to the formation of (?) *triaminoanthrachryson*, a black substance which is unchanged below 295°, whereas sodium hyposulphite gives the sodium salt of a triaminoanthrachryson, $\text{C}_{14}\text{H}_7\text{O}_6\text{N}_3\text{Na}_4$. Tetranitroanthrachryson reacts readily with aromatic bases in alkaline solution, giving dark dyes from which a homogeneous material could not be isolated.

The probability of the participation of the hydroxy-groups in the reactions just described has led to the preparation of 1:3:5:7-tetramethoxyanthraquinone, slender, yellow needles, m. p. 238°, by the action of methyl sulphate on anthrachryson in alkaline solution. The ether is transformed readily into 2:4:6:8-tetranitro-1:3:5:7-tetramethoxyanthraquinone, slender yellow needles, m. p. 258° (decomp.) after darkening at 220°, which is not affected by alcoholic potassium hydroxide solution. It is readily converted by aniline and aqueous sodium carbonate solution into 2:6-dinitro-4:8-dianilino-1:3:5:7-tetramethoxyanthraquinone, slender, dark

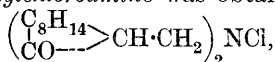
blue needles, which gradually decompose without melting above 300°. H. W.

The Carbamides of Anthraquinone. M. BATTEGAY and J. BERNHARDT (*Chim. et Ind.*, 1922, **8**, 305—306).—The three isomeric dianthraquinonylcarbamides, 1:1', 1:2', and 2:2' show a gradation in properties in which the 1:2'-isomeride approaches more nearly to the 2:2'- than to the 1:1'-isomeride. The 1:2'- and the 2:2'-isomerides may be used as vat dyes by preliminary reduction in alkaline medium, but under similar conditions the 1:1'-isomeride very rapidly undergoes hydrolysis unless the temperature is kept below 18—20°, and then the carbamide is so little soluble as to render it useless as a dye. If, however, two hydroxy-, methoxy-, or benzoylamino-groups are substituted in it in positions para to the carbamide-group, then the products are no longer sensitive to destruction during reduction, and may be used as dyes. W. G.

The Urethanes of Anthraquinone. M. BATTEGAY and J. BERNHARDT (*Chim. et Ind.*, 1922, **8**, 307).—The group $\text{NH}\cdot\text{CO}_2\text{Et}$ exercises a greater auxochrome effect when introduced into the anthraquinone molecule than does the group $\text{NH}\cdot\text{COPh}$, both in the 1- and the 2-derivatives. The 1-urethanes, like the 1:1'-carbamides, are very sensitive to alkaline reduction, the product undergoing immediate hydrolysis. The introduction of a nitro-, a hydroxy-, a methoxy-, or a benzoylamino-group into the para-position in the urethanes does not check this hydrolysis as it did that of the carbamide (cf. previous abstract). W. G.

Reduction Products of Hydroxymethylenecamphor. V. COUPLING of Hydroxylamine with Methylenecamphor. H. RUPE and H. SCHMID (*Helv. Chim. Acta*, 1922, **5**, 778—785).—Reaction between hydroxylamine and methylenecamphor in alcohol takes place between one molecule of the former and two molecules of the latter with formation of *di-camphomethylhydroxylamine* ($\text{C}_8\text{H}_{14}\text{CO} \rightarrow \text{CH}\cdot\text{CH}_2$)₂N·OH, crystallising in colourless leaflets, m. p. 109·5—110·5°; its *hydrochloride* crystallises in fine, white leaflets decomposed by hot water; the neutral *oxalate* $(\text{C}_{22}\text{H}_{35}\text{O}_3\text{N})_2\cdot\text{C}_2\text{H}_2\text{O}_4$ forms white, microscopic leaflets, m. p. 169—169·5°. By stannous chloride and hydrochloric acid, the hydroxylamine derivative is reduced to di-camphomethylamine (cf. Rupe and Kussmaul, A., 1920, i, 622). Di-camphomethylhydroxylamine is readily oxidised by cupric acetate in alcoholic solution, but no definite products could be isolated. Better results were obtained with ferric chloride, and from the product was isolated a *compound*, $\text{C}_{11}\text{H}_{17}\text{O}_2\text{N}$, white, microscopic crystals, sintering at 195°, m. p. 208—210°. Molecular-weight determinations by cryoscopic methods indicate a molecular weight from twice to four times that represented by the formula. Hydroxymethylenecamphor was expected to be present in the oxidation product, but was not found.

By the action of thionyl chloride on di-camphomethylhydroxylamine, *di-camphomethylchloroamine* was obtained,

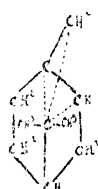


a white, crystalline powder, becoming yellow at 135°, m. p. 202—250° (decomp.). E. H. R.

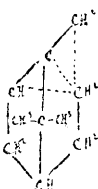
The Formulæ of Dicyclic Terpenes. GEORGES DUPONT (*Bull. Soc. chim.*, 1922, [iv], **31**, 897—909).—A theoretical discussion which the author maintains that the usually accepted formulæ for dicyclic terpenes are based mainly on the products obtained on oxidation with permanganate and do not accord with other reactions of the hydrocarbons. The suggestion is made that their properties are more consistently expressed by the introduction of free valencies or oscillating bonds into the formulæ: each terpene is dealt with from this point of view. On the above hypothesis, the formulæ—which are compared with the Bacyer benzene formula—should be written :



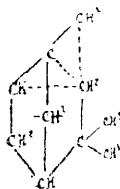
Pinene.



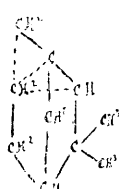
Nopinene.



Camphene.



Fenchene I.



Fenchene II.



Sabinene.

H. J. E.

Melting Point of Commercial Terpin. JOSÉ MARÍA CLAVERA (*Anal. Fís. Quím.*, 1922, **20**, 243—246).—The melting point of freshly crystallised terpin hydrate, determined with rapid heating is 118.2°, which is higher than the previously accepted value. The anhydrous terpin has m. p. 104.7°. The melting point of terpin hydrate is considerably changed by small variations in the amount of water of crystallisation present. A curve is given showing the initial and final melting points of a series of mixtures varying from anhydrous terpin to terpin hydrate. The melting point is an untrustworthy criterion of purity. G. W. R.

The Preparation of Bornylene. HANS MEERWEIN and JACOB JOUSSEN (*Ber.*, 1922, **55**, [B], 2529—2533).—The elimination of hydrogen chloride from bornyl chloride has previously led to the isolation of camphene instead of the expected bornylene. Since a high temperature (about 230°) is necessary for this process, its course can readily be explained in the light of the work of Meerwein and van Emster (this vol., ii, 751) according to which the loss of the acid is preceded by the transformation of bornyl chloride into *isobornyl* chloride and camphene hydrochloride. The successful preparation of bornylene depends therefore on the discovery of conditions under which this change does not occur or only takes

place very slowly. Preliminary work in this direction has been carried out with the more reactive *isobornyl* chloride, since the transformations occur in the same manner with either substance and the results obtained with *isobornyl* chloride are directly applicable to *bornyl* chloride.

The rate of decomposition (velocity of transformation) of *isobornyl* chloride by alkali alkoxides is found to diminish with increasing concentration of the alkali, with diminution of the water content of the mixture and with increase in the molecular weight of the alcohol employed. By applying these conditions to *bornyl* chloride, it is found possible to prepare nearly pure *bornylene* (solidifying temperature $108-107^{\circ}$ instead of 113° as recorded in the literature for the pure material) by the action of a 10% solution of potassium amyloxide in amyl alcohol at 230° . The high temperature necessary for the change is remarkable. Under similar conditions, *bornyl* bromide loses hydrogen bromide almost instantaneously at about 190° with the formation of an equally pure *bornylene*.
H. W.

The Constitution of the Terpene Present in the Essential Oil from *Andropogon Jwarancusa*, Jones. JOHN LIONEL SIMONSEN (T., 1922, **121**, 2292—2299).

The Composition of the Essential Oil of Turpentine. M. VÈZES and G. DUPONT (*Chim. et Ind.*, 1922, **8**, 318—319).—Physical constants of the essential oil of Aleppo turpentine (from *Pinus halepensis*) are given, and it is shown that the composition of the fresh oil depends only on the variety of the conifer which has produced it.
W. G.

Essential Oils from *Myrica Gale*, L. M. SCHOOPS (*J. Pharm. Belg.*, 1921, **3**, 769—773; from *Chem. Zentr.*, 1922, **i**, 1340—1341).—The following data were obtained for two essential oils obtained from *Myrica Gale*, L., by steam distillation. The first oil, separating directly from the distillate, has d^{15}_{20} 0.9068; $[\alpha]_D -8^{\circ} 46'$; n^{25}_D 1.4820; acid number, 1.5; saponification number, 17.8; ester number, 16.3; acetyl number, 39.2; combined alcohols ($C_{10}H_{18}O$), 4.4%; ester (linalyl acetate), 5.6%; free alcohols ($C_{10}H_{18}O$), 11.106%; iodine number, 168.84. The second oil, extracted from the aqueous distillate, has d^{15}_{20} 0.8956; $[\alpha]_D -5^{\circ} 9'$; n^{25}_D 1.4656; acid number, 1.8; saponification number, 18.19; ester number, 16.39; acetyl number, 36.4; combined alcohols ($C_{10}H_{18}O$), 4.5%; ester (linalyl acetate), 5.73%; free alcohols ($C_{10}H_{18}O$), 7.06%; iodine number, 56.70.
G. W. R.

Isoprene and Caoutchouc. V. The Hydrogenation of Caoutchouc and its Constitution. H. STAUDINGER and J. FRITSCHI (*Helv. Chim. Acta*, 1922, **5**, 785—806).—The hydrogenation of caoutchouc and the decomposition products of the hydrogenation product were studied to get more evidence regarding the constitution of the substance. According to one theory, the caoutchouc molecule is composed of aggregations of comparatively
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simple molecules, ring compounds formed from two or more isoprene molecules, held together by partial valencies. According to an opposing theory, the whole colloid molecule is formed by polymerisation of isoprene molecules in chains of such size that the unsaturated character of the molecule is lost. The experimental evidence cannot be reconciled with the first theory, but favours the second. The hydrogenation of caoutchouc was accomplished by heating it with hydrogen in presence of platinum at 270° and about 100 atm. Nickel did not promote complete hydrogenation under these conditions. The hydrogenated product has the composition $(C_5H_{10})_x$ and retains the completely colloidal character of caoutchouc. It is stable towards bromine, but in sunlight becomes slowly brominated, the brominated product still having the properties of caoutchouc. Were the first theory of the constitution of caoutchouc correct, hydrogenation would be expected to destroy the partial or residual valencies holding the large molecules together, giving products of simpler constitution. Hydrocaoutchouc can be regarded as a high molecular paraffin hydrocarbon with so large a molecule that, in effect, $C_nH_{2n+2} = C_nH_{2n}$.

The distillation of caoutchouc and of the hydrogenated material in a high vacuum was studied. The decomposition of caoutchouc is less far-reaching in a vacuum than under normal pressure. At a pressure of 0.1 to 0.3 mm., distillation takes place between 275° and 320° . The products obtained were isoprene, about 3.1%, dipentene, about 8.8%, a hydrocarbon, $C_{15}H_{24}$, about 4.4%, and small quantities of hydrocarbons, $C_{20}H_{32}$ and $C_{25}H_{40}$. The compound $C_{15}H_{24}$ contains two double bonds, and is probably a hydrogenaphthalene derivative, whilst $C_{20}H_{32}$ contains three double bonds and probably has a long aliphatic side chain. The depolymerisation of caoutchouc to form these products can be understood if the molecule contains a long chain of the form

$\cdot CH_2 \cdot CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot CMe \cdot CH \cdot CH_2 \cdot CH_2 \cdot$ etc., which may split into sections containing 4, 8, 12, etc., carbon atoms in a chain, the sections then forming closed ring systems. When hydrocaoutchouc is distilled, a higher decomposition temperature, $350-390^{\circ}$, is necessary. The decomposition products have the composition $(C_5H_{10})_x$ and in each case have only one double bond. The lowest product found was a pentene, b. p. $30-40^{\circ}$, which appeared to be β -methyl- Δ^4 -butylene since it gave methylethylketone on oxidation. From the higher boiling fractions were isolated, among others, a hydrocarbon, $C_{15}H_{20}$, and, as the highest boiling constituent, $C_{50}H_{100}$. The presence of such substances as the last in the decomposition products shows that hydrocaoutchouc itself must have an exceedingly high molecular weight. It cannot be vulcanised, and this fact supports the view that the vulcanisation of caoutchouc is a truly chemical process depending on the ethylene linkings and not an adsorption phenomenon. It is shown that in latex the caoutchouc is present in its normal molecular form and not in the form of simpler molecules which in the coagulation process combine to form caoutchouc.

E. H. R.

Betulin. HEINRICH SCHULZE and KURT PIEROH (*Ber.*, 1922, 55, [B], 2332—2346).—An extended investigation of betulin indicates that it is a member of a particular class of phytosterol-like dihydroxy-alcohols. The substance crystallises with one or one-half molecular proportion of ethyl alcohol which is very firmly retained and has been overlooked by previous workers. The empirical formula is $C_{32}H_{52}O_2$ or $C_{33}H_{54}O_2$. When heated with formic acid, it undergoes a remarkable transformation into *allobetulin* which appears to be closely related to β -amyrin and lupeol, whereas betulin shows great similarity to onocol isolated from *Ononios spinosa*.

Birch bark is extracted with aqueous ammonia and the dry residue is exhaustively treated with boiling alcohol. The bulk of the alcohol is removed and the residue is treated with an excess of lead acetate and evaporated to dryness. The dry mass is extracted with boiling benzene from which crude betulin separates. It is purified by crystallisation from alcohol from which it separates when the solutions are rapidly cooled in slender needles resembling asbestos (+2EtOH) or on slow cooling in coarse, lustrous, rhombic needles (+EtOH). It has m. p. 251—252°, $[\alpha]_D^{25} +19.96^\circ$ in pyridine solution. The diacetate crystallises in coarse, rhombic prisms, m. p. 216—217°, $[\alpha]_D^{25} +21.99^\circ$ in chloroform solution. Betulin is converted by phthalic anhydride into *betulin hydrogen phthalate*, slender, matted needles (from aqueous alcohol, +EtOH or +2H₂O), m. p. (not quite definite) 180—182° (decomp.), $[\alpha]_D^{25} +24.48^\circ$ when dissolved in chloroform; the corresponding *silver* salt is described.

Betulin is transformed by boiling formic acid (90—95%) into *allobetulin formate*, coarse, rhombic needles, m. p. 311—312°, $[\alpha]_D^{25} +51.08^\circ$ in chloroform solution, which is hydrolysed by alcoholic potassium hydroxide solution to *allobetulin*, monoclinic or triclinic platelets, m. p. 260—261°, $[\alpha]_D^{25} +48.25^\circ$ when dissolved in chloroform. Analysis of the substance and its derivatives are in agreement with the formula, $C_{32}H_{52}O_2$ or $C_{33}H_{54}O_2$, for *allobetulin* which appears to be isomeric with betulin. It contains only one hydroxyl group, the second oxygen atom being in ethereal linking. The conversion of betulin into *allobetulin* is not a specific action of formic acid, but appears to depend on the hydrogen-ion concentration; it can also be effected by acetic acid containing a little concentrated hydrochloric acid. In comparison with betulin, *allobetulin* and its derivatives are characterised by their higher melting point, smaller solubility, higher specific rotation, and greater stability towards chemical reagents. *allobetulin acetate* crystallises in hexagonal platelets belonging to the rhombic system; it has m. p. 277—278°, $[\alpha]_D^{25} +54.16^\circ$ in chloroform solution. *allobetulin* is converted by benzoic anhydride at 170° into *allobetulin benzoate*, apparently monoclinic platelets, m. p. 275—276°, $[\alpha]_D^{25} +70.26^\circ$, when dissolved in chloroform, by phthalic anhydride into *allobetulin hydrogen phthalate*, slender needles, m. p. 260—261° (slight gas evolution), $[\alpha]_D^{25} +58.20^\circ$ in chloroform (the *silver* salt is described), and by molten succinic anhydride into *allobetulin hydrogen succinate*, slender, lustrous leaflets, m. p. 265—266°, $[\alpha]_D^{25} +48.01^\circ$,

when dissolved in chloroform (the *silver* salt was analysed). *allo-Betulin* is oxidised by chromic acid in glacial acetic acid solution to *allobetulone*, colourless, rhombic needles, m. p. 230—231°, $[\alpha]_D^{25} + 84.40^\circ$ in chloroform [*oxime*, leaflets, m. p. 285—290° (decomp.) when rapidly heated, *phenylhydrazone*, pale yellow leaflets, m. p. 223° (decomp.) after softening at 220°]. *alloBetulin* is converted by phosphorus pentachloride in the presence of chloroform into *apoallobetulin*, $C_{32}H_{50}O$ or $C_{33}H_{52}O$, lustrous, rhombic needles, m. p. 198—200°, $[\alpha]_D^{25} + 74.78^\circ$ in chloroform solution. *Oxyallobetulin acetate*, $C_{32}H_{48}O_3Ac$ or $C_{33}H_{50}O_3Ac$, is prepared by the oxidation of *allobetulin acetate* dissolved in glacial acetic acid with chromic acid; it crystallises in leaflets which do not melt below 360°, $[\alpha]_D^{25} + 54.34^\circ$ when dissolved in chloroform. It is hydrolysed by alcoholic potassium hydroxide solution to *oxyallobetulin*, slender, matted needles which sublime before melting.

H. W.

Tannins and Similar Compounds. X. The Tannin of the Native Oak. KARL FREUDENBERG and ERICH VOLLBRECHT (*Ber.*, 1922, 55, [B], 2420—2423).—The tannin of the oak, isolated from the fresh leaves by means of the lead salt, is purified from free ellagic acid and admixed quercetin glucosides by extraction with ethyl acetate in a vacuum. It is accompanied by its own condensation products, from which it is freed by fractional precipitation from its alcoholic solution with ether. It is an amorphous, reddish-yellow material, freely soluble in water, alcohol, or acetone. It is strongly acidic. It has $[\alpha]_D$ about -35° . It contains 23—25% of combined ellagic acid, and about 5% of combined dextrose; the remainder of the molecule is an amorphous acid, termed *quercussic acid*. Warm, dilute mineral acids cause a more ready elimination of dextrose than of ellagic acid, the inactive hydrolytic product containing the residue of a compound of ellagic and quercussic acids. Continued hydrolysis effects the complete removal of ellagic acid. Dilute alkalis remove the whole of the ellagic acid in the cold, without, however, separating the dextrose. It appears, therefore, that oak tannin is a glucoside of quercussic acid which is esterified to a depside with ellagic acid. Acid or alkaline hydrolysis of oak tannin results in the considerable destruction of quercussic acid. Tannase acts very slowly, but gives a uniform product which closely resembles the original material in physical properties, and is optically inactive and not hydrolysed by acid or alkali. Quercussic acid appears to be a bibasic acid of molecular weight about 800.

The degradation of oak tannin by tannase to quercussic acid is too tedious for preparative purposes. It is found, however, that, under definite conditions, *Aspergillus niger* grows on the solutions and thereby completes the degradation without decomposing the quercussic acid. Since, in addition, it is found that the galls of *Quercus pedunculata* contain the same tannin as the leaves, a convenient method of preparing quercussic acid is obtained. Treatment of it with molten potassium hydroxide has not led to the

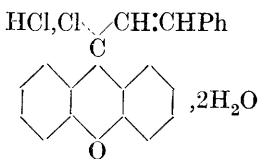
isolation of definite products. Phloroglucinol is not formed; its isolation by earlier workers from oak tannin is probably attributable to the presence of quercetin. H. W.

Constitution of Elsholtzic Acid. YASUHIKO ASAHINA and SATORU KUWADA (*J. Pharm. Soc. Japan*, 1922, No. 485, 565—579; cf. *ibid.*, 1918, No. 431).—For the complete determination of the constitution of elsholtzic acid, 2-methylfuran-3-carboxylic acid was prepared from dichloroethyl ether, acetoacetic ester, and ammonia by Benary's method (A., 1911, i, 319). It was converted into its chloride, brominated, hydrolysed by boiling with water and oxidised by means of silver oxide (Hill and Sawyer, A., 1894, i, 442), and the bromine atom contained in the nucleus removed by warming with ammonium chloride and zinc dust. The furan-2 : 3-dicarboxylic acid so obtained, colourless prisms, m. p. 221°, was proved to be identical with that obtained from elsholtzic acid. The constitution of elsholtzic acid and elsholtzic ketone are therefore, respectively, $\begin{array}{c} \text{CH} \cdot \text{CMe} \\ | \quad \diagup \\ \text{CH} - \text{O} \end{array} > \text{C} \cdot \text{CO}_2\text{H}$ and $\begin{array}{c} \text{CH} \cdot \text{CMe} \\ | \quad \diagup \\ \text{CH} - \text{O} \end{array} > \text{C} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CHMe}_2$.

Methyl furan-2 : 3-dicarboxylate forms white crystals, m. p. 34°; the *monoanilide* crystallises in light yellowish-brown needles, m. p. 169—170°; the *dianilide* was not obtained. The product of the hydrolysis mentioned above was *bromo-2-hydroxymethylfuran-3-carboxylic acid*, fine, yellow needles, m. p. 116° (*monoacetate*, white needles, m. p. 94—95°). From the mother-liquor an *oxime* (impure) was obtained, which was converted into a nitrile, and then into furan-2 : 3-dicarboxylic acid. K. K.

Poly-arylated Vinyl Carbinols and their Derivatives. II. Diarylstyryl Carbinols and the Products of their Transformations. KARL ZIEGLER and CURT OCHS (*Ber.*, 1922, 55, [B], 2257—2277; cf. this vol., i, 151).—The recent publications of Meyer and Schuster (this vol., i, 540) and Skraup and Freundlich (this vol., i, 539) on halochromic phenomena with carbinols has caused the authors to give a further account of their work.

9-Styrylxanthyl chloride hydrochloride (annexed formula) is obtained by treating a solution of 9-styrylxanthenol in benzene with concentrated hydrochloric acid. It forms small, coarse red crystals or golden leaflets which are stable in a closed vessel, but rapidly decompose on exposure to air. Its behaviour when heated varies greatly with the conditions of heating. The corresponding *bromide hydrobromide*, coarse red crystals, is prepared in an analogous manner. The chloride forms an extensive series of double salts with the chlorides of the heavy metals such as zinc chloride, mercuric chloride, ferric chloride, antimony trichloride, stannous chloride, and stannic chloride, of which the *zinc* compound, $\text{C}_{21}\text{H}_{15}\text{OCl}_2 \cdot \text{ZnCl}_2$, long, red needles, decomp. 188° after darkening

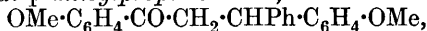


at 100°, and *ferric* compound, $C_{21}H_{15}OCl, FeCl_3$, carmine-red leaflets which gradually melts and decomposes at 160—180° after darkening at 145°, are described in detail. Analogous *salts* are formed from the bromide. The perhaloids, *chloride-perchloride*, *chloride-perbromide*, and *bromide-perbromide*, are characterised by the ease with which they lose the per-halogen, so that they could not be isolated in an analytically pure condition. 9-*Styrylxanthenol*, small, colourless crystals, m. p. 158—159°, is prepared by shaking an ethereal solution of the perchlorate or hydrochloride with sodium hydroxide or sodium carbonate; if traces of acid vapours and elevation of temperature are not scrupulously avoided during removal of the ether, *di-9-styrylxanthyl ether*, a colourless, micro-crystalline powder, m. p. 172°, is obtained. 9-Styrylxanthenyl chloride is converted by cold, absolute ethyl alcohol into 9-*styrylxanthyl ethyl ether*, small cubes or short prisms, m. p. 168—169° after previous darkening. The action of boiling glacial acetic acid on 9-styrylxanthenol, its ethers, or its chloride hydrochloride rapidly leads to the formation of a *substance*, colourless prisms, m. p. 241—242°; analyses of the product are in harmony with the formula, $O\langle C_6H_4 \rangle C:C:CHPh$, but this simple constitution is not in accord with determinations of the molecular weight and with the inability of the product to re-form the perchlorate when treated with perchloric acid; it is probably to be regarded as a polymerised allene derivative. 9-Styrylxanthenyl perchlorate, on the other hand, is converted by boiling glacial acetic acid into a new stable *perchlorate*, dark brownish-red leaflets, decomp. 248°, which is transformed by boiling alcohol into the xanthen derivative, m. p. 241—242° (see above). Attempts to prepare 9-styrylxanthyl by the action of phenyl magnesium bromide on 9-styrylxanthenyl perchlorate did not lead to the desired result. The reaction takes place energetically but without development of a trace of colour. The production of diphenyl cannot be established. The product appears to be 9-*phenyl-9-styrylxanthenol*, $O\langle C_6H_4 \rangle CPh:CH:CHPh$, colourless, microscopic prisms, m. p. 142—143°. (The analogous reaction between 9-phenylxanthenyl perchlorate and magnesium phenyl bromide appears to yield 9-phenylxanthyl.)

Di-p-anisylstyryl carbinol, $(OMe \cdot C_6H_4)_2C(OH) \cdot CH:CHPh$, a voluminous, pale yellow powder which has not been caused to crystallise, is prepared in the same manner as 9-styrylxanthenol (the double *salts* of di-*p*-anisylstyrylmethyl chloride with ferric chloride and antimony trichloride have been prepared). The carbinol appears to be stable towards boiling ethyl alcohol containing a little acid; it is transformed by boiling glacial acetic acid into a *substance*, $(C_{23}H_{20}O_2)_2$, long needles, m. p. 188°, which is probably a polymerised allene derivative.

9-Styryldi- $\beta\beta'$ -naphthaxanthenyl perchlorate (this vol., i, 152) has now been isolated as a stable, coffee-brown powder which darkens at 140°, slowly melts between 140 and 160°, and decomposes at 174°.

γ-Phenyl-α-γ-di-p-anisylpropane-α-one,



colourless crystals, m. p. 89—90°, is prepared by the action of magnesium *p*-anisyl bromide on *p*-anisyl styryl ketone. 2:4:4'-Trimethoxybenzophenone, colourless needles, m. p. 70—71°, is readily obtained from *p*-anisoyl chloride and resorcinyl dimethyl ether by Friedel and Crafts' reaction. 2:2'-Dimethoxybenzhydrol, colourless crystals, m. p. 85—86°, is prepared from salicylaldehyde methyl ether and magnesium *o*-anisyl bromide.

[With G. BREMER and F. THIEL.]—Halochromic salts, particularly perchlorates, can be obtained readily from tetra-arylallyl alcohols if the aryl groups are suitably chosen. Thus, *di-p-anisyl-(ββ-diphenylvinyl)methyl perchlorate*, m. p. 130—131°, is prepared in the same manner as *di-p-anisylstyrylmethyl perchlorate* from ββ-diphenylvinyl bromide and *di-p-anisyl ketone*. Free *diphenyl-di-p-anisylallyl alcohol* is an amorphous substance which appears to lose water with great readiness. The perchlorate is rapidly transformed by pyridine into pyridine perchlorate and *γγ-diphenyl-αα-di-p-anisylallene*, $\text{C}(\text{C}_6\text{H}_4 \cdot \text{OMe})_2 \cdot \text{C} : \text{CPh}_2$, colourless crystals, m. p. 102—103°, which is smoothly converted by perchloric acid into the original perchlorate.

9-ββ-Diphenylvinylxanthyl perchlorate, $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C} \langle \text{CH} : \text{CPh}_2, \text{ClO}_4 \rangle$,

red needles, m. p. 166° (decomp.), is obtained smoothly by the action of ββ-diphenylvinyl bromide and magnesium on xanthone. It is readily hydrolysed to 9-ββ-diphenylvinylidenexanthene,

$\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C} : \text{C} : \text{CPh}_2$, m. p. 205—206°, from which the original

perchlorate is easily re-formed. The allene derivative becomes isomerised when subjected to the protracted action of boiling glacial acetic acid, giving a *product*, $\text{C}_{27}\text{H}_{18}\text{O}$, coarse, colourless cubes, m. p. 173—174°. ββ-Diphenylvinylxanthyl chloride hydrochloride, $\text{C}_{21}\text{H}_{20}\text{OCl}_2$, dark red, very unstable needles, is prepared by passing hydrogen chloride into a solution of 9-ββ-diphenylvinylidenexanthene in benzene to which a little acetyl chloride has been added. 9-ββ-Diphenylvinylxanthyl perchlorate reacts energetically with an ethereal solution of magnesium phenyl bromide, giving an intensely green solution from which colourless

crystals of 9-ββ-diphenylvinylxanthyl, $\text{O} \langle \text{C}_6\text{H}_4 \rangle \text{C} \cdot \text{CH} : \text{CPh}_2$,

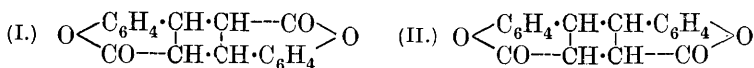
separate. The substance gives a pale yellow solution in cold benzene which becomes dark brown when heated, but returns to its original colour when again cooled. It is converted by air into the corresponding *peroxide*. The original green colour of the ethereal solution cannot at present be explained; it appears, however, to be due to a radicle, since it is discharged by contact with air.

H. W.

Biscoumaric Acids. A. W. K. DE JONG (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, 25, 175—178).—In a recent communication (A., 1918, i, 303), the author has shown that the product

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of the action of light on coumarin is not identical with the hydrodicoumarin of Fittig and Dyson (T., 1887, **51**, 66). The author assumes that the product of illumination is formed from coumarin in the same way as α - and β -truxillic acids are formed from normal cinnamic acid by the production of a tetramethylene ring between the doubly linked carbon atoms of the two molecules. On this basis, four different biscoumarins may be formed, two of which are represented by each of the formulæ I and II.



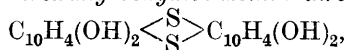
In addition to the biscoumarin of the author and hydrodicoumarin of Fittig and Dyson, a further biscoumarin has been isolated by Ström (A., 1904, i, 505), which, since it is formed from coumaric acid in the same way as α -truxillic acid from α -cinnamic acid, the author, in conformity with the names and structures assigned to the truxillic acids (A., 1918, i, 172), has termed α -biscoumarin, and the acid from which it is derived α -biscoumaric acid. This acid changes into α -biscoumarin at 250° and α -biscoumarin melts with decomposition at 318°. Methylation of α -biscoumaric acid with methyl sulphate gives the dimethyl ester of the dimethyl ether, which crystallises in needles, m. p. 133°, and is sparingly soluble in ether. The dimethyl ether, obtained by boiling the ester with alkali, melts at 261–262° and when heated with acetic anhydride at 210° yields the anhydride of the dimethyl ether of γ -biscoumaric acid, which crystallises in large, bright yellow crystals, m. p. 186–187°. The dimethyl ether melts at 234°. Heating α -biscoumaric acid with potassium hydroxide yields the acid corresponding with β -cocaic acid, m. p. 212°; this acid is named ζ -biscoumaric acid. The biscoumaric acid of the product of illumination of coumarin is termed λ -biscoumaric acid, and yields a dimethyl ester of the dimethyl ether which melts at 112–113°. Heating the dimethyl ether of λ -biscoumaric acid with acetic anhydride at 210° yields a non-crystallisable syrup, which on boiling with alkali yields the dimethyl ether of ϵ -biscoumaric acid, m. p. 203°. This transformation shows that the coumarin rings of the product of illumination are situated on different sides of the tetramethylene ring, and since the two coumarin rings are on different sides of the tetramethylene ring in α -biscoumarin, it follows that λ -biscoumarin has the structure II, and by removing a carboxyl group from one side of the tetramethylene ring to the other, an *o*-dihydroxy- ϵ -truxillic acid is formed. On melting λ -biscoumaric acid with potassium hydroxide, δ -biscoumaric acid is formed, m. p. 157°. J. F. S.

Dibenzothianthrenediquinone and Dinaphthathiophendiquinone. (Conversion of the Dithiin Ring into the Thiophen Ring.) KURT BRASS and LUDWIG KÖHLER (*Ber.*, 1922, **55**, [B], 2543–2568).—An account is given of the more extended examination of dibenzothianthrenediquinone, $C_{10}H_4O_2 \begin{array}{c} \diagup S \\ \diagdown \end{array} C_{10}H_4O_2$ (cf.

Brass and Köhler, A., 1921, i, 435). The most remarkable property of the substance is the readiness with which it is converted into dinaphthathiophendiquinone, $S < \begin{smallmatrix} C_{10}H_4O_2 \\ C_{10}H_4O_2 \end{smallmatrix}$, the dithiin being transformed into the thiophen ring.

The preparation of dibenzothianthreniquinone is most conveniently effected by agitating an aqueous suspension of 2:3-dichloro- α -naphthaquinone (the method of obtaining the latter by chlorination of α -naphthaquinone in glacial acetic acid in the presence of iodine is described in detail) with the calculated quantity of sodium sulphide solution in the absence of air at the atmospheric temperature. Reaction occurs in accordance with the equation $8C_{10}H_4O_2Cl_2 + 12Na_2S + 3H_2O = 2NaSH + Na_2S_2O_3 + 16NaCl + 4C_{10}H_4O_2 < \begin{smallmatrix} S \\ S \end{smallmatrix} > C_{10}H_4(OH) \cdot ONa$. The green *monosodium* salt of the quinhydrone is separated and treated with dilute nitric acid or chromic acid, whereby it is converted into the blue quinhydrone, which is oxidised further in the boiling solution to the quinone. Alternatively, an alkaline suspension of 2:3-dichloro- α -naphthaquinone is treated with hydrogen sulphide; in this case, reduction proceeds to the quinol stage, and the product is then oxidised as just described. The product has m. p. 302° (decomp.) after incipient decomposition at 280° , dinaphthathiophendiquinone being produced. A similar decomposition occurs slowly in the presence of boiling nitrobenzene. 1:14-*Dihydroxydibenzothianthrenquinone*,

$C_{10}H_4O_2 < \begin{smallmatrix} S \\ S \end{smallmatrix} > C_{10}H_4(OH)_2$, is obtained by the action of dilute acid on the green sodium salt described above. It crystallises in dark blue needles which are stable when dry, but readily oxidised to the quinone when moist. In consequence of atmospheric oxidation, it melts at 302° (m. p. of diquinone) when heated in an open capillary tube. Only one of its hydroxyl groups is capable of salt formation (the monosodium salt is described above). Both hydroxyl groups are readily acylated by acetyl or benzoyl chloride in the presence of pyridine, giving, respectively, 5:14-*diacetoxydibenzothianthrenquinone*, dark, olive-green crystals with a red reflex, m. p. (indefinite) 265 — 268° , and 5:14-*dibenzoyloxydibenzothianthrenquinone*, red rodlets or leaflets with a green reflex, m. p. (indefinite) 290° . 5:7:12:14-*Tetrahydroxydibenzothianthren*,



is obtained in colourless crystals by the action of carbon dioxide on a solution of its sodium salt in water; it is decidedly unstable and readily oxidised to the blue quinol. It forms a colourless methyl ether. Its acyl compounds are also colourless; 5:14-*dihydroxy-7:12-diacetoxydibenzothianthren* has m. p. about 262° after previous decomposition, whereas 5:7:12:14-*tetra-acetoxydibenzothianthren* crystallises in needles, m. p. (indefinite) 300 — 340° , and 5:7:12:14-*tetrabenzoyloxydibenzothianthren* forms rhombic plates, m. p. (indefinite) about 360° .

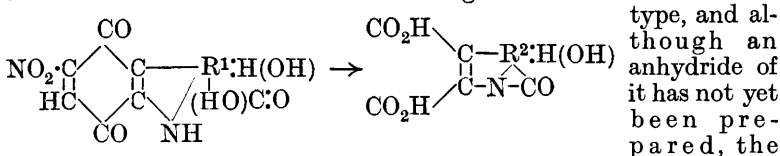
Dibenzothianthreniquinone is quantitatively converted by a

mixture of nitric acid (d 1.52) and water into *dibenzothianthren-diquinone sulphoxide*, $C_{10}H_4O_2 \begin{smallmatrix} S^- \\ \diagup \diagdown \\ SO \end{smallmatrix} C_{10}H_4O_2$, yellow, hygroscopic needles. It is stable at the atmospheric temperature, but with rise in temperature exhibits a marked tendency to lose the sulphoxide sulphur atom and form the thiophen ring. It is reduced by hydrogen bromide to dibenzothianthrendiquinone, in which respect it differs from other sulphoxides. Hydrogen chloride acts similarly but more slowly. Zinc dust and glacial acetic acid or hydrogen iodide and glacial acetic acid convert it into the blue quinhydrone; since dibenzothianthrendiquinone is not formed during the process, it follows that the reduction of the keto-group precedes the loss of oxygen from the sulphonic group. *Dinaphthathiophendiquinone* is most conveniently prepared (with intermediate formation of the sulphoxide) by gradually heating dibenzothianthrendiquinone with fuming nitric acid (d 1.52). It crystallises in very stable, yellow needles, m. p. 278° ; it sublimes at a higher temperature. It is reduced by stannous chloride in the presence of glacial acetic acid to 5:13-*dihydroxydinaphthathiophen*-6:11-quinone, $S \begin{smallmatrix} C_{10}H_4(OH)_2 \\ \diagup \diagdown \\ C_{10}H_4O_2 \end{smallmatrix}$, dark green needles, m. p. (indefinite) about 265° , which yields a *monoacetate*, blue rodlets or plates, m. p. (indefinite) about 290° , and a *diacetate*, pale red needles, m. p. (indefinite) 254° . 5:6:11:13-*Tetrahydroxydinaphthathiophen* is prepared by the reduction of dinaphthathiophendiquinone by hydrogen iodide in hot glacial acetic acid solution; it forms pale green needles which readily undergo oxidation; the corresponding *tetra-acetate* forms pale yellow plates, m. p. (indefinite) 271° (decomp.), whereas the *tetrabenzoate* crystallises in pale yellow, prismatic aggregates, m. p. about 330° (decomp.). H. W.

The Preparation of Histidine from Blood. S. DEMJANOVSKI (*Z. physiol. Chem.*, 1922, **122**, 93—97).—Details are given of a method by which a yield of 90 grams of crude histidine dihydrochloride may be obtained from $8\frac{1}{2}$ litres of defibrinated blood. The hydrolysis is carried out in an autoclave with hydrochloric acid, at $1\frac{1}{2}$ atmospheres pressure. W. O. K.

Strychnos Alkaloids. XXXIII. The Degradation of Cacotheline by Bromine. HERMANN LEUCHS, HANS MILDBRAND, and W. ROBERT LEUCHS (*Ber.*, 1922, **55**, [B], 2403—2415).—The degradation of cacotheline by bromine has been investigated previously by Hanssen (A., 1887, 505), who obtained a product which, on account of its behaviour towards sodium hydroxide, and of the formation of a mono-silver salt, be regarded as a mono-carboxylic acid. To this substance the empirical formula, $C_{19}H_{22}O_6N_2 \cdot 2H_2O$, is now assigned and the presence in it of two carboxyl groups is established, one of which is neutralised in the compound by the basic nitrogen atom. Four of the oxygen atoms are thus present in the carboxyl groups, whilst the fifth and sixth atoms are present in the acid amide and secondary alcoholic groups

of brucine, since the presence of aldehydic or ketonic groups could not be detected. One of the nitrogen atoms is present in the acid amide group, whilst the second is a basic, tertiary atom which enables the formation of quaternary ammonium salts and betaines. The probable course of the oxidative process is indicated by the annexed scheme. The new acid belongs thus to the maleic acid



presence of the double bond is established by the ready addition of two, but not more, atomic proportions of hydrogen. A remarkable point in the scheme outlined above is that the residue R^2 must contain two more atoms of hydrogen than R^1 , and that these can only be added as the result of an unusual reaction. In this connexion, it is recalled that cacotheline undergoes autoredaction in boiling aqueous solutions with production of a violet dihydro-derivative.

An aqueous solution of cacotheline, treated with hydrobromic acid and six atomic proportions of bromine, is heated on the water-bath and finally boiled until a clear solution is obtained, from which a yellow substance separates on cooling; this is purified by repeated treatment of its boiling aqueous solution with animal charcoal and precipitation with hydrobromic acid, whereby the hydrobromide, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2\cdot\text{HBr}\cdot 2\text{H}_2\text{O}$, is obtained in colourless prisms or rectangular leaflets. The latter can be converted into the acid, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2$, by boiling with lead oxide or silver carbonate in poor yield; decomposition is effected preferably with *N*-alkali hydroxide in boiling solution and evaporation of the solution until copious crystallisation has occurred in the boiling liquid. In this manner, the dihydrate is obtained as oblique prisms or four- or six-sided plates which dissolve in 26–27 parts of boiling water. Crystallisation from an ice-cold solution gives a *hexahydrate*, slender needles, which dissolve freely in warm water. The acid (as sodium salt) has $[\alpha]_D^{20} - 37.0^\circ$ in aqueous solution. The *silver* salt, $\text{C}_{19}\text{H}_{21}\text{O}_6\text{N}_2\text{Ag}$, the *hydrochloride*, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2\cdot\text{HCl}$, needles and prisms, the *hydrogen sulphate*, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2\cdot\text{H}_2\text{SO}_4$, and the *nitrate*, $[\alpha]_D^{20} - 30.0^\circ$ in aqueous solution, are described. The action of a methyl alcoholic solution of methyl iodide on the silver salt leads to the formation of the *methylbetaine* of the acid, $\text{C}_{20}\text{H}_{24}\text{O}_6\text{N}_2$, colourless prisms, $[\alpha]_D^{18} - 5.6^\circ$ in aqueous solution, and a sparingly soluble product which is probably either an isomeric betaine or the acid, $\text{C}_{19}\text{H}_{22}\text{O}_6\text{N}_2$; it gives a sparingly soluble nitrate which has $[\alpha]_D^{18} - 30.8^\circ$ in water, agreeing in this respect with the nitrate of the acid, from which, however, it differs in its water content. Treatment of the betaine with aqueous hydriodic acid gives the *methiodide* of the acid, $\text{C}_{20}\text{H}_{25}\text{O}_6\text{N}_2\cdot\text{I}\cdot 2\text{H}_2\text{O}$, pale yellow needles or prisms.

The *monomethyl ester hydrochloride*, $\text{C}_{20}\text{H}_{24}\text{O}_6\text{N}_2\cdot\text{HCl}$, slender,

colourless needles, is prepared by the action of methyl alcoholic hydrogen chloride on the acid at 20° . The corresponding free ester could not be caused to crystallise, whereas the *methiodide* forms pale yellow, oblique prisms. More drastic treatment of the acid with methyl-alcoholic hydrogen chloride gives the *dimethyl ester hydrochloride*, $C_{21}H_{26}O_6N_2 \cdot HCl$, coarse, rectangular prisms; the free ester crystallises in prisms, the *methiodide* in colourless, thick, hexagonal plates.

An aqueous solution of the hydrobromide of the acid, $C_{19}H_{22}O_6N_2$, is reduced by sodium amalgam; the resultant *acid*, however, cannot be caused to crystallise, and is isolated as its *methyl ester*, $C_{21}H_{28}O_6N_2$, colourless prisms, m. p. $143-147^{\circ}$ (decomp.) after softening at 138° , m. p. about $132-135^{\circ}$ in a vacuum. The preparation of the methyl ester *nitrate*, $C_{21}H_{28}O_6N_2 \cdot HNO_3$, coarse prisms, *hydrochloride*, rectangular prisms or leaflets, and *methiodide*, small prisms or long, rectangular plates, is described. The ester hydrochloride is hydrolysed by 12*N*-hydrochloric acid to the corresponding *acid hydrochloride*, $C_{19}H_{24}O_6N_2 \cdot HCl \cdot 3H_2O$, quadratic leaflets.

If the solution obtained by the oxidation of cacotheline with bromine is saturated with sulphur dioxide and preserved at 0° , crystals are deposited which evolve sulphur dioxide when boiled with water; these are converted by boiling 2*N*-hydrobromic acid solution into the *hydrobromide*, $C_{17}H_{26}O_3N_2Br_2 \cdot HBr$, colourless, hexagonal plates. The corresponding *nitrate*, $C_{17}H_{26}O_3N_2Br_2 \cdot HNO_3$, crystallises in rectangular leaflets or prisms. The free *base* is a granular powder which is decomposed by boiling water with re-formation of the hydrobromide. H. W.

Pyrroles and Hydroxypyrroles. HANS FISCHER and MARIANNE HERMANN (*Z. physiol. Chem.*, 1922, **122**, 1-25).—The following pyrrole compounds have been prepared as being related or analogous to certain derivatives of bilirubin.

Ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate, prepared from α -methyl- β -acetylsuccinic acid (*phenylhydrazone*, colourless crystals, m. p. 85°), forms a *diacetyl* derivative on boiling with acetic anhydride containing a trace of sulphuric acid, almost colourless needles, m. p. 220° (decomp.). Ethyl 2-hydroxy-3:5-dimethylpyrrole-4-carboxylate, which yields a colourless *monoacetyl* derivative, m. p. 118° , is reduced by hydrogen iodide and acetic acid, yielding practically all its nitrogen as ammonia, and so resembling bilirubic acid.

The nitro-derivative of ethyl 2-hydroxy-5-methylpyrrole-4-carboxylate on reduction with zinc dust yields *ethyl 3-amino-2-hydroxy-5-methylpyrrole-4-carboxylate*, colourless prisms, m. p. 244° .

Ethyl 3-hydroxy-5-methylpyrrole-4-carboxylate condenses with benzaldehyde in presence of a small quantity of potassium hydrogen sulphate to yield *ethyl 3-hydroxy-2-benzylidene-5-methylpyrrole-4-carboxylate*, glistening, yellow needles, m. p. 228° ; with *p*-dimethylamino-benzaldehyde to yield *ethyl 3-hydroxy-2-p-dimethylaminobenzylidene-*

5-methylpyrrole-4-carboxylate, ochre-yellow needles, m. p. 214° ; with acetic anhydride there is formed a *monoacetyl* derivative, colourless needles, m. p. 123° , and with benzoyl chloride in pyridine a tarry mass, from which has been isolated rhombohedral, colourless crystals, m. p. 127° . Similarly with diazobenzene chloride, a yellow *dye* is formed, $C_{14}H_{15}O_3N_3$, yellow scales, m. p. 240° ; with diazotised *p*-dichloroaniline, a similar *compound*, long, yellow needles, aggregated in bundles, m. p. 265° , is formed; and analogous compounds are obtained from *p*-nitroaniline and diazobenzene-sulphonic acid.

o-Nitrophenyl chloromercaptan condenses in benzene solution with ethyl 2 : 4-dimethylpyrrole-3-carboxylate to yield *ethyl 5-o-nitrophenylthiol-2 : 4-dimethylpyrrole-3-carboxylate*, yellow octahedra, m. p. 191 — 192° . Similarly, from ethyl 2 : 5-dimethylpyrrole-3-carboxylate is obtained *ethyl 4-o-nitrophenylthiol-2 : 5-dimethylpyrrole-3-carboxylate*, fine, yellow prisms, m. p. 189° ; from 3-acetyl-2 : 4-dimethylpyrrole, *5-o-nitrophenylthiol-3-acetyl-2 : 4-dimethylpyrrole*, greenish-yellow crystals, m. p. 252° ; from 2 : 4-dimethyl-5-acetylpyrrole, *3-o-nitrophenylthiol-5-acetyl-2 : 4-dimethylpyrrole*, a green compound, m. p. 217 — 218° ; and from 2 : 3 : 5-trimethylpyrrole, *4-o-nitrophenylthiol-2 : 3 : 5-trimethylpyrrole*. No definite compound could be isolated from the action of *o*-nitrophenyl chloromercaptan on bilirubin, the hæmatoporphyrin from urine or fæces, or mesohæmatoporphyrin, whilst it does not react with ethyl 1-phenyl-2 : 5-dimethylpyrrole-3-carboxylate or ethyl 3-acetyl-2 : 4-dimethylpyrrole-5-carboxylate.

Ethyl 2 : 4-dimethylpyrrole-3-carboxylate condenses in dry ether with sulphur monochloride to yield *ethyl 5-disulphido-bis-2 : 4-dimethylpyrrole-3-carboxylate*, fine, pale yellow prisms, m. p. 195° , and with sulphur dichloride to yield *ethyl 5-sulphido-bis-2 : 4-dimethylpyrrole-3-carboxylate*, almost colourless, long needles, m. p. 197° , and also the monosulphide. Similarly, from ethyl 2 : 5-dimethylpyrrole-3-carboxylate is obtained *ethyl 4 : 4-sulphidobis-2 : 5-dimethylpyrrole-3-carboxylate*, pale yellow leaflets, m. p. 272° , and impure *ethyl 4 : 4'-sulphido-bis-2 : 5-dimethylpyrrole-3-carboxylate*; whilst from 5-acetyl-2 : 4-dimethylpyrrole, only *bis-5-acetyl-2 : 4-dimethylpyrrole-3'-disulphide*, small prisms, m. p. 317° , could be obtained.

W. O. K.

Pyrroles. III. Ketones, Ketonic Acid Esters, and Ketonic Acid Nitriles of Substituted Pyrroles. HANS FISCHER, KARL SCHNELLER, and WERNER ZERWECK (*Ber.*, 1922, 55, [B], 2390—2403).—The Gattermann synthesis of aldehydes with hydrocyanic acid and the Hoesch synthesis of ketones have been applied to a series of substituted pyrroles. In many cases, reaction proceeds very smoothly. The nitriles used include acetonitrile, benzonitrile, mono-, di-, and tri-chloroacetonitriles, cyanogen, malonitrile, ethyl cyanoacetate, and ethyl cyanoformate. With dinitriles, only a one-sided condensation is achieved. Chloroacetonitrile promises to be particularly useful on account of its

great reactivity and the readiness with which the halogen atom in the new compound is replaced by other groups. It appears likely to be useful in the examination of the products of the degradation of blood and bile pigments.

Ethyl 5-acetyl-2:4-dimethylpyrrole-3-carboxylate, m. p. 142°, is obtained by passing a slow current of dry hydrogen chloride into a mixture of ethyl 2:4-dimethylpyrrole-3-carboxylate and acetonitrile dissolved in anhydrous ether and subsequent decomposition of the *imine hydrochloride* primarily formed (orange-coloured crystals, m. p. 240°), with warm water. Ethyl 5-benzoyl-2:4-dimethylpyrrole-3-carboxylate, colourless needles, m. p. 108°, and the intermediate *imine hydrochloride*, lemon-yellow needles, m. p. 232°, are prepared similarly. Chloroacetonitrile and ethyl 2:4-dimethylpyrrole-3-carboxylate give an *imine hydrochloride*, m. p. 110°, and ethyl 5-chloroacetyl-2:4-dimethylpyrrole-3-carboxylate, $\text{NH} < \begin{smallmatrix} \text{C}(\text{CO} \cdot \text{CH}_2\text{Cl}) \cdot \text{CMe} \\ \text{CMe} = \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$, colourless needles, m. p. 187°,

(*phenylhydrazone*, yellow needles, m. p. 164°). The chloro-compound is converted by a solution of dimethylamine in absolute alcohol into ethyl 5-dimethylaminoacetyl-2:4-dimethylpyrrole-3-carboxylate, colourless crystals, m. p. 95°. Ethyl 2:4-dimethylpyrrole-3-carboxylate condenses with ethyl cyanoacetate in the usual manner giving an *imine hydrochloride* and ethyl 3-carbethoxy-2:4-dimethylpyrrole-5-acetate, colourless needles, m. p. 145°. Cyanogen condenses with ethyl 2:4-dimethylpyrrole-3-carboxylate with the formation of 3-carbethoxy-2:4-dimethylpyrrole-5-glyoxylonitrile, $\text{NH} < \begin{smallmatrix} \text{C}(\text{CO} \cdot \text{CN}) \cdot \text{CMe} \\ \text{CMe} = \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$, silvery leaflets, m. p. 165°, but does not

appear to react under similar conditions with 3-acetyl-2:4-dimethylpyrrole, or with ethyl 2:5-dimethylpyrrole-3-carboxylate; a crystalline substance could not be obtained from 2:4-dimethylpyrrole. Ethyl 5-cyanoacetyl-2:4-dimethylpyrrole-3-carboxylate, almost colourless needles, m. p. 234°, is prepared from ethyl 2:4-dimethylpyrrole-3-carboxylate and malononitrile or from ethyl 5-chloroacetyl-2:4-dimethylpyrrole-3-carboxylate and potassium cyanide.

Ethyl 2:5-dimethylpyrrole-3-carboxylate and chloroacetonitrile give an *imine hydrochloride*, coarse, pale yellow needles, which is converted by cold water into ethyl 4-chloroacetyl-2:5-dimethylpyrrole-3-carboxylate, colourless crystals, m. p. 130°. 2:4:5-Trimethylpyrrole is transformed in a similar manner into 3-chloroacetyl-2:4:5-trimethylpyrrole, colourless crystals, m. p. 193°, which is transformed by potassium cyanide into 3-cyanoacetyl-2:4:5-trimethylpyrrole, colourless crystals, m. p. 178°.

Ethyl cyanoformate transforms ethyl 2:4-dimethylpyrrole-3-carboxylate into ethyl 3-carbethoxy-2:4-dimethylpyrrole-5-glyoxylate, $\text{NH} < \begin{smallmatrix} \text{C}(\text{CO} \cdot \text{CO}_2\text{Et}) \cdot \text{CMe} \\ \text{CMe} = \text{C} \cdot \text{CO}_2\text{Et} \end{smallmatrix}$, dark yellow crystals, m. p. 82·5°, which is readily hydrolysed by aqueous sodium hydroxide to the corresponding acid, m. p. 192° (decomp.). When treated similarly,

ethyl 2:5-dimethylpyrrole-3-carboxylate gives an *imine hydrochloride*, and *ethyl 3-carbethoxy-2:5-dimethylpyrrole-4-glyoxylate*, $\text{NH} \begin{smallmatrix} \text{CMe}=\text{C}\cdot\text{CO}\cdot\text{CO}_2\text{Et} \\ \text{CMe}=\text{C}\cdot\text{CO}_2\text{Et} \end{smallmatrix}$, colourless needles, m. p. 102°; 3-

acetyl-2:4-dimethylpyrrole yields an *imine hydrochloride*, coarse needles, and *ethyl 3-acetyl-2:4-dimethylpyrrole-5-glyoxylate*, colourless crystals, m. p. 120°, which is readily hydrolysed to the corresponding *acid*, pale yellow crystals, m. p. 178° (decomp.).

[With MAX SCHUBERT.]—A mixture of crude hæmopyrrole and chloroacetonitrile dissolved in ether is converted by dry hydrogen chloride into an imine hydrochloride which is transformed by hot water into a *chloroacetyl* derivative, $\text{C}_{10}\text{H}_{14}\text{ONCl}$, pale pink needles, m. p. 127°; the latter is converted by hydriodic and glacial acetic acids into hæmopyrrole [2:3-dimethyl-4-ethylpyrrole] identified as the picrate, m. p. 121°. H. W.

“**Graphites**” from Pyrrole and from Thiophen. R. CIUSA (*Gazzetta*, 1922, 52, ii, 130—131).—Following Ciamician and Ciusa’s supposition (A., 1921, i, 329) that the existence of saturated complexes, C_6 , C_4HN , and C_4S , is possible, the author pointed out (*Atti R. Accad. Lincei*, 1921, [v], 30, i, 468) that such complexes should exhibit a marked tendency to polymerise to graphite from benzene and to the compounds $(\text{C}_4\text{HN})_n$ and $(\text{C}_4\text{S})_n$, which might be termed graphites from pyrrole and thiophen, respectively. It is now found that tetra-iodopyrrole yields at 150—200° the compound $(\text{C}_4\text{HNI})_{2n}$, and at an incipient red heat the compound $(\text{C}_4\text{HN})_n$, which forms black, graphitic scales and may be regarded as graphite from pyrrole. Similarly, when heated to incipient redness in a current of inert gas, tetra-iodothiophen gives the graphitic compound $(\text{C}_4\text{S})_n$. An analogous compound was obtained by Pauly (A., 1913, i, 1311) from tetra-iodoglyoxaline. With each of these tetra-iodo-derivatives, three iodine atoms are expelled simultaneously at a comparatively low temperature, whilst the fourth atom is eliminated in a succeeding phase at a higher temperature. Further, *tetra-iodofuran*, m. p. 145°, begins to lose iodine at 160° and decomposes at 262°, leaving a black residue similar to the other “graphites.” T. H. P.

The 4-Piperidone Ring. L. RUZICKA and C. F. SEIDEL (*Helv. Chim. Acta*, 1922, 5, 715—720).—If the polymerisation of 4-piperidone is due to reaction between the keto- and the imino-groups, replacement of the hydrogen of the latter group by another radicle should prevent it. Such a substituted piperidone was prepared as follows. Ethyl $\beta\beta'\beta''$ -nitrilotripropionate (A., 1921, i, 53), $\text{N}(\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et})_3$, was condensed in benzene solution with sodium ethoxide and from the product was prepared *ethyl 4-ketopiperidinepropionate*, a viscous, colourless oil, b. p. 100—110°/0.5 mm. This ester can be distilled unchanged in a vacuum and does not polymerise. By reduction with hydrogen and platinum black in acetic acid solution, it gave *ethyl 4-hydroxypiperidinepropionate*, b. p. 125°/0.5 mm., *benzoate*, m. p. 195°.

An attempt was made to prepare the compound in the pyrrolidine

series analogous to 4-piperidone. By condensing ethyl β -iodopropionate with ethyl glycine, the *ethyl iminoacetatepropionate*, $\text{CO}_2\text{Et}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, was obtained, b. p. 100—105°/0.1 mm. This was condensed by means of sodium, as in the preparation of 4-piperidone (*loc. cit.*), but, although the reaction appeared to proceed normally, pure products could not be isolated. Similarly, the condensation of the *benzoyl* derivative (b. p. 170—180°/0.3 mm.) gave no result. On the other hand, condensation of ethyl benzoyl- $\beta\beta'$ -iminodipropionate with sodium went normally and from the product was prepared the previously described dibenzylidene-4-piperidone (*loc. cit.*).

E. H. R.

Preparation of Dialkylamides of Nicotinic Acid. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 184625).—Dialkylamides of nicotinic acid are prepared by the interaction of a haloid or ester of the acid and a dialkylamine (cf. this vol., i, 860). Thus *nicotinodipropylamide* is obtained by heating nicotinyl chloride with dipropylamine hydrochloride at 180°. It is a yellow oil, b. p. 184°/17 mm. Similarly, the *piperidide* of nicotinic acid is obtained as a viscid oil, b. p. 310°, by heating the acid bromide with piperidine hydrobromide.

G. F. M.

New Isomerism in the Isatin Series. V. GUSTAV HELLER (*Ber.*, 1922, **55**, [B], 2681—2697).—Previous investigations in the isatin series have shown that, in addition to the lactam form,

$\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO} \\ \text{NH}\end{smallmatrix}\rangle\text{CO}$, which is common to isatin and its substitution

products, the lactim form, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{CO} \\ \text{N}\end{smallmatrix}\rangle\text{C}\cdot\text{OH}$, has an independent existence in the case of 5:7-dimethylisatin, and that the third (isatole) form, $\text{C}_6\text{H}_4\langle\begin{smallmatrix}\text{C}(\text{OH}) \\ \text{N}\end{smallmatrix}\rangle\text{CO}$, is obtainable in several instances.

The problems of the series are further complicated by the formation of a fourth form of unknown constitution which is characterised by its high melting point and insolubility in alkali and of bimolecular isatins (isatoids) which are at present known only as their *O*-alkyl ethers. The present communication is mainly devoted to a description of dihalogenated isatins.

The course of the action of benzoyl chloride on isatin silver salts, in so far as isomerides of the isatins are concerned, is characterised by the primary production of the lactim form which only remains in a stable condition in the case of 5:7-dimethylisatin; with isatin, 5-chloro-, 5-bromo-, 5:7-dichloro-, and 4:5:7-trimethyl-isatin, the action proceeds further to the isatole, and with 5:7-dibromo-isatin, 4-chloro-5-bromoisatin, and to a less extent with 5:7-dichloroisatin, to its final stage, thereby producing the form which is insoluble in alkali. Dimethylisatin lactim can be converted by alkali into the isatole, which, like dichloro- and trimethyl-isatole, is transformed into the fourth variety by recrystallisation from glacial acetic acid. This treatment does not have the same effect with the simplest isatole, and, in this case, the "insoluble" isomeride is yet unknown.

[With WALTER BENADE and OTTO HOCHMUTH.]—5 : 7-Dibromoisatin is readily converted by warm sodium carbonate solution into *sodium dibromoisatoate*; the corresponding *acid*, m. p. 248—249°, gives a somewhat sparingly soluble *bisulphite* compound. 5 : 7-Dibromoisatin silver, a greyish-violet substance, prepared by the action of a hot aqueous silver acetate solution on 5 : 7-dibromoisatin dissolved in hot alcohol, is transformed by benzoyl chloride in the presence of benzene mainly into 5 : 7-dibromo-N-benzoylisatoic acid, aggregates of needles, m. p. 207—208° (decomp.); in addition, a small quantity of the *fourth dibromoisatin*, slender needles, m. p. above 300°, is obtained. 5 : 7-Dibromo-N-benzoylisatin is prepared by the action of acetic anhydride on dibromobenzoylisatoic acid; it forms coarse, yellow crystals, m. p. 161—162°. 5 : 7-Dibromo-N-acetylisatin, yellow plates, m. p. 133°, is prepared by the action of acetyl chloride on the corresponding silver salt in the presence of benzene; it is converted by dilute sodium hydroxide solution into 5 : 7-dibromo-N-acetylisatoic acid, colourless needles, m. p. 204°. 5 : 7-Dibromoisatin silver is transformed by methyl iodide in the presence of benzene into the corresponding *lactim ether*, red crystals, m. p. 164—165°, which could not be converted smoothly into an isatoid. It is transformed by phenylhydrazine in the presence of light petroleum into 5 : 7-dibromoisatin- α -phenylhydrazone, dark red needles, m. p. 218° (decomp.), and by aniline into a mixture of 5 : 7-dibromoisatin- α -anilide, short brown rods, m. p. 189°, and 5 : 7-dibromoisatinanil, pale blue needles, m. p. 174—175°; the *di-anil*, $C_{30}H_{13}N_3Br_2$, dark red needles, m. p. 236—237°, is prepared by the further action of aniline on the anilide. 5 : 7-Dibromoisatin-dianil silver, a blue precipitate, is prepared by the action of silver acetate on an alcoholic solution of the di-anil. The salt is particularly remarkable because it does not contain oxygen, and its formation is precisely analogous to salt formation with oxygenated isatins. The *sodium* and *potassium* salts of 5 : 7-dibromoisatin are described; the compounds are much more stable than the corresponding isatin derivatives.

4-Chloro-5-bromoisatin silver, a bluish-grey salt, is mainly converted by benzoyl chloride in the presence of benzene into 4-chloro-5-bromo-N-benzoylisatin, coarse, yellow crystals, m. p. 196°, which is converted by warm dilute alkali into 4-chloro-5-bromo-N-benzoylisatoic acid, m. p. 186°. A dark-coloured, non-crystalline substance which does not dissolve in alkali is also produced in small amount; it probably belongs to the fourth series of isatin isomerides. Treatment of the silver salt with methyl iodide in the presence of benzene causes the slow formation of the corresponding *O-methyl ether*, m. p. (indefinite) 173°, which could not be obtained in the pure condition. It is converted by phenylhydrazine into 4-chloro-5-bromoisatin-2-phenylhydrazone, slender, dark red needles, m. p. 235° (decomp.), and by aniline into the corresponding *anilide*, m. p. 276—277° (decomp.).

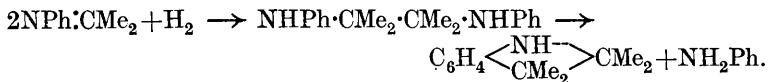
5 : 7-Dichloroisatin silver is converted by acetyl chloride in the presence of benzene into 5 : 7-dichloro-N-acetylisatoic acid, prisms, m. p. 204° (decomp.), which is transformed by acetic

anhydride into 5 : 7-dichloroisatin. The silver salt is converted by benzoyl chloride mainly into 5 : 7-dichloro-N-benzoylisatoic acid, $\text{NHBz} \cdot \text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{CO}_2\text{H}$, colourless needles, m. p. 215° (decomp.). In addition to the primary product of the change, 5 : 7-dichloro-N-benzoylisatin, $\text{C}_6\text{H}_2\text{Cl}_2 \cdot \text{CO} \cdot \text{NHBz}$, yellow plates, m. p. 146° , is formed in very small quantity; it is obtained readily by the action of acetic anhydride on 5 : 7-dichloro-N-benzoylisatoic acid. 5 : 7-Dichloroisatole, m. p. 205° (slight decomp.), is also produced; its properties are similar to those of the simplest isatoles in that it does not give the indophenin reaction, does not combine with phenylhydrazine, and dissolves in dilute sodium hydroxide solution to a carmine red solution which yields dichloroisatin on addition of mineral acids. 5 : 7-Dichloroisatole is unstable in solutions in organic media and is transformed by recrystallisation from glacial acetic acid into 5 : 7-dichloroisatin IV, red crystals, m. p. 313° . 5 : 7-Dichloroisatin methyl ether, red prisms, m. p. 158° , is prepared in the usual manner from the silver salt and methyl iodide (this reaction does not appear to be influenced by the presence of substituents); it is very stable towards light. The corresponding α -phenylhydrazone crystallises in dark red needles, m. p. $217\text{--}218^\circ$ (decomp.). The lactim ether is converted with relative ease by acetic anhydride into tetrachloromethylisatoid, m. p. 127° , followed by re-solidification at about 180° and re-melting at about 222° , which is transformed by hydrogen bromide and glacial acetic acid into dichloroisatin.

Re-examination of the action of benzoyl chloride on 5 : 7-dimethylisatin silver has shown that N-benzoyl-5 : 7-dimethylisatoic acid, colourless tetrahedra, m. p. 208° (decomp.), is produced during the action. 5 : 7-Dimethylisatin O-methyl ether, dark red prisms, m. p. $140\text{--}141^\circ$ [α -phenylhydrazone, red rodlets, m. p. 234° (decomp.)] is very stable towards light; it is converted by acetic anhydride or boiling toluene into 5 : 7-dimethylisatoid, red, crystalline plates, m. p. 237° (previously described as dimethylisatin-II methyl ether).

7-Methylisatin dissolved in alcohol does not give a normal silver salt with silver acetate; the product when heated with acetyl chloride or benzoyl chloride in the presence of benzene regenerates methylisatin. In other respects, the compound exhibits little activity, the only readily preparable derivative being N-acetyl-7-methylisatin, yellow platelets, m. p. 163° , which is converted by alkali into N-acetyl-7-methylisatoic acid, m. p. 175° . H. W.

Keto-anils. IV. Reduction Products of Keto-anils. E. KNOEVENAGEL (*Ber.*, 1922, **55**, [B], 2309—2321; cf. this vol., i, 750, 751).—The reduction of acetoneanil with sodium and alcohol leads to the formation of 2 : 2 : 3 : 3-tetramethylindoline, in accordance with the scheme :



Acetone-*p*-tolil and acetone- α -naphthil behave similarly; the latter

case is of particular interest, since the intermediate compound can be isolated.

Acetoneanil is reduced by sodium and boiling ethyl alcohol to 2 : 2 : 3 : 3-*tetramethylindoline*, a colourless, crystalline substance, m. p. 39·5°. The base dissolves readily in cold dilute acetic acid, but does not yield a carbonate. It is stable towards hydrogen chloride at 240—280°, and towards mercuric acetate at 150°. It readily reduces alkaline potassium permanganate solution. It gives a *hydrochloride*, m. p. 201—207° (decomp.), a *picrate*, m. p. 74°, and an *acetyl* derivative, m. p. 83°. It is converted by molecular quantities of sodium nitrite and hydrochloric acid into the *nitroso*-derivative, m. p. 44·5°, which is readily isomerised by hydrochloric acid to 5-*nitroso*-2 : 2 : 3 : 3-*tetramethylindoline hydrochloride*, unstable, green crystals, m. p. (indefinite) 170° (decomp.). Attempts to reduce acetoneanil electrolytically at a lead cathode were unsuccessful.

Acetone-*p*-tolil is reduced by sodium and ethyl alcohol or, less advantageously, by zinc and hydrochloric acid (20%) to *p*-toluidine and 2 : 2 : 3 : 3 : 5-*pentamethylindoline*, a yellow liquid which does not solidify after prolonged preservation in a freezing mixture. The *hydrochloride*, m. p. 201—205° (decomp.), *acetyl* derivative, a pale yellow substance, m. p. 51°, b. p. 165—167°/14—15 mm., *nitroso*-compound, pale brown crystals, m. p. 48·5°, *picrate*, a reddish-brown salt, m. p. 144°, and *oxalate* are described.

Acetone- α -*naphthil*, a viscous, yellow liquid, b. p. 200—203°/12 mm., which could not be caused to crystallise, is prepared by heating a mixture of acetone and α -naphthylamine with a little iodine. It is hydrolysed by boiling hydrochloric acid (20%). The corresponding *hydrogen oxalate*, m. p. 167·5°, and *picrate*, slender, pale yellow needles, m. p. 210°, are described. It is reduced by sodium and ethyl alcohol at a temperature not exceeding 105° to acetone-*ar*-*tetrahydro*- α -*naphthil*, a greenish-yellow liquid which darkens gradually on exposure to air, b. p. 193—196°/14—15 mm. It does not form a carbonate. The corresponding *hydrochloride* forms coarse crystals, m. p. 199° (*acetone*- α -*naphthil hydrochloride* crystallises in slender, matted needles, m. p. 215°, after darkening and incipient decomposition at 180°); the *hydrogen oxalate*, colourless needles, m. p. 152—153°, and the *picrate*, yellowish-brown crystals, m. p. 175—185° (decomp.), are described. The *tetrahydronaphthil* is hydrolysed by boiling hydrochloric acid (20%) to acetone and *ar*-*tetrahydro*- α -*naphthylamine*. Reduction of acetone- α -*naphthil* at a higher temperature (see above), either with sodium and ethyl alcohol under increased pressure or with sodium and amyl alcohol, leads to the formation of 2 : 2 : 3 : 3-*tetramethyl*-*ar*-*tetrahydro*- α -*naphthindoline*, a pale yellow liquid which is stable towards light; the colourless *hydrogen oxalate*, m. p. 183°, and the *picrate*, m. p. (indefinite) 163° after darkening at 150°, are described.

H. W.

The Quaternary Salts of Quinaldinic Acid. WILLIAM HOBSON MILLS and FRANCES MARY HAMER (T., 1922, 121, 2008—2014).

Doebner's Reaction. IV. R. CIUSA (*Gazzetta*, 1922, **52**, ii, 43—48; cf. A., 1915, i, 894, 895; 1921, i, 195).—2-Phenyltetrahydro- β -naphthacinchonic acid, now obtained in larger quantity, crystallises in white scales, m. p. 226°, and, like its methyl ester, m. p. 134°, and its salts, gives solutions exhibiting slight blue fluorescence; the alkali metal salts are oily and the silver and lead salts of abnormal constitution. On prolonged boiling with alcohol, the acid yields phenyl- β -naphthaquinoline, m. p. 188°, together with other compounds not identified. This reaction is similar to that observed by Simon and Mauguin (A., 1907, i, 725; 1908, i, 296), who found that when dihydro-2-phenyl- β -naphthaquinoline-3:4-dicarboxylic acid is heated in alkaline solution, 2-phenyl- β -naphthacinchonic acid and 2-phenyl- β -naphthaquinoline are formed; as already shown, the dihydro-acid loses a carboxyl group from the β -position and then oxidises itself to 2-phenyl- β -naphthacinchonic acid, with simultaneous formation of the tetrahydrogenated acid, which is transformed into the corresponding non-hydrogenated base on boiling.

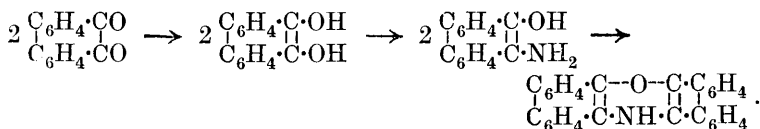
The action of benzylidene- α -naphthylamine on ethyl oxalacetate (cf. Simon and Mauguin, *loc. cit.*) yields: (1) 2-Phenyl- β -naphthaquinoline-3:4-dicarboxylic acid, m. p. 152°; Simon and Mauguin gave m. p. 162°. (2) A *dimeride* of benzylidene- β -naphthylamine which crystallises in colourless needles, m. p. 200°, yields benzaldehyde (2 mols.) and β -naphthylamine (2 mols.) when hydrolysed $\text{C}_{10}\text{H}_7\text{N}-\text{CHPh}$ by means of dilute sulphuric acid, and may be represented provisionally by the annexed formula. $\text{C}_{10}\text{H}_7\text{N}-\text{CHPh}$ (3) Ethyl 2-phenyl- β -naphthaquinoline-3:4-dicarboxylate, already described by Simon and Mauguin (*loc. cit.*).

α -*Pyrrylcinchonic acid*, $\text{C}_{14}\text{H}_{10}\text{O}_2\text{N}_2$, prepared by condensation of 2-acetylpyrrole with isatin in presence of potassium hydroxide, crystallises in small, yellow needles, and blackens without melting at 310°; its *sodium salt* (+2½H₂O) was analysed.

α -*Furylcinchonic acid*, $\text{C}_{14}\text{H}_9\text{O}_3\text{N}$, similarly prepared from 2-acetylfuran and isatin, forms yellow needles, m. p. 149°. T. H. P.

Preparation and Mechanism of Formation of Phenanthroxazine. B. FORESTI (*Gazzetta*, 1922, **52**, ii, 90—96; cf. this vol., ii, 524).—In the preparation of 9-amino-10-hydroxyphenanthrene by the reduction of phenanthraquinone monoxime in alcoholic solution by means of hydrogen sulphide, sulphur and impure phenanthroxazine are precipitated, the aminohydroxyphenanthrene undergoing condensation at the boiling point of the alcohol. This condensation takes place more rapidly and yields a purer product if a suspension of the hydrochloride of the base in nitrobenzene or naphthalene is boiled for a few minutes; if a solvent having a lower boiling point, such as xylene, is used, the reaction occurs more slowly and yields a mixture of phenanthroxazine and phenanthrazine. These results indicate that, in the formation of phenanthroxazine by the action of phenylhydrazine on phenanthraquinone (Bamberger and Grob, A., 1901, i, 280), the latter is first reduced to phenanthraquinol, which is transformed by the

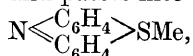
action of ammonia into 9-amino-10-hydroxyphenanthrene, this then undergoing condensation to phenanthroxazine with elimination of water and ammonia :



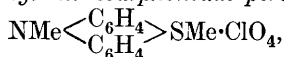
The action of aqueous ammonia on dihydroxyphenanthrene (Schmidt and Lumpp, A., 1910, i, 312; ii, 450; Foresti, this vol., ii, 524) yields first 9-amino-10-hydroxyphenanthrene, which gives (1) phenanthroxazine, and (2) diaminophenanthrene, which readily condenses to phenanthrazine. T. H. P.

Sulphonium Bases Derived from Thiodiphenylamine and Analogous Substances. F. KEHRMANN and JEAN HENRI DARDEL (*Ber.*, 1922, 55, [B], 2346—2359; cf. A., 1918, i, 308, and previous abstracts).—The formation of sulphonium salts from aromatic sulphides containing a cyclic sulphur atom has been examined.

Thiodiphenylamine is obtained conveniently and in 82% yield by heating a mixture of diphenylamine and sulphur with a trace of iodine at 170°. It unites with methyl sulphate at 80° to yield the salt, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{SMe} \cdot \text{O} \cdot \text{SO}_3\text{Me}$, which is converted into the corresponding *perchlorate*, $\text{C}_{13}\text{H}_{12}\text{NSClO}_4$, a crystalline powder which is very unstable towards light. It is converted by sodium hydroxide solution into the colourless *base*, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{SMe} \cdot \text{OH}$, which readily loses water and passes into the *anhydride*,



an unstable, yellow substance which is reconverted by carbon dioxide into the colourless *carbonate* of the sulphonium type. NS-*Dimethylthiodiphenylaminesulphonium perchlorate*,

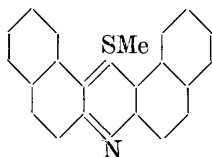


colourless, thin prisms, is prepared in an analogous manner from methylthiodiphenylamine. The corresponding free *base* is colourless and soluble in water; it does not yield an anhydride, but is decomposed in hot solution into methyl alcohol and the methylated original material.

Thiophenyl- β -naphthylamine, sulphur-yellow needles, m. p. 178°, is obtained in 80% yield by heating phenyl- β -naphthylamine and sulphur with iodine at 200°/12—15 mm. It is converted in the usual manner into S-*methylthiophenyl- β -naphthylaminesulphonium perchlorate*, $\text{NH} \langle \text{C}_6\text{H}_4 \rangle \text{SMe} \cdot \text{ClO}_4$, colourless, lustrous needles (the corresponding yellow *picrate* and colourless *ferrocyanide* are described). It is transformed by sodium hydroxide into a yellow

base which could not be obtained in a homogeneous condition, but appears to be an anhydride. NS-Dimethylthiophenyl- β -naphthylaminesulphonium perchlorate is a colourless, crystalline powder which is not affected by cold sodium hydroxide solution, but is decomposed by warm alkali into methylthiophenyl- β -naphthylamine. S-Methylthiophenyl- α -naphthylaminesulphonium perchlorate is decomposed by sodium carbonate solution with separation of a yellow anhydride. Attempts to obtain a *N*-methylated thiophenyl- α -naphthylamine were unsuccessful.

Thiodi- β -naphthylamine, pale yellow needles, m. p. 233°, is readily prepared in 85% yield by heating a mixture of di- β -naphthylamine and sulphur with a little iodine at 180–200°. It is transformed in the usual manner into S-methylthiodi- β -naphthylaminesulphonium perchlorate, $\text{NH} \langle \text{C}_{10}\text{H}_6 \rangle \text{SMe} \cdot \text{ClO}_4$, a colourless, crystalline powder (the corresponding chloride, colourless leaflets, platinichloride, and picrate are described). The salts are converted by sodium hydroxide solution into the corresponding anhydride (annexed formula), pale orange-coloured needles, m. p. 160–165° (partial decomp.), which is reconverted by acids (including carbon dioxide) into colourless sulphonium salts. NS-Dimethylthiodi- β -

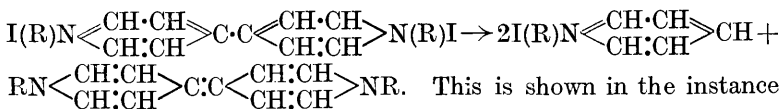


naphthylaminesulphonium perchlorate, $\text{NMe} \langle \text{C}_{10}\text{H}_6 \rangle \text{SMe} \cdot \text{ClO}_4$, colourless crystals, is not decomposed by cold sodium hydroxide solution, but is converted by the hot reagent into *N*-methylthiodi- β -naphthylamine.

Thiodi- α -naphthylamine is obtained in 60–70% yield by heating a mixture of di- α -naphthylamine, sulphur, and a little iodine at 155–180°, and is conveniently purified through the black, crystalline picrate. It is transformed in the usual manner into S-methylthiodi- α -naphthylaminesulphonium perchlorate, a colourless, crystalline powder from which the corresponding anhydride (annexed formula), golden-yellow needles, m. p. 141°, is obtained. The latter substance is relatively stable towards dry air, but readily absorbs acid vapours with formation of colourless sulphonium salts.

H. W.

1 : 1'-Dialkyltetrahydro-4 : 4'-dipyridyls. BRUNO EMMERT and OTTO VARENKAMP (*Ber.*, 1922, 55, [B], 2322–2326; cf. A., 1920, i, 331; this vol., i, 680).—The recent observations of Dimroth and Frister (this vol., i, 678), that 1 : 1'-diacetyltetrahydro-4 : 4'-dipyridyl and 4 : 4'-dipyridyl react in acetic anhydride solution to form pyridine and diacetyldihydrodipyridyl, render it probable that dialkyltetrahydrodipyridyls could be converted by 4 : 4'-dipyridyldialkylidides into 1 : 1'-dialkyldihydrodipyridyls in accordance with the scheme: $\text{RN} \langle \text{CH}:\text{CH} \rangle \text{CH}:\text{CH} \langle \text{CH}:\text{CH} \rangle \text{NR} +$



This is shown in the instance of dibenzyltetrahydro-4 : 4'-dipyridyl and 4 : 4'-dipyridyl dibenzyl iodide to be the case; benzylpyridinium iodide is produced, but the second product is a merquinonoid substance formed by the union of molecular proportions of dibenzyl-dihydrodipyridyl and dipyridyl dibenzyl iodide.

1 : 1'-Dibenzyltetrahydro-4 : 4'-dipyridyl is conveniently prepared by the addition of sodium amalgam to a solution of benzylpyridinium chloride in water covered with a layer of ether in an atmosphere of hydrogen. When dissolved in ethyl alcohol and gradually treated with an aqueous solution of dipyridyl dibenzyl iodide in an atmosphere of hydrogen, it gives benzylpyridinium iodide and the *quinhydrone*, $\text{C}_{48}\text{H}_{44}\text{N}_4\text{I}_2$, a dark violet powder, m. p. 180—185°, when rapidly heated, which is relatively stable towards air and dissolves in alcohol, aniline, pyridine, or acetic anhydride with the formation of dark blue solutions which become brown on exposure to air. It is prepared more conveniently, but in a less pure condition, by the action of a large excess of sodium amalgam on an aqueous solution of dipyridyl dibenzyl iodide. H. W.

Formaldehyde Derivatives of 2 : 5-Diketopiperazine. EMILE CHERBULIEZ and EMANUEL FEER (*Helv. Chim. Acta*, 1922, 5, 678—687).—Protein substances are known to form compounds with formaldehyde, and it is suggested that combination takes place at the *N*-substituted amido-groups characteristic of these substances. To test this hypothesis, experiments have been made with 2 : 5-diketopiperazine, which is the simplest derivative of an α -amino-acid containing nitrogen only in the form of a substituted acid amide. 2 : 5-Diketopiperazine readily combines with formaldehyde to give 2 : 5-diketo-1 : 4-di-hydroxymethylpiperazine, small, colourless prisms, m. p. 178° (decomp.). It is a relatively stable substance forming a neutral aqueous solution, but dissolving more readily, without decomposition, in aqueous alkali. Its constitution is established by the preparation from it of the known 2 : 5-diketo-1 : 4-dibenzylpiperazine. It can be methylated with methyl sulphate to form 2 : 5-diketo-1 : 4-di-methoxymethyl-2 : 5-piperazine, colourless spangles, m. p. 99—100°, which is perfectly stable in aqueous solution. Benzoylation is best carried out with benzoic anhydride in pyridine; 2 : 5-diketo-1 : 4-di-benzoylmethylpiperazine forms brilliant spangles, m. p. 182°. With piperidine, diketodi-hydroxymethylpiperazine condenses to give 2 : 5-diketo-1 : 4-di-piperidinomethylpiperazine, long prisms, m. p. 156—157°, readily hydrolysed by hot water to diketopiperazine, formaldehyde, and piperidine.

By the action of phosphorus pentachloride on the diketodi-hydroxymethylpiperazine, 2 : 5-diketo-1 : 4-di-chloromethylpiperazine is formed, m. p. about 162° (decomp.). The chlorine atoms of this compound are extraordinarily reactive, in consequence of which

derivatives are formed with the greatest ease. The compound is decomposed by water with regeneration of the di-hydroxymethyl-compound, whilst with alcohols the alkoxy-derivatives are formed; 2 : 5-diketo-1 : 4-diethoxymethylpiperazine forms rhombic crystals, m. p. 92—93°. By the Friedel-Crafts' reaction with benzene, it gives 2 : 5-diketo-1 : 4-dibenzylpiperazine, and when heated alone with naphthalene, or with the addition of a little copper, at 150—160°, it condenses to form 2 : 5-diketo-1 : 4-di-naphthylmethylpiperazine, a white, crystalline powder, m. p. 189—192°. With β -naphthol, the dichloro-compound readily condenses, giving 2 : 5-diketo-1 : 4-di-(β -hydroxy- α -naphthylmethyl)piperazine, a crystalline powder, m. p. 285—286°; the *dibenzoyl* derivative forms fine needles, m. p. 267—268°. E. H. R.

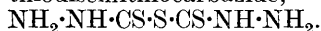
Preparation of Aromatic Selenium Compounds. FARBERWERKE VORM. MEISTER, LUCIUS, & BRÜNING (D.R.-P. 348906 and 350376; from *Chem. Zentr.*, 1922, iv, 46).—An earlier patent (A., 1918, i, 218) is modified by using selenic acid instead of selenium or selenium dioxide and by substituting other solvents for sulphuric acid or working in the absence of solvents. The compound obtained from *o*-nitrophenol and selenic acid in the presence of sulphuric acid, is a yellow powder containing 16% of selenium, and exploding on heating. Antipyrine gives with selenic acid a compound containing 17% of selenium; it forms small crystals, m. p. about 238°, with discoloration. By the action of selenious oxide on *p*-nitroantipyrine in formic acid solution, *di-p-nitroantipyrinyl selenide* is obtained; it forms yellow crystals, m. p. about 260° (decomp.). *Di-p-tolylantipyrinyl selenide*, (C₁₂H₁₃ON₂)₂Se, prepared from *p*-tolylantipyrine and selenious acid in alcoholic solution, forms colourless crystals, m. p. about 255° (decomp.). The compound obtained by the action of selenious acid on resorcinol in aqueous solution is a brown powder. G. W. R.

Preparation of Water-soluble Compounds of Diethylbarbituric Acid and its Homologues. JOHANN A. WÜLFING (D.R.-P. 345361; from *Chem. Zentr.*, 1922, ii, 1080—1081).—Solutions of diethylbarbituric acid or its homologues are treated with the theoretical amount of calcium hydroxide, magnesium hydroxide, or freshly precipitated calcium carbonate, if necessary with heating, and after filtration, if required, evaporated to dryness in a vacuum. The *calcium* salt and the *magnesium* salt of diethylbarbituric acid are mentioned, and also the *calcium* salt and the *magnesium* salt of phenylethylbarbituric acid. The products have therapeutical uses and form stable mixtures with alkaline earth salts of *o*-acetoxybenzoic acid. G. W. R.

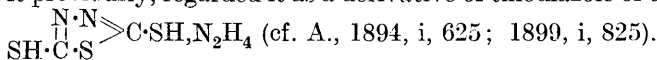
3-Hydroxy-2-phenylindazole. GUSTAV HELLER (*Ber.*, 1922, 55, [B], 2680).—In reply to von Auwers and Hüttenes (this vol., i, 682), the author maintains the individuality of the isomeric form of 3-hydroxy-2-phenylindazole described by him (A., 1917, i, 219). H. W.

The Interaction of Aniline and Acraldehyde. FREDERICK GEORGE MANN (T., 1922, **121**, 2178—2182).

Dithiocarbazinic Acid. II. SIMA M. LOSANITCH (*Glas. Acad. Sci. Belgrade*, 1922, **103**, 1—9).—In a previous communication (T., 1921, **119**, 763), it was shown that the dithiocarbazates decompose slowly when heated in aqueous or alcoholic solution, yielding hydrogen sulphide, ammonium sulphide, ammonia (or an amine), sulphur, and a white, crystalline product of acid reaction. This decomposition yields in the beginning hydrogen sulphide, semithiocarbazide, and thiocarbazide. Subsequently, the products of the first decomposition interact with the dithiocarbazinate and form ammonia and thiodisemithiocarbazide,



The latter product then suffers transformation into the white, crystalline acid product mentioned in the first communication. For this compound the author suggests the constitution $\text{S}[\text{C}(\text{SH}) \cdot \text{N} \cdot \text{NH}_2]$, or $\text{S}(\text{C} \begin{smallmatrix} \text{N} \\ \text{S} \end{smallmatrix} \text{NH}_3)_2$, whilst Busch, who obtained it previously, regarded it as a derivative of thiodiazole of the formula



It forms colourless needles and plates, decomp. about 170° , m. p. 225° , and is soluble in water, less so in alcohol. With methyl iodide, it yields a *dimethyl* ester, colourless crystals, m. p. 136 — 137° . It also forms a mono-, di-, and poly-sulphide. The disulphide has been already described by Ziegele (A., 1899, i, 827). The *monosulphide* is formed if the aqueous or alcoholic solution of the acid is boiled; it crystallises in yellow needles, m. p. 178° (decomp.), and forms salts with bases. The salts of the alkalis and ammonium are soluble in water; those of the heavy metals insoluble. The ammonium salt yields with methyl iodide the *monosulphide methyl* ester, a white substance, soluble in alcohol; m. p. 71° . The *polysulphide*, ($\text{C}_4\text{H}_4\text{N}_4\text{S}_7$), is formed together with the disulphide by the method employed by Ziegele (*loc. cit.*); it is insoluble even in boiling alcohol, forms yellow crystals, m. p. 186° , and is not identical with the polysulphide ($\text{C}_2\text{H}_2\text{N}_2\text{S}_3$) described by Ziegele. S. S. M.

The Cyanine Dyes. VI. Dyes containing a Quinoline and a Benzothiazole Nucleus. The Thioisocyanines. WALTER THEODORE KARL BRAUNHOLTZ and WILLIAM HOBSON MILLS (T., 1922, **121**, 2004—2008).

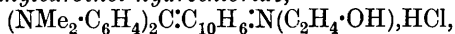
Formation of Triphenylpararosaniline Hydrochloride from Diphenylamine and Chloralammonia. RIKI HORIUCHI (*Mem. Coll. Sci. Kyōtō*, 1921, **5**, 1—7).—The small yield of triphenylpararosaniline hydrochloride obtained by heating diphenylamine and chloralammonia directly at 130° , is greatly increased by maintaining the temperature at 100° for some time prior to heating at 130° . The author has investigated the reaction of diphenylamine with various compounds containing CCl_3 and CHO groups, respectively, and concludes that compounds containing the former

group are alone concerned in the formation of diphenylamine-blue, the chlorine atoms being replaced by the phenyl group, and the resulting product reacting with part of the hydrogen chloride produced.

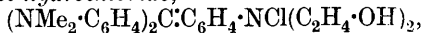
J. S. G. T.

Preparation of New Triarylmethane Colouring Matters.

BRITISH DYESTUFFS CORPORATION, LTD., ARTHUR GEORGE GREEN, KENNETH HERBERT SAUNDERS, and STANLEY CHARLES BATE (Brit. Pat. 185612).—New triarylmethane dyes containing an hydroxyalkyl group attached to nitrogen are obtained by condensing Michler's ketone or Michler's hydrol with an arylhydroxyalkylamine, an aryl dihydroxyalkylamine, an arylalkylhydroxyalkylamine, or an arylaralkylhydroxyalkylamine, and, where the hydrol is used, oxidising the leuco-compound first produced to the dyestuff in the usual way. For example, *tetramethylethanoltriaminodiphenyl naphthylcarbinol hydrochloride*,



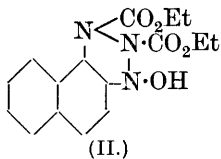
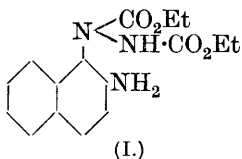
is obtained by adding 23 parts of α -naphthylethanolamine to the product of the action of 20 parts of phosphorus oxychloride on 30 parts of tetramethyldiaminodiphenyl ketone in presence of toluene as diluent. The dye crystallises on cooling in green crystals, which have the same properties as Victoria-Blue-R except that the solubility is much superior. *Tetramethyldiethanoltriaminotriphenylcarbinol hydrochloride*,



prepared from Michler's hydrol and diethanolaniline, and subsequent oxidation of the resulting leuco-compound with lead peroxide, is a coppery powder which dyes tanned cotton bright purple shades. Other shades of purple are obtained by substituting for the diethanolaniline other hydroxyalkylarylamines such as ethanolaniline, diethanol-*o*-toluidine, etc.

G. F. M.

The Structure of the Compounds Obtained by the Oxidation of the Additive Products of β -Naphthylamine and Azocarbonates. OTTO DIELS and HARALD WACKERMANN (*Ber.*, 1922, 55, [B], 2443—2450).—The additive compound of β -naphthylamine and ethyl azodicarboxylate (annexed formula I) has been observed to be converted by oxidation into a yellow compound to which the formula II

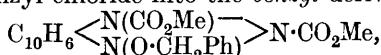


amine and ethyl azodicarboxylate (annexed formula I) has been observed to be converted by oxidation into a yellow compound to which the formula II

has been assigned (cf. A., 1921, i, 280). The correctness of the second formula is established by a series of experiments starting from the corresponding methyl ester.

The compound $\text{C}_{10}\text{H}_6 \begin{smallmatrix} \text{N}(\text{CO}_2\text{Me}) \\ \text{N}(\text{OH}) \end{smallmatrix} > \text{N} \cdot \text{CO}_2\text{Me}$, brownish-yellow prisms, m. p. 117° (decomp.), is prepared by the addition of hydrogen peroxide to a hot solution of the additive compound of β -naphthylamine and methyl azodicarboxylate in glacial acetic acid. The presence in it of a mobile hydrogen atom is established

by the formation of an additive *compound*, $C_{18}H_{18}O_8N_4$, m. p. 138° , with carbethoxycarbimide and by its conversion by potassium ethoxide and benzyl chloride into the *benzyl* derivative,



colourless crystals, m. p. 187° . Cautious treatment of the product of the oxidation of the methyl or ethyl ester with dilute alkali hydroxide solution causes hydrolysis, loss of carbon dioxide, and formation of the *acid*, $C_{10}H_6 \begin{array}{c} \text{NH} \\ \text{N}(\text{OH}) \end{array} \text{N}\cdot\text{CO}_2\text{H}$, pale yellow needles,

m. p. 128° ; the alternative formula, $C_{10}H_6 \begin{array}{c} \text{N}(\text{CO}_2\text{H}) \\ \text{N}(\text{OH}) \end{array} \text{NH}$, is excluded since the acid does not immediately lose water and carbon dioxide with the formation of 1 : 2-azimidonaphthalene. The latter substance, m. p. $178\text{--}179^\circ$, is, however, produced when the acid is treated with methylamine (40%).

A similar conclusion is drawn from an attempt to obtain the methyl ether of the oxidation product by means of diazomethane; normal methylation appears to take place in the first instance, but the methyl ether is unstable, immediately losing carbon dioxide and, presumably, dimethyl ether with consequent formation of *methyl* $\alpha\beta$ -aziminonaphthalenecarboxylate, $C_{10}H_6 \begin{array}{c} \text{N}(\text{CO}_2\text{Me}) \\ \text{N} \end{array} \text{N}$, pale, reddish-brown prisms, m. p. $132\text{--}133^\circ$; the identity of the latter compound is established by its production from azimino-naphthalene and methyl chloroformate in the presence of benzene and pyridine.

H. W.

Addition of Azoimide at Contiguous Double Linkings.
VIII. 5-Anilino-1-phenyltetrazole and the Azide of Dithiocarbamic Acid. E. OLIVERI-MANDALÀ (*Gazzetta*, 1922, 52, ii, 139—144; cf. A., 1913, i, 961).—The action of azoimide on carbodiphenyldi-imide yields 5-anilino-1-phenyltetrazole, $\text{N} \begin{array}{c} \text{N}\cdot\text{NPh} \\ \text{N}:\text{C}\cdot\text{NPh} \end{array}$, which forms slender, white, acicular crystals,

m. p. 162° , and yields an *acetyl* compound, m. p. 87° , and a *silver* derivative, $C_{13}H_{10}N_5\text{Ag}$. This compound, which is undoubtedly formed by way of the azide, $\text{NPh}\cdot\text{C}\cdot\text{NPh} + \text{N}_3\text{H} \rightarrow \text{NPh}\cdot\text{C}(\text{N}_3)\cdot\text{NPh} \rightarrow C_{13}H_{11}N_5$, is identical with that obtained by Busch and Bauer (A., 1900, i, 414) by the action of nitrous acid on aminodiphenylguanidine and regarded by these authors as phenyliminophenyldihydropyrazole, $\text{N} \begin{array}{c} \text{N}-\text{NPh} \\ \text{NH}\cdot\text{C}\cdot\text{NPh} \end{array}$; from its mode of preparation, its

marked stability towards concentrated solutions of acids and bases, and its formation of an acetyl derivative, the compound must, however, be regarded as a tetrazole derivative, although it is not improbable that in the formation of salts it may undergo transformation into the phenyliminophenyltetrazolone. When heated above its melting point, 5-anilino-1-phenyltetrazole decomposes, yielding carbylamine, azoimide, and 1-phenyltetrazole, m. p. 65° (Freund and Paradies, A., 1901, i, 770; Oliveri-Mandalà and

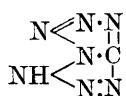
Alagna, A., 1911, i, 243), the last resulting from the interaction of the phenylcarbylamine and azoimide.

Azoimide combines also with carbon disulphide giving an explosive *compound*, which corresponds in behaviour with the azides of thiocarbamic acids and has probably the structure, $\text{SH}\cdot\text{CS}\cdot\text{N}_3$. It forms a *sodium* salt, $\text{CN}_3\text{S}_2\text{Na}$, and when heated gently with dilute hydrochloric acid decomposes losing two atoms of nitrogen and one atom of sulphur, $\text{SH}\cdot\text{CS}\cdot\text{N}_3 \rightarrow \text{S} \begin{smallmatrix} \diagup \\ \text{N} \end{smallmatrix} \text{C} \cdot \text{SH} \rightarrow$

$\text{HS}\cdot\text{C}\equiv\text{N}$, and, if concentrated solutions are used, yields the insoluble, yellow compound, $\text{C}_2\text{H}_2\text{N}_2\text{S}_3$, obtained on decomposition of aqueous thiocyanic acid solutions. Some of the salts of the explosive azide were prepared by Sommer (A., 1916, ii, 29).

The above results, together with those published in the author's previous papers, show (1) that with carbylamines, ketens, esters of isocyanic and thiocyanic acids, carbodiphenyldi-imide and carbon disulphide, which contain two contiguous double linkings, azoimide readily unites, the triazo-group becoming attached always to the carbon atom and the hydrogen to the nitrogen atom; that, in the first two cases, integral addition of the azoimide molecule at the double linking may result in the formation of tetrazole derivatives. (2) That the unsaturated groupings, $\cdot\text{N}:\text{C}(\text{N}_3)\cdot$ and $:\text{C}:\text{C}(\text{N}_3)\cdot$, undergo rapid isomerisation to the corresponding heterocyclic compounds, $\text{N} \begin{smallmatrix} \diagup \text{N} \cdot \text{C} \\ \diagdown \text{N} \cdot \text{N} \end{smallmatrix}$ and $\text{N} \begin{smallmatrix} \diagup \text{N} \cdot \text{C} \\ \diagdown \text{N} \cdot \text{C} \end{smallmatrix}$. The only known compound

of this type with which isomerisation of the triazo-group does not occur is vinylazoimide (Forster and Newman, T., 1910, 97, 2570), which does not undergo isomeric change to *isotriazole*. On account of the ease with which the three nitrogen atoms, even when forming part of a nucleus, are eliminated as azoimide, the compound described by Thiele and Ingle (A., 1896, i, 107) as tetrazylazoimide



must be regarded as composed of two tetrazole nuclei (annexed formula). (3) That diphenylcarbodi-imide reacts more readily than phenylcarbimide with azoimide. This is in accordance with the observations of Staudinger and Meyer (A., 1920, i, 228), who

found that replacement of the carbonyl group in $\text{NPh}:\text{C}:\text{O}$ by $:\text{C}:\text{NPh}$ causes marked increase in the reactivity. T. H. P.

The Influence of Hydrogen-ion Concentration on the Solubility of Uric Acid. A. JUNG (*Helv. Chim. Acta*, 1922, 5, 688—702).—Experiments were made to determine whether slight changes in the degree of acidity in the neighbourhood of the neutral point, such as can be obtained by the use of buffer systems, have any influence on the solubility of uric acid. It is found that the influence is considerable. The solubility is lowest with low p_{H} values, that is, in acetate mixtures, and highest in phosphate and borate mixtures. It rises from 0.59 gram per litre at p_{H} 7.09 to 1.54 grams per litre at p_{H} 7.6, and continues to rise rapidly above this p_{H} value. It appears probable that the character of the anion in the buffer salt has a chemical influence; complex

salts may be formed, for instance, between the uric acid and borates or phosphates. In the case of all solutions having a p_H value higher than 7.6, when the saturated solution was kept for fourteen days almost the whole of the uric acid was precipitated. This precipitate may be a complex salt or may be sodium biurate precipitated through decomposition of a complex compound. Uric acid is completely precipitated from solution by animal charcoal, and since at the same time there is generally a slight fall in the p_H value of the solution, it appears that uric acid salts are adsorbed by the charcoal.

E. H. R.

Preparation of Carboxylic Acids of the Purine Series.

E. MERCK, OTTO WOLFES, and ERICH KORNICK (D.R.-P. 352980; from *Chem. Zentr.*, 1922, iv, 160—161).—Salts of mono- or dialkylated xanthines are treated with salts of monohalogenated aliphatic carboxylic acids. By heating sodium theobromine in aqueous alkaline solution with monochloroacetic acid, *theobromine-1-acetic acid* is obtained as colourless crystals, m. p. 260°. Theophylline and monochloroacetic acid give *theophylline-7-acetic acid*, crystals, m. p. 271° (corr.). 3-Methylxanthineacetic acid forms needles, m. p. 306° (decomp.). Sodium 3-methylxanthine and β -iodopropionic acid give *3-methylxanthinepropionic acid*, lustrous leaflets, m. p. 308—309° (decomp.). The *N*-alkyl-carboxylic acids of mono- and di-alkyl xanthines and their salts have therapeutic uses.

G. W. R.

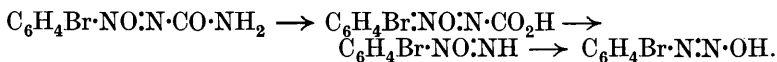
Azoxyamides and Diazo-compounds. A. PIERONI (*Gazzetta*, 1922, 52, ii, 32—43).—Since only one phenylazocarbonamide is obtainable from phenylazocarbonamide, although Angeli's results (A., 1916, i, 679) indicate that two isomerides should exist, the author has investigated *p*-bromo- and *p*-nitro-phenylazocarbonamides and the corresponding azoxy-derivatives. For the preparation of these azocarbonamides, Widman's general method (A., 1895, i, 603) yields unsatisfactory results. *p*-Bromophenylazocarbonamide may, however, be obtained by diazotising *p*-bromoaniline, treating the diazonium salt with aqueous potassium cyanide solution, and treating the nitrile thus formed in moist ethereal solution with a current of hydrogen chloride; under these conditions, the nitrile unites with a molecule of water. The compounds thus obtained, namely, *p*-bromo-, *p*-nitro-, and 2:4-dibromophenylazocarbonamides, and *p*-bromo- and *p*-nitro-phenyldiazonitriles, were subjected to the action of hydrogen peroxide in acetic acid solution. Of the azoxyamides prepared in this way, none could be obtained in two isomeric forms, and the method of formation and also the behaviour indicate in all cases the formula $O:NR:N\cdot CO\cdot NH_2$; that they are not more complex compounds is shown by their cryoscopic behaviour. The constitution of *p*-bromophenylazoxycarbonamide is confirmed by the readiness with which it is reduced, by means of zinc dust and acetic acid, to the original azocarbonamide. Treatment of aqueous *p*-bromophenylazoxycarbonamide with an alkaline solution of potassium hypobromite

and subsequently with β -naphthol results in evolution of gas and formation of bromophenylazo- β -naphthol-red.

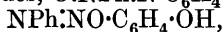
The fact that *p*-bromo- and *p*-nitro-benzodiazonitriles are oxidised by hydrogen peroxide in acetic acid solution, yielding mainly the corresponding azoxyamides, indicates that the action of hydrogen peroxide on *p*-chlorobenzodiazonitrile proceeds, not in the manner supposed by Bamberger and Baudisch (A., 1912, i, 733), but in the two stages described by Angeli (*loc. cit.*): $C_6H_4Cl \cdot N \cdot N \cdot CN + H_2O_2 = C_6H_4Cl \cdot NO \cdot N \cdot CN + H_2O$ and $C_6H_4Cl \cdot NO \cdot N \cdot CN + H_2O = C_6H_4Cl \cdot NO \cdot NOH + HCN$.

Under the ordinary experimental conditions, 2:4-dibromophenylazocarbonamide is not oxidised to the corresponding azoxy-derivative by hydrogen peroxide, and no azoxy-compound has been obtainable from benzoylazo-*p*-bromobenzene.

All the azoxyamides obtained exhibit close analogy to aromatic diazo-compounds. In slightly alkaline solution, they react with β -naphthol to give the corresponding benzeneazonaphthols, and they also react in alkaline solution with pyrrole and its derivatives, with phenols, with ethyl acetoacetate, and with nitroethane. With saturated aqueous potassium hydroxide solution, the *p*-bromo-azoxyamide reacts in accordance with the scheme:



Since the two isomerides, $O \cdot NPh \cdot N \cdot C_6H_4 \cdot OH$ and



yield the compound $NPh \cdot N \cdot OH$ as final product when oxidised with permanganate, and since also the nitrosoamine of phenyl-carbamide, $NH_2 \cdot CO \cdot NPh \cdot NO$, which is isomeric with phenylazoxycarbonamide, reacts in alkaline solution with β -naphthol like diazo-derivatives and azoxyamides, giving phenylazonaphthol, the existence of the two isomerides $O \cdot NPh \cdot NH$ and $NPh \cdot NH \cdot O$ may be assumed. The normal diazotates will therefore be represented by the general formulæ $O \cdot NR \cdot NH$ and $NR \cdot NH \cdot O$ (cf. Angeli, A., 1916, i, 679), and the behaviour of these compounds is explained better by the presence of conjugated double linkings than by Hantzsch's view that normal and iso-diazotates are spacial isomerides of the formula, $NR \cdot N \cdot OH$.

Phenylazoxycarbonamide, $O \cdot NPh \cdot N \cdot CO \cdot NH_2$, forms long needles, m. p. 150° (decomp.), reddening in the air, and exhibits normal cryoscopic behaviour in acetic acid solution.

2:4-Dibromophenylazocarbonamide, $C_6H_3Br_2 \cdot N \cdot N \cdot CO \cdot NH_2$, crystallises in long, orange-yellow, silky needles, m. p. 194° .

p-Bromophenylazocarbonamide, $C_6H_4Br \cdot N \cdot N \cdot CO \cdot NH_2$, forms crystals, m. p. 175° (decomp.).

p-Bromophenylazoxycarbonamide, $C_6H_4Br \cdot NO \cdot N \cdot CO \cdot NH_2$, crystallises in pale yellow needles, m. p. 201° (decomp.).

p-Nitrophenylazoxycarbonamide, $C_7H_6O_4N_4$, forms pale yellow needles, m. p. 203° (decomp.), and readily undergoes change owing to the presence of the nitro-group, which tends to expel the less highly negative and less stable azoxy-group. With β -naphthol in

alkaline solution, the amide readily reacts with formation of the deep red *p*-nitrophenylazo- β -naphthol.

Potassium p-bromobenzeneazoxycarboxylate, $C_6H_4Br \cdot NO \cdot N \cdot CO_2K$, is a yellow, crystalline compound, but could not be obtained pure, as it readily undergoes alteration. T. H. P.

Certain Salts with para-, ortho-, and meta-Quinonoid Structure. III. R. CIUSA and G. RASTELLI (*Gazzetta*, 1922, 52, ii, 121—125; cf. A., 1920, i, 256; 1921, i, 63).—The authors have completed the optical investigation of *p*- and *o*-nitrophenylhydrazones and the corresponding alkali metal salts.

The *monosodium* salt of *pyruvic acid p-nitrophenylhydrazone*, $CO_2Na \cdot CMe \cdot N \cdot NH \cdot C_6H_4 \cdot NO_2$, forms lustrous, pale yellow scales; the *monopotassium* salt, similar scales; the *disodium* salt, small, violet crystals, and the *dipotassium* salt, small, violet needles. All these salts yield the original hydrazone on hydrolysis.

Pyruvic acid o-nitrophenylhydrazone forms yellow needles, m. p. 221° , the *mono-sodium* and *potassium* salts yellow scales, and the *di-sodium* and *potassium* salts blue crystals with metallic lustre; these salts also give the original hydrazone when hydrolysed.

Solutions of these quinone-nitronic acids are moderately stable, and in the experimental conditions employed obey Beer's law sufficiently well. Spectrographic examination shows that the salification is accompanied by profound structural change; the benzenoid form of benzaldehyde-*p*-nitrophenylhydrazone is altered to a para-quinonoid structure, the characteristic band at 2100, which is shown by ordinary quinone, becoming evident. Similarly, pyruvic acid *p*-nitrophenylhydrazone and its monometallic salts are benzenoid, and its dimetallic salts quinonoid, in character. The *o*-nitrophenylhydrazones exhibit the same behaviour.

T. H. P.

Certain Salts with para-, ortho-, and meta-Quinonoid Structure. IV. R. CIUSA and G. RASTELLI (*Gazzetta*, 1922, 52, ii, 126—128; cf. preceding abstract).—The action of methyl iodide on the potassium salt of benzaldehyde-*p*-nitrophenylhydrazone yields, not a quinonoid methyl ether of the hydrazone, but *benzaldehyde-p-nitrophenylmethylhydrazone*, $CHPh \cdot N \cdot NMe \cdot C_6H_4 \cdot NO_2$, which separates in either red or canary-yellow crystals, m. p. 131° , yields *as-p*-nitrophenylmethylhydrazine on hydrolysis, exhibits an absorption spectrum similar to that of benzaldehyde-*p*-nitrophenylhydrazone, and in acetone solution gives no coloration with alkali.

as-p-Nitrophenylmethylhydrazine, $NH_2 \cdot NMe \cdot C_6H_4 \cdot NO_2$, forms yellowish-brown, acicular crystals or silky, yellow needles, m. p. 156° , reduces Fehling's solution, gives a silver mirror with ammoniacal silver nitrate, and condenses with aldehydes and ketones to the corresponding hydrazones. This constitution was suggested by Charrier (A., 1915, i, 905) for a compound, m. p. 142° . The hydrazine forms a *picrate*, $NH_2 \cdot NMe \cdot C_6H_4 \cdot NO_2 \cdot C_6H_3O_7 \cdot N_3$, m. p. 131° (decomp.), and with ferric chloride solution yields a small proportion of a *compound*, m. p. 145 — 146° , which is possibly the corresponding tetrazone.

Pyruvic acid as-p-nitrophenylmethylhydrazone forms both red and yellow modifications, m. p. 153°. T. H. P.

Protein Precipitants. ALMA HILLER and DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1922, **53**, 253—267).—With the object of ascertaining the extent to which proteins and protein products are precipitated by different protein precipitants, the action of a number of these substances both on blood and Witte's peptone has been studied. The results with the latter substance indicate that tungstic acid and picric acid precipitate protein intermediate products relatively completely without precipitating the amino-acids; trichloroacetic acid removes proteins only, nearly all the protein products passing into the filtrate; whilst metaphosphoric acid, colloidal iron, and mercuric chloride occupy an intermediate position with regard to their action on protein products. With blood, all the substances studied removed proteins completely, and all, with the exception of alcohol, allowed similar amounts of amino-acids to pass into the filtrates. The recovery of added mixed monoamino-acids was, however, incomplete in the cases of metaphosphoric acid and alcohol. E. S.

The Colloidal Behaviour of Serum Globulin. DAVID I. HITCHCOCK (*J. Gen. Physiol.*, 1922, **5**, 35—44).—The globulin of ox serum behaves stoichiometrically as an amphoteric electrolyte, like other proteins which have been investigated, such as gelatin. The potential differences and osmotic pressures across membranes separating acid solutions of this protein from water are largely explicable by Donnan's theory of membrane equilibrium. W. O. K.

Effect of Acids and Alkalis on some Chemical and Physical Properties of Hæmoglobin. G. QUAGLIARIELLO (*Arch. Sci. biol.*, 1921, **2**, 423—472; *Ber. ges. physiol.*, 12, 82—83; from *Chem. Zentr.*, 1922, iii, 52—53).—The author has studied the effect of lactic acid, hydrochloric acid, and sodium hydroxide on the surface tension of protein solutions, and in particular of hæmoglobin solutions, by stalagmometric measurements. The effect of lactic acid is similar to that of hydrochloric acid. Both acids and alkali exert the same effect on hæmoglobin solutions as on solutions of other proteins. No evidence was found for an aggregation of the hæmoglobin molecule. The surface tension, like the solubility, osmotic pressure, viscosity, and swelling power, shows a minimum at the isoelectric point, all these properties being connected with the degree of dissociation of the ampholyte. The free ions are hydrated more easily than the molecules. The marked depression of the surface tension at the isoelectric point appears abnormal, since the less stable is a colloidal solution the more does the surface tension approach that of the solvent. The lowering in concentration consequent on molecular aggregation must be balanced by increased surface activity. G. W. R.

Hæmocyanin. VI and VII. The Action of some Gases on Hæmocyanin. CH. DHÉRE and A. SCHNEIDER (*J. physiol. path. gén.*, 1922, **20**, 1—13; 34—40).—An examination of the action of

hydrogen, nitrogen, carbon dioxide, carbon monoxide, nitric oxide, methane, acetylene, and ethylene on hæmocyannin. The oxy-hæmocyannins from the various species used are as easily and rapidly reduced by treatment with an inert gas at 15° to 20° as by a vacuum at 40°. Hæmocyannin forms with nitric oxide a crystallisable, green pigment which is less unstable than oxyhæmocyannin. Reduced hæmocyannin at 20° does not form coloured compounds with methane, ethylene, or acetylene.

CHEMICAL ABSTRACTS.

Preparation and Analysis of Animal Nucleic Acid. P. A. LEVENE (*J. Biol. Chem.*, 1922, **53**, 441—447).—The author's method (A., 1921, i, 821) for the preparation of animal nucleic acid has been improved. The ground glands (10 lb.) are boiled for thirty-five minutes with 5 litres of water containing 250 grams of sodium hydroxide. The mixture is then neutralised with acetic acid, treated with a colloidal solution (50 c.c.) of iron, filtered, and left over-night. Addition of a double volume of methyl alcohol containing 2% of hydrochloric acid precipitates the nucleic acid. The method has been applied to thymus gland, spleen, kidney, pancreas, and liver. In the latter case, the product contains considerable amounts of glycogen and must be further purified. Nucleic acids from the above organs have the same elementary composition, which corresponds with that of a hexose tetranucleotide. Estimations of the purine bases also agree with the tetranucleotide theory. E. S.

Some Properties of Dialysed Gelatin. DOROTHY JORDAN LLOYD (*Biochem. J.*, 1922, **16**, 530—540).—The influence of hydrochloric acid, sodium hydroxide, and sodium chloride on the gelling power of gelatin purified by dialysis at the isoelectric point (cf. A., 1920, i, 452, 895) has been followed. For comparative purposes, the minimum concentration of gelatin necessary to produce a gel after keeping for forty-eight hours at 15° has been taken as an inverse measure of the gelling power. Under these conditions, pure gelatin requires a minimum concentration of 0.8% to form a gel. Hydrochloric acid decreases the gelling power, the diminution passing through a maximum at P_H 2—3 and again beyond P_H 0.7. Sodium hydroxide slightly decreases the gelling power between P_H 10—12, and completely prevents gelation above P_H 12. Neutral salts diminish the influence of hydrogen ions on gelling power; no other simple relationship between sodium chloride content and gelling power appears to exist.

The influence of hydrochloric acid, sodium hydroxide, and sodium chloride on the production of turbid gels, and the effect of temperature on the optical rotation of gelatin have also been studied. Finally, the theory of gelation is discussed. E. S.

Thermal Expansion of Gelatin Gels. ALAN TAFFEL (T., 1922, **121**, 1971—1984).

Saccharase. E. CANALS (*Bull. Soc. chim.*, 1922, [iv], **31**, 921—928; cf. Tribot, A., 1909, i, 73).—An attempt to verify the author's hypothesis that magnesium behaves as a catalytic agent

with regard to saccharase in a manner analogous to that of manganese with regard to oxydases. Analysis of saccharases from various sources shows that all specimens contain a considerable proportion of magnesium and of phosphoric acid, similar results being obtained from a filtered solution made from each specimen. Other substances found in the ash are potassium, sodium, iron, aluminium, calcium, chlorine, and sulphur (as sulphate), but in some cases one or more of these elements are missing or present only in traces. The magnesium and phosphate content when examined quantitatively shows wide variation.

H. J. E.

A Silver Compound of Saccharase. H. VON EULER and K. JOSEPHSON (*Ber.*, 1922, **55**, [B], 2416—2420).—Previous investigations on the inactivation of saccharase by silver salts (Euler and Svanberg, A., 1921, i, 68, 202; Euler and Myrbäck, this vol., i, 693) have made it very probable that a compound of saccharase and silver is formed; such a product has now been isolated in a somewhat impure condition.

A saccharase solution is concentrated in a vacuum until it is approximately 1% and treated with an excess of silver nitrate; after some hours, the solution becomes brown, but remains clear. Addition of concentrated alcohol causes the separation of a brown precipitate which can be readily removed by centrifuging; it is purified by solution in water and re-precipitation with alcohol. It contains approximately 50% of carbohydrates, which are derived mainly from the original yeast. Analysis of the product gives silver 2.5%, phosphorus 0.81%, nitrogen 4.5%, carbon 41.5%, hydrogen, 7.6%, and oxygen 43.1%. It is remarkable that the atomic ratio of phosphorus to silver is 1 : 1. This is in agreement with the value deduced from the experiments of Euler and Myrbäck (*loc. cit.*).

H. W.

The Inactivation of Saccharase by Iodine. H. VON EULER and STURE LANDERGREN (*Biochem. Z.*, 1922, **131**, 386—389).—Addition of iodine in potassium iodide solution to two different saccharase preparations of different activity reduced the activity to one-half. Sodium thiosulphate cannot reactivate the saccharase.

H. K.

Effect of Filtration on Amylases. JEAN EFFRONT (*Compt. rend. soc. Biol.*, 1922, **86**, 271—273; from *Chem. Zentr.*, 1922, iii, 177; cf. this vol., i, 184).—Ptyalin retained from saliva by filter-paper cannot be removed by water or by sugar solution. It is removable, however, in the presence of sodium chloride or starch paste. This absorption increases with rise of temperature and affects, not only diastases, but also inhibitory substances accompanying them. Diastases may thus be purified by filtration. Many inactive plant juices may be activated by filtration.

G. W. R.

Characteristic Properties of Amylases of Different Origin. JEAN EFFRONT (*Compt. rend. soc. Biol.*, 1922, **86**, 274—275; from *Chem. Zentr.*, 1922, iii, 177; cf. preceding abstract).—Amylases

of animal origin, from bacteria, and from seeds are readily isolated by maceration. Amylases from green plant materials are isolated with difficulty, but more readily in the presence of sodium chloride or starch paste. Animal amylases, and amylases from germinated seeds quickly form sugar from starch grains, 72—74% being changed within an hour. Amylases from resting seeds and from vegetative portions of plants are less active. The optimum temperature for animal and bacterial amylases and for amylases from vegetative portions of plants is 40°. For amylases of certain germinated seeds, the optimum temperature is 60°. Resistance to heat and chemical effects (acids) varies with origin. G. W. R.

The Asymmetric Action of Emulsin in the Benzaldehyde-cyanohydrin Synthesis. E. NORDEFELDT (*Biochem. Z.*, 1922, **131**, 390—410; cf. this vol., i, 66).—The author has made a detailed examination of the most favourable conditions for the formation of optically active cyanohydrin and records some properties of emulsin. For the production of optically active cyanohydrin, emulsin is necessary. With small quantities of emulsin, there is proportionality between the rotation attained and the amount of emulsin present, but with larger quantities the rotation rises more slowly than would be expected. The *d*-cyanohydrin is labile and its rotation falls off spontaneously. This velocity of autoracemisation increases with rise of temperature and with increasing acidity within the range P_H 3 to 6.5. At the neutral point the velocity of racemisation equals the velocity of formation of the cyanohydrin and the product is inactive. H. K.

Mechanism of Action of Oxidising and Reducing Ferments. F. BATELLI and L. STERN (*Arch. internat. Physiol.*, 1921, **18**, 403—418; *Ber. ges. Physiol.*, 1922, **11**, 431—432; from *Chem. Zentr.*, 1922, i, 1203—1204).—Ferments are divided into three groups, according to the behaviour of the ions of water to the substrate, namely hydratases, for example, the ferment concerned in the reversible change fumaric acid to maleic acid; hydrolases producing esterification or hydrolysis; and oxydoreductases in which the hydrogen and hydroxyl ions of water give reduction and oxidation products respectively. Catalase is regarded as an oxydoreductase. G. W. R.

The Action of Poisons on Enzymic Processes. VII. Metal Catalysis and Catalase Action. VIII. The Volumetric Method for the Estimation of Catalase. C. G. SANTESSON (*Skand. Arch. Physiol.*, 1922, **47**, 129—181, 191—208).—VII.—The amount of catalyst is of importance when the material acted on is constant; colloidal metals in minute amounts are often ineffective. Frog muscle catalase shows similar properties, although not so regularly; the effective amount of catalase may be of the order 0.06 mg. A low temperature (0.6—0.9°) markedly decreases the evolution of oxygen caused by colloidal silver; heating the solution also inhibits its activity. Muscle catalase is similarly affected. The effect of a series of ions on the activity of colloidal silver and muscle catalase is widely different in the two cases.

VIII.—A criticism of the methods available for the determination of catalase activity. The use of 0.211% (0.062*N*) hydrogen peroxide is preferred.

CHEMICAL ABSTRACTS.

The Anaerobic and Aerobic Oxidation of Xanthine and Hypoxanthine by Tissues and by Milk. E. J. MORIAN, C. P. STEWART, and F. G. HOPKINS (*Proc. Roy. Soc.*, 1922, [*B*], **94**, 109—131).—Milk and certain animal tissues contain a catalytic system which can bring about the rapid oxidation of xanthine and hypoxanthine to uric acid either anaerobically in the presence of methylene-blue (which is thereby reduced), or aerobically in its absence. The action of the enzyme is highly specific; thus, neither guanine, caffeine, theobromine, uracil, thymine, cytosine, nor histidine is able to induce the reduction of methylene-blue in milk. Adenine does so slowly, but this is due to the presence of adenase, which converts the adenine into hypoxanthine. Under anaerobic conditions uric acid is produced at the same rate from both xanthine and hypoxanthine; when aerobic conditions prevail, however, the time required for the complete conversion of hypoxanthine into uric acid is twice that necessary in the case of xanthine. This is probably due to the fact that the system is homogeneous in the former, and heterogeneous in the latter, case. With moderate concentrations of base present the oxidation proceeds at a linear rate.

E. S.

Enzyme Action. XXIII. Homo- and Hetero-lytic Enzymes. HENRY E. ARMSTRONG (*Proc. Roy. Soc.*, 1922, [*B*], **94**, 132—133).—The author considers that the conversion of xanthine and hypoxanthine into uric acid by the milk enzyme (cf. preceding abstract) is a hydrolytic change. The action of the enzyme differs from that of ordinary hydrolytic enzymes, which induce the distribution of the elements of water between two sections of a single molecule, in that these elements are distributed between two distinct molecules. It is suggested that the terms *homo-* and *hetero-lytic* be used to distinguish between these two classes of enzymes.

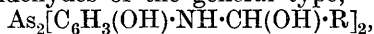
E. S.

Further Experiments on the Isolation of the Antineuritic Vitamin. ATHERTON SEIDELL (*J. Amer. Chem. Soc.*, 1922, **44**, 2042—2051; cf. Seidell, *J. Ind. Eng. Chem.*, 1921, **13**, 1111).—The preparation of the vitamin solution is modified in that, instead of subjecting fresh yeast to autolysis and filtering the thick, slimy liquid thus obtained, the yeast is treated for a few minutes with boiling water and the mixture is then centrifuged. The aqueous solution thus obtained contains a greater proportion of the total vitamin than is present in the filtrate from autolysed yeast, and, in addition, is free from adenine and other products of the autolytic decomposition. The vitamin is adsorbed by fuller's earth from its acid solution (cf. Seidell, *U.S. Public Health Repts.*, 1922, **37**, 801), thus giving an "activated solid" which is extracted with barium hydroxide solution and the barium eliminated by acidifying with sulphuric acid. The extract is subjected to precipitation with

saturated lead acetate solution and filtered. The filtrate is freed from excess of lead by means of hydrogen sulphide and concentrated by distillation under diminished pressure (the treatment with lead acetate prevents the otherwise excessive foaming during distillation). The residue is precipitated successively with silver nitrate and ammoniacal silver nitrate. Approximately one-third of the solids of the extract is precipitated as silver compounds, and these contain somewhat more than one-half of the antineuritic vitamin. The incomplete precipitation of the vitamin base is believed to be due to the considerable solubility of its silver compound.

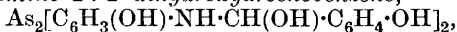
The vitamin fractions are found to be quite stable both in solution and in the dried condition. They dialyse almost completely through a collodion membrane and physiological tests show that all the vitamin is in the diffusate, thus indicating that the vitamin molecule is of relatively simple constitution. Using nitrogen estimations as a criterion of purity, it is concluded that the highly active fractions contain vitamin and one or more analogous nitrogenous bases, and that these cannot be advantageously separated from one another by silver precipitation. H. W.

Condensation Products of Arsphenamine [Salvarsan] with Aldehydes. GEORGE W. RAIZISS and A. C. BLATT (*J. Amer. Chem. Soc.*, 1922, **44**, 2023—2027).—A series of compounds of salvarsan with aldehydes of the general type,



has been prepared by dissolving 3 : 3'-diamino-4 : 4'-dihydroxyarsenobenzene dihydrochloride in methyl alcohol, transformation of the latter into its di-sodium salt by the addition of four molecular proportions of aqueous sodium hydroxide and addition of slightly more than two molecular proportions of the requisite aldehyde. The mixture is in some cases agitated mechanically for two hours in an atmosphere of nitrogen, in others heated under a reflux condenser for a similar period. The product is precipitated by neutralising the solution with hydrochloric acid. The additive compounds are in general solids which vary in colour from yellow to reddish-brown. They cannot be crystallised readily from the customary organic media, and are in general merely washed and dried before being analysed.

The following individual substances are described : 3 : 3'-Bis-o- α -dihydroxybenzylamino-4 : 4'-dihydroxyarsenobenzene,



m. p. 182°, and the corresponding *dihydrochloride*, an orange-yellow substance. 3 : 3'-Bis- α -hydroxy-p-methoxybenzylamino-4 : 4'-dihydroxyarsenobenzene, a yellow powder which softens at 80° and decomposes gradually when further heated. 3 : 3'-Bis-p- α -dihydroxy-m-methoxybenzylamino-4 : 4'-dihydroxyarsenobenzene, from salvarsan and vanillin, a reddish-brown, amorphous solid, m. p. 175—176°. 3 : 3'-Bishydroxymethylamino-4 : 4'-dihydroxyarsenobenzene *dihydrochloride*, $\text{As}_2[\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CH}_2\cdot\text{OH}]_2\cdot 2\text{HCl}$, from salvarsan and formaldehyde, decomp. 185—190°. 3 : 3'-Bis- α -hydroxy-m-nitro-

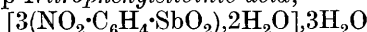
benzylamino-4 : 4'-dihydroxyarsenobenzene, a yellow powder, decomp. 247—250°. 3 : 3'-*Bis- α -hydroxy- γ -phenylallylamino-4 : 4'-dihydroxyarsenobenzene*, $\text{As}_2[\text{C}_6\text{H}_3(\text{OH})\cdot\text{NH}\cdot\text{CH}(\text{OH})\cdot\text{CH}:\text{CHPh}]_2$, from salvarsan and cinnamaldehyde, a yellow powder, decomp. 195—200°. Disodium salvarsan did not give products with benzaldehyde or *p*-chlorobenzaldehyde which were sufficiently pure for analysis.

H. W.

A Sulphonated Naphthylarsinic Acid. A. ELIZABETH HILL and A. K. BALLS (*J. Amer. Chem. Soc.*, 1922, **44**, 2051—2054).— α -Naphthylarsinic acid, creamy-white needles, m. p. 197°, is prepared conveniently by addition of a diazotised solution of α -naphthylamine to an aqueous solution of sodium arsenite and decomposition of the diazonium product at the atmospheric temperature. It is not affected by dilute or concentrated sulphuric acid, but is readily transformed by the fuming acid (20%) into a *monosulphonic acid*, colourless, somewhat hygroscopic, glistening plates, which remains unchanged below 250° (three *potassium* salts have been prepared). The substance is oxidised readily by alkaline potassium permanganate, but the viscous, yellow, hygroscopic liquid which is thereby obtained could not be purified; it is shown, however, to contain arsenic and sulphur in equal atomic proportion. The position of the sulphonic group in the naphthalene molecule has not been elucidated.

H. W.

***p*-Nitrophenylstibinic Acid.** G. CHARRIER (*Gazzetta*, 1922, **52**, ii, 16—18).—*p*-Nitrophenylstibinic acid,

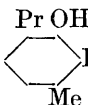


(cf. Schmidt, A., 1920, i, 901), prepared by treating antimony trichloride with *p*-nitrophenyldiazonium chloride and subjecting the additive compound, $\text{NO}_2\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{SbCl}_4$, thus formed (cf. May, T., 1912, **101**, 1037), to the action of sodium hydroxide (cf. Bort, A., 1913, i, 115), forms an amorphous, chrome-yellow powder decomposing, without melting, at about 300°.

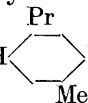
T. H. P.

Mercuriation in the Aromatic Series. II. Thymolmercuriacetates and their Derivatives. EFISIO MAMELI and ANNA MAMELI-MANNESSIER (*Gazzetta*, 1922, **52**, ii, 1—16; cf. this vol., i, 695).—By treating thymol with mercuric acetate under various conditions, the authors have obtained, besides the thymoldimercuriacetate already known (cf. Dimroth, A., 1902, i, 850; Rupp, A., 1917, i, 670; Paolini, A., 1921, i, 902), also the two new compounds, thymol-2- and thymol-6-monomercuriacetates. The constitutions of these compounds are shown by the fact that they yield respectively an internal oxide and an ordinary oxide when treated in alkaline solution, which contains the corresponding hydroxides, with carbon dioxide. Confirmation of these structures is obtained by examining the behaviour of the compounds towards coupling with diazonium salts, Dimroth (*loc. cit.*) having shown that mercury groups in the ortho-position to a phenolic hydroxyl persist, whereas those in the para-position are often displaced by the azo-group. With thymol-6 mercuriacetate, not only is this

displacement observed, but a second azo-group enters in the ortho-position, the resulting compound being 2:6-bisbenzeneazothymol. The action of mercuric acetate on either thymol-2- or thymol-6-mercuriacetate yields thymoldimercuriacetate, which is the 2:6-compound.

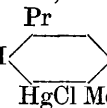
Thymol-2-mercuriacetate,  $\text{Hg}\cdot\text{OAc}$, forms a lustrous,

crystalline, white powder, m. p. 147° on rapid heating, decomposing at 182° . It gives no coloration with ferric chloride, behaves towards sulphuric acid like its para-isomeride, and yields a black precipitate with ammonium sulphide in a few minutes and with hydrogen sulphide only when hydrochloric acid is present.

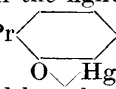
Thymol-6-mercuriacetate,  $\text{Hg}\cdot\text{OAc}$, forms small, lus-

trous crystals, m. p. 163° (bath initially at 150°), decomposing at 178 — 180° . It gives no coloration with ferric chloride, but dissolves in cold concentrated sulphuric acid, yielding a yellow coloration changing to reddish-brown. With benzenediazonium chloride, it gives (1) 2:6-bisbenzeneazothymol, m. p. 181° (cf. Mazzara and Pozzetto, A., 1885, 893; Auwers and Michaelis, A., 1914, i, 744), and (2) a small proportion of a cream-yellow azo-compound, which is possibly 2-benzeneazothymol-6-mercuriacetate.

Thymol-2-mercurichloride, $\text{OH}\cdot\text{C}_6\text{H}_2\text{MePr}\cdot\text{HgCl}$, has m. p. 144 — 145° , and decomposes at about 160° . The 6-isomeride crystallises in slender, white needles, m. p. 188° , and decomposes at 195° .

Thymol-2:6-dimercurichloride,  HgCl , has m. p. 210 —

211° (decomp.).

Thymol-2-mercuribromide forms a white, crystalline powder, contracting at 140° and reddening and subliming at 180° . The *sulphate*, $(\text{OH}\cdot\text{C}_6\text{H}_2\text{MePr}\cdot\text{Hg})_2\text{SO}_4$, is obtained as an amorphous, white powder, which reddens, without melting, at 220° . The *nitrate* forms a pale pink powder, turning violet in the light, m. p. 148 — 150° , decomposing at 155° . The *oxide*,  Me , forms a

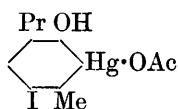
white precipitate, m. p. 195° (decomp.), and has the normal molecular weight in freezing phenol.

Thymol-6-mercuribromide is a white compound, m. p. 149° (decomp.). The *sulphate* forms a white, amorphous powder, decomposing, without melting, at 235° , and dissolves in concentrated sulphuric acid to a yellow solution; careful addition of ferrous sulphate solution to this acid solution gives a wine-red ring or, on shaking, a greenish-blue coloration. The *nitrate* is a white, pulverulent substance with pale pink reflexion, m. p. 167°
pp*

(decomp.), and dissolves in concentrated sulphuric acid to a straw-yellow solution which, with ferrous sulphate solution, gives a blood-red ring or, on agitation, a bluish-violet or intense blue

coloration. The *oxide*, $\left[\begin{array}{c} \text{Pr} \\ \text{OH} \text{---} \text{C}_6\text{H}_3 \text{---} \text{Hg} \text{---} \text{O} \\ \text{Me} \end{array} \right]_2$, forms a white powder, blackens at 180° , decomposes into a gummy mass at about 205° , and exhibits normal cryoscopic behaviour in phenol solution. The *hydroxide* is a white compound, m. p. $190\text{--}195^\circ$ (decomp.). T. H. P.

Mercuriation in the Aromatic Series. III. Mercuriated Derivatives of 6-Iodothymol. EFISIO MAMELI (*Gazzetta*, 1922, 52, ii, 18—23).—The action of mercuric acetate on 6-iodothymol, which has only one free ortho-position with respect to the hydroxyl, readily yields the monomercuri-derivative, 6-iodothymol-2-mercuri-



acetate (annexed formula), from which the corresponding chloride and bromide are obtainable. That the mercuri-group in all these compounds occupies the ortho-position with respect to the hydroxyl is shown by the formation of an internal oxide when the

iodothymolmercurihydroxide is treated with carbon dioxide. The action of iodine in presence of potassium iodide on 6-iodothymol-2-mercuriacetate yields a product identical with aristol; this result confirms the view that the iodine atom in aristol occupies the para-position with respect to the phenolic or quinonic oxygen and that the thymolic groups are united at the ortho-positions to this oxygen, these being the only free positions. Compounds showing the same behaviour as aristol are obtained also by the action of iodine and potassium iodide on thymol-2- and thymol-6-mercuriacetates (see preceding abstract).

6-Iodothymol-2-mercuriacetate forms white crystals, reddening at 170° , m. p. 175° (decomp.), yields 6-iodothymol when heated with concentrated hydrochloric acid, and gives with concentrated sulphuric acid a red coloration changing to green and later to brown. The corresponding *chloride*, $\text{OH} \cdot \text{C}_6\text{HMePrI} \cdot \text{HgCl}$, forms white crystals, turning yellow at 119° , m. p. $122\text{--}124^\circ$; the bromide is a white powder, turning yellow at 102° , m. p. $105\text{--}108^\circ$. The internal *oxide*, $\text{C}_6\text{HMePrI} \text{---} \text{Hg} \text{---} \text{O}$, forms crystals, m. p. $162\text{--}165^\circ$ (decomp.), and exhibits normal cryoscopic behaviour in phenol.

T. H. P.

Mercuriation in the Aromatic Series. IV. Dimercuriated Derivatives of Guaiacol. EFISIO MAMELI (*Gazzetta*, 1922, 52, ii, 23—27).—The action of mercuric acetate on guaiacol yields mono- and di-mercuriacetates in proportions varying with the experimental conditions; the principal product obtained in alcoholic acetic acid solution is guaiacol-4:6-dimercuriacetate. The positions of the two $\text{Hg} \cdot \text{OAc}$ groups are shown by the fact that the

action of nitric acid on this compound yields 4 : 6-dinitroguaiacol (cf. Cousin, A., 1900, i, 179).

With the dimercuriacetate and the corresponding dichloride and dinitrate, the acid residue united to the mercury is replaced with great readiness. For instance, replacement by hydroxyl is effected, not only by sodium hydroxide, but also by water or aqueous alcohol.

A dimercuri-derivative of 5-iodoacetylguaiacol has also been prepared and is being investigated.

Guaiacol-4 : 6-dimercuriacetate, $\text{OMe} \begin{array}{c} \text{OH Hg}\cdot\text{OAc} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_2 \\ \diagdown \quad \diagup \\ \text{Hg}\cdot\text{OAc} \end{array}$, forms white

crystals, and turns yellow and then red, without melting, when heated; by concentrated sulphuric acid it is turned first green and then blue, and by water or aqueous alcohol it is converted into a white, infusible compound which is probably guaiacolmonomercuriacetate.

Guaiacol-4 : 6-dimercurihydroxide-3-oxide, $\text{OMe} \begin{array}{c} \text{OH Hg}\cdot\text{OAc} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_2 \\ \diagdown \quad \diagup \\ \text{O} \quad \text{Hg} \end{array}$, ob-

tained by the action of 5% sodium hydroxide solution on the dimercuriacetate, forms an infusible, heavy, white precipitate and turns brown at 200—210°.

Guaiacol-4 : 6-dimercurichloride, $\text{OMe}\cdot\text{C}_6\text{H}_2(\text{OH})(\text{HgCl})_2$, forms a white, crystalline powder and begins to turn brown, without melting, at 179—180°; the *nitrate*, $\text{OMe}\cdot\text{C}_6\text{H}_2(\text{OH})(\text{Hg}\cdot\text{NO}_3)_2$, is an infusible, white, crystalline compound. T. H. P.

Mercuriation in the Aromatic Series. V. Binary and Ternary Systems relating to Mercuriation. E. MAMELI and G. COCCONI (*Gazzetta*, 1922, 52, ii, 113—120; cf. preceding abstracts).—To explain the mechanism of mercuriation in derivatives of benzene, it has been suggested that the first phase of the reaction consists in the formation of an unstable intermediate compound either by substitution or addition. In order to ascertain if this is really the case in the mercuriation of phenol, the authors have investigated the freezing-point diagrams of the four systems, (1) $\text{Ph}\cdot\text{OH}-\text{Hg}(\text{OAc})_2$, (2) $\text{Ph}\cdot\text{OH}-\text{CH}_3\cdot\text{CO}_2\text{H}$,

(3) $\text{CH}_3\cdot\text{CO}_2\text{H}-\text{Hg}(\text{OAc})_2$,

and (4) the ternary system. The diagram of state of system (1) exhibits a curve corresponding with the separation of phenol and ceasing at the concentration 50% at 17°; this curve indicates the formation of no product of combination. System (2) yields a complete curve which shows that the two components are miscible in the liquid condition and form no compound, and reveals a eutectic at 15.3°. For system (3), only the beginning of the curve corresponding with the separation of acetic acid is realisable. The ternary system is capable of development only for solutions rich in phenol, and is represented by a series of isothermal lines which indicate the formation of no additive product and come to an end

at the saturation curve of mercuric acetate in the phenol-acetic acid mixtures; this curve, separating the regions of saturated and unsaturated solutions, was confirmed by a series of measurements of solubility at 15°. No ternary eutectic point was observed. Further, the system aniline-mercuric acetate, within the limits of solubility of mercuric acetate in aniline, gives no indication of the formation of an additive product.

T. H. P.

Physiological Chemistry.

The Respiratory Exchange in Fresh-water Fish. III. Gold Fish. JOHN ADDYMAN GARDNER, GEORGE KING, and EDWIN BOOTH POWERS (*Biochem. J.*, 1922, **16**, 523—529).—Measurements were made with the apparatus previously described (A., 1914, i, 1149). The consumption of oxygen was roughly proportional to the temperature. Gold-fish require much less oxygen per kilo. than trout, and appear to react to temperature over a wider range. The respiratory quotient showed unaccountable variations. E. S.

Relation between Age and the Concentrations of Protein Fractions in the Blood of the Calf and Cow. PAUL E. HOWE (*J. Biol. Chem.*, 1922, **53**, 479—494).—Estimations of the proteins in calves' blood from birth onwards indicate that the quantity and composition of the blood proteins are dependent on the diet during the first four to six weeks, but are afterwards independent of this factor. E. S.

Nature of the Reducing Substance in Human Blood. EVELYN ASHLEY COOPER and HILDA WALKER (*Biochem. J.*, 1922, **16**, 455—459).—The reducing power of blood is only occasionally increased by hydrolysis (cf. A., 1921, i, 698). In the estimation of dextrose by MacLean's method, the presence of chlorides, bromides, iodides, or citrates inhibits the reduction of the copper carbonate; this action is not shown by sulphates or phosphates. Iodometric methods are not suitable for the estimation of blood sugar. Exercise frequently produces a considerable increase in the concentration of sugar in the blood. E. S.

Isolation of the Coagulating Enzyme from Blood-serum. MAX BLEIBTREU (*Pflüger's Archiv*, 1922, **194**, 318—322; from *Chem. Zentr.*, 1922, iii, 179).—A modification of an earlier method (Bleibtreu and Atzler, A., 1920, i, 783). Serum casein is prepared by the addition of one gram of casein powder to 100 c.c. of ox-serum and precipitation by acetic acid. The precipitate after separation is reduced to a powder. Ten to 12.5 c.c. of 0.2—0.25 *N*-sodium hydroxide solution are added to 10 grams of serum casein in 50 c.c. of water. After addition of 100 c.c. of water

and neutralisation with *N*-hydrochloric acid, 15 c.c. of a diluted solution of "Liq. ferri oxyd. dialys.," 2.5 c.c. of saturated magnesium sulphate solution and half the volume of ethyl alcohol are added. The coagulating enzyme is obtained in the filtrate.

G. W. R.

Electrochemical Study of the Condition of Several Electrolytes in the Blood. B. S. NEUHAUSEN and E. K. MARSHALL, jun. (*J. Biol. Chem.*, 1922, **53**, 365—372).—Electrometric methods have been used to estimate the concentrations of sodium, chlorine, and calcium ions in blood. The results indicate that sodium and chlorine are not bound to any appreciable extent, but are present as in an aqueous solution of sodium chloride and sodium hydrogen carbonate of the same concentration. About 80% of the calcium, however, is in the non-ionised form.

E. S.

The Action of the Phosphate-ion on Blood and Urinary Sugar. H. ELIAS and ST. WEISS (*Wiener Arch. inn. Med.*, 1922, **4**, 29—58).—Intravenous injections of hypertonic solutions of sodium dihydrogen phosphate and sodium monohydrogen phosphate usually lower the sugar content of the blood in diabetic and alimentary hyperglycæmia, whilst the sugar content of normal blood is unaltered; the effect is accompanied and followed by a decreased excretion of sugar in the urine, and is due to the phosphate-ion. It cannot be ascribed to a decrease in the phosphorus content of the blood-serum, to the formation of dextrose diphosphoric acid or to oxidative glycolysis in the blood; the sugar must be removed either through some process of combustion or through the storing up of a carbohydrate or carbohydrate phosphoric acid in the tissues.

CHEMICAL ABSTRACTS.

Effect of Ether Anæsthesia on the Acid-base Balance of the Blood. DONALD D. VAN SLYKE, J. HAROLD AUSTIN, and GLENN E. CULLEN (*J. Biol. Chem.*, 1922, **53**, 277—292).—During ether anæsthesia, the blood of dogs showed an increased hydrogen-ion concentration, a decreased alkaline reserve, and, with one exception, an increased carbon dioxide tension. A true acidosis thus occurs, due, apparently, either to the introduction of acid into the blood or the withdrawal of base from it. The latter change is not a secondary effect produced to balance an acapnia (cf. Henderson and Haggard, A., 1918, i, 201).

E. S.

Effects of Ether Anæsthesia alone or Preceded by Morphine on the Alkali Metabolism of the Dog. R. L. STEHLE, W. BOURNE, and H. G. BARBOUR (*J. Biol. Chem.*, 1922, **53**, 341—348).—During ether anæsthesia the blood showed an increased hydrogen-ion concentration and a decreased alkali reserve. At the same time, the rate of excretion of sodium and potassium was lowered; this was probably due to the anuria which accompanies ether anæsthesia, for the total excretion of sodium and potassium during the day of the experiment was abnormally high. When administration of morphine preceded the ether anæsthesia, the increase in hydrogen-ion concentration was much less marked, whilst there

was practically no change in the alkali reserve. There was, however, a large increase in the rate of excretion of sodium and potassium.

E. S.

Erythropoietic Action of Germanium Dioxide. FREDERICK S. HAMMETT, JOSEPH E. NOWREY, jun., and JOHN H. MÜLLER (*J. Exptl. Med.*, 1922, **35**, 173—180).—Germanium dioxide causes a marked and sustained rise in the number of erythrocytes in blood which ranged from 1 to nearly 5 millions. The size of the dose did not seem to be important. The effect seems to be quick in making its appearance. The oxide also tends to increase the coagulability of the blood.

CHEMICAL ABSTRACTS.

Osmotic Resistance and Phosphatides of the Blood. New Quantitative Methods. R. BRINKMAN (*Arch. Néerland. Physiol.*, 1922, **6**, 451—515).—The author discusses in detail the various factors which affect the osmotic resistance of the red blood corpuscles. It is shown that whereas the resistance curves obtained when hypotonic solutions of sodium chloride are employed for estimating the osmotic resistance of the corpuscles show a gradual and continuous increase in hæmolysis with decreasing concentrations of salt, those obtained when equilibrated solutions containing physiological concentrations of calcium- and hydrogen-ions are employed consist of three distinct parts—a small fraction representing the old and least resistant corpuscles, a large fraction (80%) of somewhat greater resistance, and a small, strongly resistant fraction consisting of the young corpuscles. That continuous curves result when the former method is employed is due to an increased permeability of the cell which results from the lyotropic action of the sodium chloride on the lipoids which constitute the cell membrane. Pure solutions of sodium chloride are thus unsuitable for estimating the osmotic resistance of the cells. Solutions of a mixture of primary and secondary phosphates may, however, be employed. Details of the method are given, and it is shown that it gives results identical with those obtained with an equilibrated saline solution. The effect of changes in the organism of the ratio phosphatides: cholesterol has been studied and the hæmolytic action of phosphatides and its inhibition by cholesterol demonstrated (cf. A., 1920, i, 782).

E. S.

Uric Acid Content of Blood Corpuscles. A. CHAUFFARD, P. BRODIN, and A. GRIGAUT (*Compt. rend. Soc. Biol.*, 1922, **86**, 31—32; from *Chem. Zentr.*, 1922, i, 1209).—The uric acid content both of blood-serum and of blood corpuscles is twice as great in gouty conditions as in normal health. In the former case, the uric acid content of the corpuscles bears a more constant relationship to the uric acid content of the serum than in the latter case (cf. Theis and Benedict, this vol., i, 82.)

G. W. R.

The Distribution of Chloride between Corpuscles and Plasma and the Influence of Carbon Dioxide. Z. DISCHE (*Biochem. Z.*, 1922, **131**, 596—600).—Contrary to the results of van Creveld (this vol., i, 287), there is no chloride in the corpuscles

of the circulating blood of normal persons or in the corpuscles of blood which has lost carbon dioxide through exposure. H. K.

Distribution of Sodium, Potassium, Calcium, and Magnesium between the Corpuscles and Serum of Human Blood. BENJAMIN KRAMER and FREDERICK F. TISDALL (*J. Biol. Chem.*, 1922, **53**, 241—252).—Analytical results, to some extent collected from previous papers, are tabulated. E. S.

Soap and Serum. ADOLF JARISCH (*Klin. Woch.*, 1922, **1**, 71).—Sodium soaps undergo hydrolysis in a medium having a p_H less than 8.5, but when soap is added to blood-serum, of which the p_H is far below this value, the liquid remains clear. To explain this fact, the author dialysed serum until it was free from salt and then added soap to one portion and colloidal fatty acid to the other. In each case a voluminous precipitate was obtained which had all the physical characteristics of euglobulin. This precipitate was completely soluble in a 0.012 *N*-solution of sodium chloride, which explains the fact that no precipitate is obtained with normal serum. Entirely similar precipitates are obtained when commercial lecithin or alcoholic extracts of tissue are added to dialysed serum. In every case, the precipitate soluble in sodium chloride solution appears to be an adsorption compound between the lipid and the pseudoglobulin of the serum. CHEMICAL ABSTRACTS.

Blood Enzymes. II. The Influence of Temperature on the Action of the Maltase of Dog's Serum. ARTHUR COMPTON (*Biochem. J.*, 1922, **16**, 460—464).—The maltase present in dog's blood has an optimum temperature (55°) which shows no variation from animal to animal; this is probably due to the constancy of the hydrogen-ion concentration of the blood. The amount of this enzyme present, however, varies with different animals, although it remains practically constant for each individual. E. S.

Action of Nucleic Acid Injected into the Organism. Immunisation by a Single Injection. M. DOYON (*Arch. internat. physiol.*, 1921, **18**, 307—312; *Ber. ges. Physiol.*, 11, 436; from *Chem. Zentr.*, 1922, i, 1206—1207; cf. this vol., i, 82).—Nucleic acid inhibits the coagulation of blood in vitro and in vivo, and increases the secretion of antithrombin similarly to peptone and other substances. A single injection in dogs confers immunity against the anticoagulating action of a second and third injection. Further effects of injection of nucleic acid are narcosis and lowering of blood pressure. An effective anticoagulating nucleoprotein (antithrombin) can be isolated from blood rendered incoagulable by nucleic acid. G. W. R.

The Action of Various Metallic Salts on Hæmolysis. HELEN A. PURDY and L. E. WALBUM (*J. Immunol.*, 1922, **7**, 35—45).—The significance of the presence of small quantities of metallic salts on the hæmolytic action of saponin on horse blood corpuscles, of staphylolysin on goat blood corpuscles and of complement-amboceptor on sheep blood corpuscles was studied. By determin-

ing the minimal dose of the individual salts (in molar solution) at which their action is demonstrable, it is possible to obtain a comparison between the action of the different salts. Whilst some salts exert an inciting action on hæmolysis, others exert an inhibitive one (positive and negative catalysis?); some show an inciting effect at one concentration and an inhibitive one at another. The anion in the salts seems to be without significance as regards their action in either favouring or inhibiting hæmolysis.

CHEMICAL ABSTRACTS.

Hæmolysis by Morphine and Homologues. HEINRICH RHODE (*Biochem. Z.*, 1922, **131**, 560—569).—Corpuscles washed with isotonic sodium chloride solution are hæmolysed by the hydrochlorides of morphine and its methyl, ethyl, and benzyl derivatives, the intensity of the action increasing in the order given. Bromides, sulphates, and phosphates of these alkaloids are weaker. Washing the corpuscles with sucrose solution instead of sodium chloride solution weakens the hæmolytic action of these alkaloids and reverses the relative hæmolytic activities of morphine, and methyl- and ethyl-morphine. A similar reversal is observed with ammonium salts.

H. K.

The Appearance of Digestive Enzymes during Foetal Life. C. PORCHER and A. TAPERNOUX (*Compt. rend. Soc. Biol.*, 1920, **83**, 619—620; *Expt. Sta. Record*, **44**, 865).—The authors report the presence of trypsin, pancreatic amylase, pancreatic lipase, pepsin, and erepsin in the digestive tracts of three calf foetuses aged seventy-five, one hundred, and one hundred and eighty days, respectively.

CHEMICAL ABSTRACTS.

The Influence of Illumination on the Metabolism of Carbohydrates. LUDWIG PINCUSSEN (*Klin. Woch.*, 1922, **1**, 174).—A general illumination, following an injection of adrenaline, gives rise to an increase in the blood-sugar concentration. A decrease in the blood-sugar concentration is obtained if eosin is given previously to illumination. Adrenaline plus eosin plus light produces an effect that is the resultant of the two activities taken separately, the blood-sugar concentration being only slightly increased. The rate of oxidation of carbohydrates and allied substances is increased, in vivo, when the eosin-treated subject is illuminated. This is proved by the fact that when diabetics are so treated, the blood-sugar concentration decreases, the excretion of sugar into the urine decreases or disappears entirely and the acetone substances also largely disappear from the urine. Hypophyseal diabetics, with a large volume output of urine, are entirely refractory to illumination. The blood-sugar concentration is not changed by illumination with X-rays.

CHEMICAL ABSTRACTS.

Metabolism of Sulphur. V. Cysteine as an Intermediary Product in the Metabolism of Cystine. HOWARD B. LEWIS and DANIEL A. MCGINTY [with LUCIE E. ROOT] (*J. Biol. Chem.*, 1922, **53**, 349—356).—Phenylcarbamidocystine, when administered to rabbits, is excreted in the urine as phenylcarbamidocysteine.

Hence the first stage in the katabolism of cystine is probably conversion into cysteine (cf. this vol., i, 487). E. S.

Considerations on the Solubility of the Phosphatides. GUILLERMO V. STUCKERT (*Anal. Asoc. Quím. Argentina*, 1922, **10**, 115—132).—The brains of oxen were fractionally extracted by various solvents. Not only are the solvent powers of different liquids mutually affected, but the solubility of constituents is affected by the order in which the material is treated by different solvents. The phosphatides and esterins cannot be separated in a state of purity by the use of neutral solvents. The lecithins obtained by fractional extraction are not chemically well-defined. Five distinct lecithin fractions are distinguished. Schemes are given showing the fractional separation of different constituents using acetone, ethyl alcohol, and ether. G. W. R.

Chemistry of the Lungs. A New Phosphosulphatide. UBALDO SAMMARTINO (*Biochem. Z.*, 1922, **131**, 411—412; cf. A., 1922, i, 296).—From an alcoholic extract of the lipoids of the lungs a crystalline phosphosulphatide has been obtained containing phosphorus, sulphur, and nitrogen in the ratio 1 : 1 : 2. It has neither acid nor basic properties. H. K.

Formation of Bilirubin in Surviving Spleen. Z. ERNST and B. SZAPPANYOS (*Klin. Woch.*, 1922, **1**, 614—615; from *Chem. Zentr.*, 1922, i, 1118).—The spleen of dogs, surviving after death, forms bile pigments when irrigated with defibrinated blood containing dissolved hæmoglobin. The pigment formed resembles bilirubin and the amount formed is about seven times the amount formed by the liver during the same period. G. W. R.

Alkaligenesis. II. Ammonia Production in Muscle. OLIVE P. LEE and S. TASHIRO (*Amer. J. Physiol.*, 1922, **61**, 244—253; from *Physiol. Abstr.*, 1922, **7**, 344).—1 Gram of resting frog's gastrocnemius gives off 3.83×10^{-7} grams of ammonia in fifteen minutes. During 360 contractions, it produced 7.56×10^{-7} grams. Tetanised and injured muscle produces none owing to the simultaneous production of volatile acid. Ammonia held by tetanised muscle is released on recovery : in injured muscle it is not. Muscle gives off 1/14 as much as nerve. W. O. K.

The Degradation of Carbohydrates in Transversely Striated Muscles. II. FRITZ LAQUER (*Z. Physiol. Chem.*, 1922, **122**, 26—45; cf. this vol., i, 298).—The rate of disappearance of glycogen and of formation of lactic acid by frog muscle has been further studied with special reference to the season of the year. It has also been observed that glycogen is converted into lactic acid more readily than dextrose, and that destruction of the cell structure by repeated freezing in liquid air results in an inability to produce lactic acid from dextrose whilst there is no decreased production from glycogen. This suggests that an intermediate precursor of lactic acid is a more reactive form of dextrose, which is produced directly in the case of glycogen. W. O. K.

Creatinine and Creatine in Muscle Extracts. III. Concerning the Presence of Enzymes in Muscle Tissue which have Creatine and Creatinine as their Substrates. FREDERICK S. HAMMETT (*J. Biol. Chem.*, 1922, **53**, 323—337; cf. A., 1921, i, 907).—The conversion of creatine into creatinine proceeds three to four times more rapidly in muscle extract than in aqueous solution. That this is not due to the presence of an enzyme in muscle extract is shown by the fact that there is no diminution in the rate in extracts which have been boiled, and only a slight diminution in those which have been centrifuged. Moreover, the amount of creatinine formed in a given time in a dialysed extract is only slightly greater than that produced, under the same conditions, in an equal volume of the dialysate (the initial concentrations of creatine and creatinine are the same, owing to the ease with which these substances dialyse). The increased rate of conversion of creatine into creatinine is apparently due to the colloids present in muscle extract. These adsorb creatinine but not creatine. Further, their state of aggregation undergoes periodic changes, corresponding with which periodic changes in the rate of formation of creatinine occur. The reaction is thus catalysed by the "milieu" provided by living tissue. Such types of catalysis are called biocatalysts in contradistinction to those which require the addition of a foreign catalyst. In its later stages, the reaction creatine \rightarrow creatinine in muscle extract is a reaction of the first order. E. S.

Cell Penetration by Acids. VI. The Chloroacetic Acids. W. J. CROZIER (*J. Gen. Physiol.*, 1922, **5**, 65—79).—The rate of penetration of the tissue of *Chromodoris zebra* by acid varies with the concentration and strength of the acid, and also with the temperature. From measurements, it is concluded that the rate of penetration is controlled chiefly by the rate of diffusion, but that chemical factors also enter in. W. O. K.

Classification of Aromatic Odours in Sub-classes. S. OHMA (*Arch. Néerland. Physiol.*, 1922, **6**, 567—590).—From numerous fatigue experiments the author concludes that the aromatic class in Linné's classification of odours must continue to form one class. Three sub-classes may, however, be distinguished, namely, the odour of benzaldehyde, the odour of camphor, and the odour of citral. The members of these sub-classes, together with transition members, are indicated. E. S.

Analysis of Camel's Colostrum. HELEN L. FALES (*J. Biol. Chem.*, 1922, **53**, 339).—The following results were obtained: fat 7.4, sugar 4.2, casein 4.1, albumin 0.5, globulins, etc., 0.8, ash 0.893, CaO 0.272, MgO 0.025, P₂O₅ 0.318, K₂O 0.164, Na₂O 0.082, Cl 0.128%. E. S.

Phosphate Excretion in the Urine during Water Diuresis and Purine Diuresis. JOHANNES BOCK and POUL IVERSEN (*K. Danske Videnskab. Selskab. Biol. Medd.*, 1921, **3**, 1—28).—In water diuresis of rabbits, there is no connexion between the amount of phosphate excreted and the volume of the urine. Profuse theo-

phylline diuresis is accompanied by an increase in the phosphate content of the urine, but appears not to be connected therewith; the phosphate content of the plasma is practically unchanged or reduced after administration of theophylline. Thus the augmented excretion of phosphate in the urine is not dependent either on an increased concentration of phosphate in the plasma or on the volume of the urine, but must be attributed to a specific action of theophylline on secretory elements of the kidney, probably other than those producing the diuresis.

CHEMICAL ABSTRACTS.

The Action of Intravenous Injections of Dextrose and Gum Arabic Solution on Diuresis. KARL CORI (*Wiener klin. Woch.*, 1921, **34**, 169—171).—Hypertonic dextrose solution administered intravenously has a strong diuretic effect on dogs, similar to molar diuresis. Abundant excretion of chloride-ion results, accompanied by a correspondingly large quantity of water. On diets containing only a small amount of chlorine, less chlorine is excreted and diuresis is also diminished. After twenty-four hours the increased flow of chlorine into the blood from the tissues can still be observed. The absorption and excretion of nitrates administered by mouth were accelerated by the effect of dextrose, as shown by Stejskal. In man, dextrose solution has no diuretic effect, as the chlorine adheres more closely to the tissues. Seven per cent. gum arabic solution injected intravenously reduces the sugar excretion of the diabetic. Simultaneously, the amount of urine decreases. In dogs, gum arabic solution causes a diminished excretion of ingested iodine as compared with control animals. The gum solution proves of weak diuretic effect in experiments on dogs and there is no increased excretion of chlorine. It is therefore a question of water diuresis as opposed to dextrose diuresis.

CHEMICAL ABSTRACTS.

The Rôle of Hexamethylenetetramine in the Production of Hæmaturia. W. A. BLOEDORN and J. E. HOUGHTON (*J. Lab. Clin. Med.*, 1922, **7**, 514—533).—A high hydrogen-ion concentration of urine favours the elimination of formaldehyde thereby and appears to be a necessary factor in the production of hæmaturia following administration of hexamethylenetetramine; in most cases, administration of suitable quantities of sodium hydrogen carbonate will prevent the liberation of formaldehyde. If hexamethylenetetramine is dependent for its antiseptic properties on the liberation of formaldehyde, these properties can never be manifested except in the genito-urinary tract.

CHEMICAL ABSTRACTS.

The Nature of Ehrlich's Diazo-reaction. III. LEO HERMANN (*Z. physiol. chem.*, 1922, **122**, 98—103; cf. A., 1921, i, 531).—After coupling with dichlorobenzendiazonium chloride, a substance, $C_{14}H_8O_4N_2Cl_2$, dark red, irregular prisms, m. p. 68—70°, has been isolated from the urine of tuberculous patients. This indicates that the substance originally present, responsible for the diazo-reaction, has the formula $C_8H_6O_4$. It has phenolic properties.

A different substance appears to be responsible for the diazo-reaction in cases of typhus, but enough could not be isolated for analysis.

Dichlorobenzenediazonium chloride couples with benzoylhistidine to yield a *bisdiazobenzoylhistidine*, $C_{25}H_{15}O_3N_7Cl_4$, a red dye, but this is not analogous to that obtained from urine. W. O. K.

Adrenaline Hyperglycæmia. BRÖSAMLEN (*Deut. Arch. klin. Med.*, 1921, **137**, 299—310; *Ber. ges. Physiol.*, **11**, 510; from *Chem. Zentr.*, 1922, i, 1252).—Subcutaneous injection of 1 mg. of adrenaline induces an increase in blood sugar of about 0.058% in healthy individuals. The hyperglycæmia begins after ten minutes, reaches a maximum after one hour, and passes after two to three hours into a slight hypoglycæmia. In diabetes mellitus, adrenaline hyperglycæmia shows no simple behaviour. The adrenaline blood-sugar curve may possibly be separable into a pancreatogenous and a neurogenous form. G. W. R.

Unsaturated Alcohols obtained from the Fat of Ovarial-dermoid Cysts. JOHANN MUCK (*Z. physiol. chem.*, 1922, **122**, 125—142).—Neither cholesterol nor *isocholesterol* is present in the fat of ovarian-dermoid cysts. An alcohol present, related to cholestol and giving similar colour reactions, yields a bromo-derivative, $C_{11}H_{20}OBr_4$, a white, sandy powder, m. p. 150° (decomp.). On boiling with alcoholic potassium hydroxide solution, the bromine is removed and a substance formed giving the colour reactions of a cholestol compound.

By reducing the mixed alcohols, no definite results have been obtained, but from the products of oxidation there has been isolated an amorphous monobasic acid, $C_{19}H_{34}O_4$, apparently formed from the cholestol compound (calcium salt, $C_{38}H_{66}O_8Ca \cdot 2H_2O$; barium salt, $C_{38}H_{66}O_8Ba \cdot 2H_2O$; silver salt, $C_{19}H_{33}O_4Ag$). W. O. K.

Amino-acid Deficiency Probably the Primary Etiological Factor in Pellagra. JOSEPH GOLDEERGER and W. F. TANNER (*U. S. Public Health Rep.*, 1922, **37**, 462—486).—Details are given of the occurrence of pellagra in a number of individuals who were known to be receiving diets containing adequate supplies of mineral elements and of the known vitamins. By eliminating these factors, the author concludes that pellagra is caused by a deficiency in the diet of some special combination or combinations of amino-acids. A large amount of literature leading to the same conclusion is quoted. Administration of cystine alone and of a mixture of cystine and tryptophan appears to produce some improvement in the disease. E. S.

Chlorine Metabolism in Pulmonary Tuberculosis. FELIX BOENHEIM (*Beitr. Klin. Tuberk.*, 1921, **49**, 233—238).—There appears to be a parallel between the severity of pulmonary tuberculosis and hypochloræmia; a diminished gastric chlorine secretion is not universal, so that the chlorine of the blood cannot be the decisive factor in gastric secretion. Since in the majority of cases gastric secretion is diminished early, the increased chlorine in the

blood is excreted by the kidneys, resulting in a condition of hypochloræmia, whilst normal or increased gastric secretion is associated with irritability of the gastric cells, the blood chlorine not utilised by the gastric glands being eliminated by the kidneys. Alternatively, the hypochloræmia may be due to anchoring of the chlorine in tissue depots. There is experimental evidence that in tuberculosis there is a dechlorination and resulting chlorine starvation of the tissues.

CHEMICAL ABSTRACTS.

Pharmacological Examination of *iso*Propyl Alcohol.

D. I. MACHT (*Arch. int. pharmacodynamie*, 1922, **26**, 285—286).—*iso*Propyl alcohol is more toxic than ethyl alcohol or methyl alcohol, and less toxic than *n*-propyl alcohol. Administration by the mouth produces narcosis, in larger doses general anæsthesia, and finally coma and death. Very little is absorbed by inhalation, and there is very little evidence of its absorption through the skin.

CHEMICAL ABSTRACTS.

Mode of Oxidation of Fatty Acids with Branched Chains.

II. The Fate in the Body of Hydratropic, Tropic, Atrolactic, and Atropic Acids together with Phenylacetaldehyde. HERBERT DAVENPORT KAY and HENRY STANLEY RAPER (*Biochem. J.*, 1922, **16**, 465—474).—The substances were administered to dogs. Tropic and atrolactic acids were not appreciably attacked. Hydratropic and atropic acids, however, were both oxidised, the former partly (66%) and the latter completely. The unchanged hydratropic acid recovered from the urine contained the *d*-form in excess. It is concluded that the first stage in the oxidation of hydratropic acid is its conversion into atropic acid. This is probably further oxidised to formylphenylacetic acid (cf. A., 1914, i, 1122), which is then completely destroyed. Dakin's observation that phenylacetaldehyde is to a large extent oxidised in the body has been confirmed.

E. S.

Fate of some of the Phenylacetylated Amino-acids in the Animal Organism. GEORGE J. SHIPLE and CARL P. SHERWIN (*J. Biol. Chem.*, 1922, **53**, 463—478).—The phenylacetyl group is apparently as effective as the benzoyl group in protecting amino-acids from oxidation in the animal organism. Thus, the phenylacetyl derivatives of glycine, alanine, leucine, glutamic acid, glutamine, aspartic acid, and ornithine are excreted unchanged in the urine after administration to man, dogs, rabbits, and chickens (cf. this vol., i, 492; Thierfelder and Sherwin, A., 1915, i, 481, 750).

Phenylacetyl-dl-alanine, feathery clusters, m. p. 150—152°, was prepared by the action of phenylacetyl chloride on alanine. *Phenylacetyl-dl-leucine*, feathery clusters, m. p. 133—134°, was similarly prepared from leucine.

E. S.

[Physiological] Effect of Cyanamide. ERICH HESSE (*Z. Ges. exp. Med.*, 1922, **26**, 337—351; from *Chem. Zentr.*, 1922, i, 1150).—Observations on the effect of cyanamide, previously administered, in modifying the physiological action of certain substances.

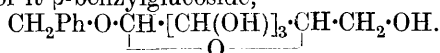
G. W. R.

The Action of the Digestive Juices on β -Benzyl-*d*-glucoside.

A. RICHAUD (*Compt. rend. soc. biol.*, 1922, **86**, 770—772).—The author incubated the macerated mucous membrane of the dog with β -benzyl-*d*-glucoside in the presence of two preservatives (toluene and sodium fluoride), but could not find any measurable trace of sugar split off even after thirty-six hours. It is therefore concluded that the substance is not attacked by the emulsin of the intestinal tract and is absorbed into the circulation unchanged.

CHEMICAL ABSTRACTS.

The Toxicity of β -Benzylglucoside obtained by Biochemical Synthesis. A. RICHAUD (*Compt. rend. Soc. Biol.*, 1922, **86**, 649—651).—The author attempted to overcome the relative toxicity of benzyl benzoate introduced by Macht as an antispasmodic by substituting for it β -benzylglucoside,



This has the advantage over benzyl benzoate in that it is more soluble in water and is less irritating to the tissues. Administered subcutaneously, the toxic dose for the mouse or guinea-pig is 11—12 grams per kilo. For the rabbit the toxic intravenous dose is 8—9 grams per kilo.

CHEMICAL ABSTRACTS.

Chemistry of Vegetable Physiology and Agriculture.

The Growth-promoting Factor of Lemon Juice. BRUNO LEICHTENTRITT and MARGARETE ZIELASKOWSKI (*Biochem. Z.*, 1922, **131**, 499—512).—The growth-promoting factor of lemon juice, for bacteria, has been submitted to a variety of experimental conditions. Lemon juice heated at 100° in acid or alkaline solution is practically unaltered in its growth-promoting factor for bacteria. Even hydrolysis with 2% hydrochloric acid is without influence, although sodium hydroxide is inimical. Exposure to ultra-violet light in Rontgen rays is without action whatever the reaction of the medium, and aeration in boiling solution is also without action. Adsorbents weaken the action but incompletely, and the bacterial growth-promoting principle is dialysable independently of the reaction of the medium. H. K.

Growth-promoting Factor of Lemon Juice. BRUNO LEICHTENTRITT and MARGARETE ZIELASKOWSKI (*Biochem. Z.*, 1922, **131**, 513—524).—There is little parallelism between the effect of external conditions and reagents on the bacterial growth-promoting principle and the antiscorbutic factor *C* of lemon juice as tested on guinea-pigs and children. Lemon juice contains an antiscorbutic factor *C* and a factor which promotes growth of bacteria and of ill-nourished children. This latter factor is termed factor or vitamin-*D*. Further experiments are necessary to determine whether *D* is identical with vitamin-*B* or not. H. K.

The Presence of Nucleic Acid in Bacteria. A. J. SCHAFER, CASPAR FOLKOFF, and S. BAYNE JONES (*Bull. Johns Hopkins Hosp.*, 1922, **33**, 151).—A nucleic acid, containing guanine and phosphorus, half of which is easily split off and half firmly bound, but no pentose, was obtained from *Bacillus coli*.

CHEMICAL ABSTRACTS.

The Elective Action of Tellurium Salts on Bacteria of the Colon-typhoid Group. G. JOACHIMOGLU (*Z. Urol.*, 1922, **16**, 97—100).—Telluric acid in concentrations of 1 in 40,000 has an elective inhibitive action on the growth of *Bacillus coli* and *B. typhosus* in cultures. It is suggested that this substance be used in colon bacillus infections of the urinary tract.

CHEMICAL ABSTRACTS.

The Darkening of Carbohydrate containing Nutrient Media by *Bacillus mesentericus* var. *niger*. ANNA MUSCHEL (*Biochem. Z.*, 1922, **131**, 570—590).—*Bacillus mesentericus* var. *niger* grows on agar devoid of carbohydrates, multivalent alcohols, or amino-acids which are not derivatives of benzene without coloration of the medium, but in presence of sugars, alcohols, and tyrosine with darkening of the media. By use of protein-free media, it is shown that the coloration is due to benzene derivatives related to *o*- and *p*-dihydroxybenzenes with possible condensation with amino-acids.

H. K.

Production of Hydrogen Peroxide by Bacteria. JAMES WALTER McLEOD and JOHN GORDON (*Biochem. J.*, 1922, **16**, 499—506).—The substance inhibitory to its own growth produced by the *Pneumococcus* in the presence of an abundant supply of oxygen (cf. *Lancet*, 1921, i, 900; *J. Path. Bact.*, 1922, **25**, 139) is hydrogen peroxide. When grown on a medium of agar and heated blood ("chocolate agar") a green coloration is produced. This is due to the action of the hydrogen peroxide which is formed; a similar action is shown by certain streptococci which also produce hydrogen peroxide. Stimulation of the growth of the *Pneumococcus* by fresh tissue fluids is probably due to the presence in the latter of catalase.

E. S.

Chemical Problems in the Bacteriology of Tubercule Bacillus. ESMOND R. LONG (*Amer. rev. tubercul.*, 1921, **5**, 705—714; *Ber. ges. Physiol.*, **12**, 299; from *Chem. Zentr.*, 1922, iii, 173).—Experiments with different strains of acid stable bacteria showed that alanine, leucine, and histidine can each serve as sole source of nitrogen supply. Tryptophan and phenylalanine are not utilised, possibly on account of the toxic character of their decomposition products. The synthesis of carbohydrate is not effected simply with the carbon of amino-acids; a further source of carbon is necessary, preferably glycerol. Propionamide and ammonia are utilised by all bacteria studied. Creatinine is only utilised by certain saprophytes. Urea is not attacked by tubercule bacilli, frog bacilli, or fish bacilli.

G. W. R.

Influence of Hydrogen-ion [Concentration] on the Growth of *Azotobacter*. P. L. GAINES and H. W. BATCHELOR (*Science*, 1922, **56**, 49—50).—The maximum hydrogen-ion concentration permitting the growth of *Azotobacter* isolated from different soils is p_H 5.9—6.0. It was found that as the hydrogen-ion concentration of the soil decreased, growth increased until p_H 6.1—6.4 was reached. The optimum reaction for the fixation of nitrogen appears to be very closely associated with that for growth. The total quantity of acid produced by the various cultures was insignificant.

A. A. E.

The Decomposition of Kaolin by Organisms. W. J. VERNADSKY (*Compt. rend.*, 1922, **175**, 450—452).—Experiments carried out to determine whether formation of hydrated aluminium oxide occurs by the action of diatoms on naturally occurring aluminium silicates showed that silicious diatoms developed in a medium in which the only source of silica was clay, whilst no action took place in the sterilised control experiment. In the former case, the clay was found to contain free aluminium hydroxide, but none was detected in the control. The author suggests that this decomposition may play a considerable part in natural processes.

H. J. E.

Nitrification. KOJI MIYAKE and S. SOMA (*J. Biochem. [Japan]*, 1922, **1**, 123—129).—Nitrification as a whole is an auto-catalytic unimolecular chemical reaction and increase of nitric acid is in accordance with the expression: $\log x - \log (A - x) = K(t - t_1)$. The decrease of ammonia compounds in the soil is also an auto-catalytic reaction following the expression: $\log (A - x) / \log (x - a) = (A - a)Kt - K_1$, where x = ammoniacal nitrogen at the end of time t , and A and a denote the original and final amounts of ammonia. K and K_1 are constants.

CHEMICAL ABSTRACTS.

Urea as a Nutrient of Yeasts and other Plants. TH. BOKORNY (*Allgem. Brauer. Hopfenztg.*, 1922, 243—246; from *Chem. Zentr.*, 1922, i, 1146; cf. A., 1917, i, 680).—In a comparison of urea and hippuric acid, it is shown that the former is an ideal plant nutrient both on account of its high nitrogen content and also because it liberates carbon dioxide. Hippuric acid is less satisfactory, since it gives benzoic acid and glycine, both of which are poisonous or harmful to plant life.

G. W. R.

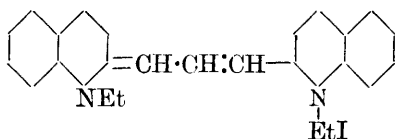
Lactic Acid Fermentation of Dextrose by Peptone. GOTTFRIED SCHLATTER (*Biochem. Z.*, 1922, **131**, 362—381).—Dextrose is converted quantitatively by peptone at 37° into inactive lactic acid, sodium hydrogen carbonate being used as buffer. This buffer substance may be replaced by sodium acetate, but not by phosphate mixtures, owing to flocculation of the peptone. During the fermentation, amino-acids appear and fermentation ceases, with flocculation of the peptone. Peptones free from phosphates, as, for example, Witte's peptone, give no fermentation; most of the observations recorded were made on Siegfried peptone. The solu-


tions are not quite sterile, although no known lactic acid forming bacteria were found. H. K.

Peptone Fermentation. EMIL BAUR and EUGEN HERZFELD (*Biochem. Z.*, 1922, **131**, 382—385).—The authors draw an analogy between the glycolytic action of plant and animal juices and the fermentation of dextrose by peptone, as revealed by their own experiments or by those of Schlatter (previous abstract). Schlatter's observations are considered an effective reply to Bau's criticism (this vol., i, 307) of their own experiments in fermentation without yeast (this vol., i, 93).
H. K.

The Oligodynamic Effect of Silver. IV. R. DOERR and W. BERGER (*Biochem. Z.*, 1922, **131**, 351—361).—The active agent in all oligodynamic effects is the silver ion. Silver surfaces lose their activity by treatment with potassium cyanide, and water activated by silver is inactivated by potassium cyanide. The inactivation is due to conversion of the deleterious silver ion into $\text{Ag}(\text{CN})_2$ ions. Carbon dioxide and oxygen are each more potent than air in developing the oligodynamic action of silver surfaces.

The Antiseptic Properties of Cyanine Dyes. C. H. BROWN-
ING, J. B. COHEN, and R. GULBRANSEN (*Brit. Med. J.*, 1922, I, 514—
515; cf. this vol., i, 612).—Certain of the cyanine dyes are extremely
potent antiseptics, for example, sensitol red (annexed formula)





for staphylococci in aqueous medium. Selective antiseptic action as between staphylococcus and *Bacillus coli* is exhibited to a higher degree by sensitol-red (for example) than by any other compound hitherto investigated, the ratios of the sterilising concentrations probably being greater than 2000 : 1. Sensitol-green is the most active of these dyes both in serum and aqueous medium for *B. coli*. Also, in the case of *B. coli*, the antiseptic action in serum is more intense than in aqueous medium.

A. A. E.

Energy Changes accompanying the Assimilation of Carbon Dioxide. O. WARBURG and ERWIN NEGELEIN (*Z. physikal. Chem.*, 1922, **102**, 235—266).—Experiments are described in which the green alga, *Chlorella vulgaris*, has been subjected, in a suitable environment, to the light from a metal filament lamp, and the proportion of the absorbed energy converted into chemical energy deduced by measuring the volume of oxygen liberated. This change occurs according to the equation $6\text{CO}_2 + 6\text{H}_2\text{O} = \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 - 674000 \text{ cal.}$ Further measurements have been made to ascertain the proportion of the chemical energy which is converted into heat. J. F. S.

Adsorption of Nutrients and Plant Growth in Relation to Hydrogen-ion Concentration. OLOF ARRHENIUS (*J. Gen. Physiol.*, 1922, 5, 81—88).—The rates of growth and of germin-

ation and of the adsorption of salts vary with the P_H of the nutrient medium. The variation is particularly marked in regard to absorption. The greatest absorption of anions occurs when the reaction is acid.

W. O. K.

Phosphorus Nutrition of Plants. M. VON WRANGELL (*Landw. Jahrb.*, 1922, **57**, 1—78; from *Chem. Zentr.*, 1922, i, 1387).—From a large number of pot-culture experiments with different plants it is concluded that the power of any species to utilise the phosphorus of relatively insoluble mineral phosphates varies directly with the ratio $\text{CaO} : \text{P}_2\text{O}_5$ in its ash. In the following series, in which the $\text{CaO} : \text{P}_2\text{O}_5$ ratio is given in brackets, phosphorus utilisation is shown in increasing degree:—wheat and rye (1·3), barley and oats (1·6), maize (3), beans, peas, and vetches (about 7), clovers (12), rape (23), tobacco, hemp, and mustard (15), buckwheat (17). Acid soil reaction favours anion absorption, whilst alkaline reaction favours cation absorption and the composition of the plant is thereby affected. Thus oats grown with acid soil reaction gave a ratio $\text{CaO} : \text{P}_2\text{O}_5$, 0·6; with neutral soil reaction, 10·0. The depressing effect of calcium ions on phosphorus absorption is postponed in the case of plants showing high calcium absorption. Where the absorption of phosphoric oxide from a fertiliser is greater than that of calcium oxide, the growth of a crop results in an excess of calcium oxide in the soil which may be undesirable. G. W. R.

Plant Chemistry. IV. *Juncus effusus*, L. JULIUS ZELLNER (*Monatsh.*, 1922, **43**, 120—123).—A record of certain analytical data for this plant.

C. K. I.

Estimation and Distribution of Chlorine in Plants. J. JUNG (*Sitzungsber. Akad. Wiss. Wien*, 1920, **129**, 297—340).—By the use of either (a) 0·5 gram of thallium acetate and 2 grams of glycerol in 7·5 grams of water, or (b) 0·1 gram of silver nitrate in 9·9 grams of 10% ammonia solution, chlorine was detected microchemically in numerous plants; it is absent from only a few plants, notably the conifers. It occurs only as chloride, and usually increases in amount from the roots to the leaves, being most abundant in succulent, parenchymatous tissues, apparently dissolved in the cell sap. It is usually scarce in the epidermis, bundles, hairs, flower parts, pollen, woody tissue, and chlorophyllous mesophyll, and abundant in fleshy roots and rhizomes. Plants which grow in rich, moist soil and in the sea are richer in chlorine than those growing in sandy soil, heaths, and fresh water. Mosses, ferns, epiphytes, parasites, and saprophytes contain little or no chlorine.

CHEMICAL ABSTRACTS.

Relation between Manganese Content and Proportion of Ash in Young and Old Leaves. F. JADIN and A. ASTRUC (*Bull. Soc. chim.*, 1922, **31**, 917—921).—A study of the comparative manganese content of young and old leaves leads to the conclusion that the figures obtained on analysis should be regarded as having only a relative value. The quantity of manganese in relation to the fresh material is less in the case of young leaves, and for the

dry material a similar result is obtained although the variations are not so great. In relation to the ash, however, the variations are in the inverse sense, although several exceptions are noted. The authors discuss the bearing of their results on those obtained by Bertrand and Rosenblatt (A., 1921, i, 759). H. J. E.

The Occurrence of Cobalt and Nickel in Plants. GABRIEL BERTRAND and M. MOKRAGNATZ (*Compt. rend.*, 1922, **175**, 458—460).—The authors have developed their method of detecting and estimating traces of cobalt and nickel, and now describe its application to the examination of the following vegetables: carrot, onion, potato, spinach, lettuce, cress, tomato, apricots, beans, lentils, buckwheat, wheat, oats, maize, rice, mushroom. Nickel was found in the ash in each case, and, with the exception of carrot and oats, cobalt also. It is pointed out that these two negative results may be reversed in working with larger quantities of ash. The proportion present is minute: that of cobalt varies from less than 0.005 mg. to 0.3 mg. per kilo. of the fresh substance, whilst in the case of nickel the values range from 0.01 mg. to 2.0 mg. H. J. E.

Anthochlor. G. KLEIN (*Sitzungsber. Akad. Wiss. Wien*, 1920, **129**, 341—394).—The yellow pigment from 300 species of flowers was examined; of these, 60 contained anthochlor, the rest mostly carotin. Its occasional simultaneous occurrence with carotin, flavone, and anthocyanin was proved, and its close relation to anthocyanin in the case of closely related plants was established. It is not a single pigment, but a group of closely related ones. It is a glucoside. Its reactions with concentrated mineral acids, alkalis, metallic salts, and reducing agents are discussed.

CHEMICAL ABSTRACTS.

Synthesis of Vitamin-A by a Marine Diatom (*Nitzschia closterium*, W. Sm.) Growing in Pure Culture. HENRY LYSTER JAMESON, JACK CECIL DRUMMOND, and KATHARINE HOPE COWARD (*Biochem. J.*, 1922, **16**, 482—485).—The marine diatom, *Nitzschia closterium*, is able to synthesise large amounts of vitamin-A when grown in Miquel's solution or in sterilised sea water.

E. S.

The Constituents of the Flowering Tops of *Artemisia afra*, Jacq. JOHN AUGUSTUS GOODSON (*Biochem. J.*, 1922, **16**, 489—493).—The following substances have been isolated: camphor, a wax-like ester which was probably ceryl cerotate, tricontane, scopoletin, and quebrachitol. The camphor had $[\alpha]_D^{20} + 9.7^\circ$ and was evidently a mixture of the two enantiomorphs. No compounds were found which could be regarded as related to santonin.

E. S.

Chemical Composition of Belladonna Leaves. A. GORIS and A. LARSONNEAU (*Bull. Sci. Pharmacol.*, 1921, **28**, 499—503; from *Chem. Zentr.*, 1922, i, 757).—Belladonna leaves are extracted with (dilute) sulphuric acid. After addition of excess of soda, the ethereal extract yields, on crystallisation, at first hyoscyamine,

mixed later with a little atropine. From the residue of the ethereal extract a volatile oil is obtained which has an odour like that of pyridine and contains pyridine, 1-methylpyrroline, and 1-methylpyrrolidine. The aqueous extract yields an unidentified 1:4-diamine of pleasant, tobacco-like odour. G. W. R.

Oils and Fats from the Seeds of Indian Forest Trees. MADYAR GOPAL RAU and JOHN LIONEL SIMONSEN (*Indian Forest Records*, 1922, **9**, Part III).—The seeds of *Chloroxylon Swietenia* yield 16% of a non-drying oil consisting of glycerides of stearic, palmitic, myristic, oleic, and linolenic acids. The seeds of *Calophyllum wightianum* yield 34% of an oil closely resembling that obtained from the seeds of *C. inophyllum* and containing about 10% of resin and glycerides of stearic, palmitic, oleic, and linolic acids. The seeds of *Mimusops elengi* yielded 16% of oil consisting of glycerides of stearic, palmitic, and oleic acids, and an unidentified saturated acid which was possibly behenic acid. The seeds of *Shorea robusta* yield 16.4% of a fat resembling Borneo tallow and consisting of glycerides of stearic and oleic acids. *Garcinia cambogia* seeds yield 31% of a fat resembling the fats from other species of *Garcinia* which should prove an excellent edible fat. It consists of glycerides of stearic and oleic acids. H. C. R.

Sand Spur, *Cenchrus tribuloides*, L. HEBER W. YOUNGKEN and CHARLES H. LA WALL (*Amer. J. Pharm.*, 1922, **94**, 567—583).—The mature fruits of the sand spur, *Cenchrus tribuloides*, L., give the following results. Moisture, 8.17%; ash, 3.95% (containing silica 10%); water-soluble extractives, 3.55% (including 0.55% of reducing sugars, the remainder being of mucilaginous character); alcoholic extractives, 3.17%, mainly chlorophyll, and resinous and oily constituents; light petroleum extractives, 2%, principally fat; ethyl ether extractives, 3.3%, having acid number 19.10, saponification number 197, and iodine number 60. Alkaloids, glucosides, and toxic or irritating substances were absent.

G. W. R.

Stearic Acid in the Latex of *Ficus fulva*, Reinw. A. J. ULTÉE (*Bull. Jard. bot. Buitenzorg*, 1922, [iii], **5**, 105—106).—The latex contains large quantities of a wax, which on hydrolysis yields stearic acid. There is but little rubber present. *Ficus elastica* latex contains much smaller quantities of a different wax. G. B.

Fluorine in Spanish Grapes. MARTINIANO LEGUIGAMÓN PONDAL (*Anal. Asoc. Quím. Argentina*, 1922, **10**, 57—73).—Fluorine is found to be a normal constituent in Spanish grapes. A method is described for its detection, using the etching action of hydrogen fluoride on glass. G. W. R.

The Influence of Light on the Formation of Anthocyanin in the Scales of Lily Bulbs (*Lilium Candidum* and *L. Martagon*). MARCEL MIRANDE (*Compt. rend.*, 1922, **175**, 496—498).—The curve of pigmentation has been traced by the use of mono-

chromatic filters, and shows a maximum in the red, a minimum in the green, and a more important maximum in the indigo-blue region. Rays in the non-luminous portion of the spectrum have no action.

H. J. E.

The Changes and Movements of the Saccharine Materials in *Mercuriale vivace* (*Mercurialis perennis*, L.) in the Course of its Annual Growth. P. GILLOT (*J. Pharm. Chim.*, 1922, [vii], 26, 250—258).—The content of reducing sugars in the aerial portions of the plant does not vary greatly from season to season. In the subterranean parts, the reducing sugar is greatest in quantity in the young growing portions. In the older organs, rhizomes, etc., it attains its maximum in the summer and a minimum at the beginning of the spring. The polysaccharides in the aerial parts of the plant appear to consist almost entirely of sucrose, and the same applies to the underground shoots. The rhizomes and roots give extracts which remain dextrorotatory even after hydrolysis by invertase, and the presence of a dextrorotatory substance in addition to sucrose is therefore postulated. The proportions of this dextrorotatory substance appear to vary with the season, existing only in small quantity at the time of inflorescence. It increases in quantity to a maximum in August. Considerable quantities of sucrose were isolated from the rhizome juices, but attempts to isolate the dextrorotatory principle have been up to the present unsuccessful.

G. F. M.

Proteins of the Lima Bean, *Phaseolus lunatus*. D. B. JONES, C. E. F. GERSDORFF, C. O. JOHNS, and A. J. FINKS (*J. Biol. Chem.*, 1922, 53, 231—240).—The lima bean contains 21.17% of protein ($N \times 6.25$). By extraction with sodium chloride solution, an α - and a β -globulin were obtained which were separated by fractional precipitation with ammonium sulphate. An albumin was also isolated. Analyses by Van Slyke's method gave the following values for basic amino-acids: α -globulin—cystine 1.60, arginine 5.67, histidine 3.71, lysine 7.84%; β -globulin—cystine 0.84, arginine 5.07, histidine 2.62, lysine 8.53%; albumin—cystine 1.07, arginine 5.74, histidine 2.54, lysine 5.97%. Positive tests were obtained for tryptophan in each case. The proteins of the lima bean are, in general, similar to those of other beans of the genus *Phaseolus* (cf. this vol., i, 504).

E. S.

Swedish Pines and Spruces. H. E. WAHLBERG (*Svensk Pappers-Tidning*, 1922; *Papierfabr.*, 1922, 20, 1097—1100, 1133—1137, 1178—1181).—The test-stems were cut up systematically and sample disks taken from definite points, these disks being further subdivided into numbered sectors. Estimations of moisture, apparent specific gravity, ash, resin, and cellulose were made in order to establish any regular variations in different portions of the tree. The most variable function is the apparent specific gravity; generally the wood having the narrowest annual rings had the highest density. The ratio of the apparent specific gravity of the autumn wood to that of the spring wood had an average value

of 1.92 throughout the tree, in spite of considerable variations in the absolute values for the different annual rings. Comparing the weather records for various years with the corresponding annual rings, it appeared that a wet, cold season tended to give rise to wood of low density. The apparent specific gravities of the freshly felled wood and of the seasoned wood were compared; shrinkages of 6.5 to 11.6% in volume were recorded during the transition from the growing tree to the air-dry condition. Cellulose and resin tended to vary inversely but generally without regular laws; the principal variation in this respect was a tendency for the cellulose to decrease and the resin to increase from the outer layers towards the heart. The resin appears to have reached a constant condition of solubility within ten days after felling [cf. *J. Soc. Chem. Ind.*, 1922, 805A]. J. F. B.

The Chemical Constituents of Green Plants. XX. The Acids of the Cherry (*Prunus avium*). HARTWIG FRANZEN and FRITZ HELWERT (*Z. physiol. chem.*, 1922, 122, 46—85).—Malic acid is much the most important acid of the cherry. There are present also traces of oxalic acid, and small quantities of succinic acid, citric acid, lactic acid, and of unsaturated acids.

W. O. K.

Mafurra Tallow, a Product of the Nuts of *Trichilia emetica*. M. RINDL (*South African J. Ind.*, 1922, 5, 415—423).—Both the husk and the kernel of Mafurra nuts from Portuguese East Africa furnish a solid fat, whilst an oil is obtained from the aril. The aril oil has the following characters: d_{15}^{20} 0.931, acid value (as oleic acid) 8.9%, saponification value 202.5, iodine value 66, saponification value of acetylated oil 235. The oil congeals if kept for some time at about 5°. The constants of the solid fat obtained from different sources vary so widely that it is certain that all the commercial material is not derived from the same species of *Trichilia*. The kernel usually contains about 60% of fat, and the husk 25—35%. It has a high m. p., ranging usually from 35—45°, and yields 7—8% of its weight of glycerol on saponification. It has a notably high acid value (40—50). G. F. M.

The Phytin Content of Foods. E. ARBENZ (*Mitt. Lebensm. Hyg.*, 1922, 13, 45—52).—Finely pulverised foods (vegetables and fruits dried first at 36°) were extracted with 0.6% hydrochloric acid, the phytin being estimated in the extracts by an adaptation of the method of Huebner and Stadler (*Biochem. Z.*, 1914, 64, 422). The percentages of phytin (as anhydrous phytic acid) in fresh and dried fruits, respectively, were: Rice bran, 3.801, 4.232; rice flour, 0.192, 0.216; wheat bran, 4.641, 5.073; whole-wheat flour, 0.498, 0.572; white flour, 0.184, 0.208; maize flour, 0.764, 0.857; lentils, 0.292, 0.326; peas, 0.498, 0.561; oat flour, 0.460, 0.506; cocoa, 2.110, 2.230. Phytin was not found in carrots, turnips, cauliflower, Brussels sprouts, kale, spinach, asparagus, apples, peaches, or figs.

CHEMICAL ABSTRACTS.

Effect of Silicic Acid on Crop Production in the Presence of Insufficient Amounts of Phosphoric Acid. O. LEMMERMANN and H. WIESSMANN (*Z. Pflanz. Düng.*, [A], 1922, 1, 185—255).—Working with sand cultures of gramineous, leguminous, and cruciferous plants, increases in yield were obtained by the use of colloidal silicic acid, particularly in the presence of insufficient phosphoric acid. In experiments with natural soils, similar results were obtained. With shortage of nitrogen or potassium, the effect of silicon is much less. The increases appear to be due to the direct action of silicic acid on plant growth. Silicon compounds, other than colloidal silicic acid, gave insignificant or negative results.

G. W. R.

The Growth of Maize as Affected by Iron and Aluminium Salts. CHAS. H. ARNDT (*Amer. J. Bot.*, 1922, 9, 47—71).—The availability of iron in ferric phosphate depends largely on the composition of the nutrient solution, the requisite quantity of ferric phosphate varying from 7 mg. per litre in one case to more than 35 mg. in another. 0.0005*N*-Ferrous sulphate gave optimum growth in one case and the addition of ferric nitrate produced a precipitate from which the plant could not obtain sufficient iron from a 0.001*N*-solution. Sulphuric, nitric, and hydrochloric acids are approximately equal in toxicity when added to the nutrient solutions in low concentrations; at higher concentrations, sulphuric acid depressed the growth of tops more than the others, but was more favourable to root development. Sand cultures required much more acid than water cultures to produce the same results. The toxicity of ferrous sulphate showed no relation to the initial hydrogen-ion concentration. Aluminium salts produced approximately the same depression in growth as a solution of ferrous sulphate of the same normality.

CHEMICAL ABSTRACTS.

Characteristic Proteins in High- and Low-protein Maize. M. F. SHOWALTER and R. H. CARR (*J. Amer. Chem. Soc.*, 1922, 44, 2019—2023).—The relative abundance of the different proteins in maize and the contents of mono- and di-amino-acids have been studied.

A considerably larger part of the protein is present as zein and globulins in high-nitrogen than in low-nitrogen maize; the zein and globulins have been formed at the expense of the amides, albumin, and glutenin. The embryo constitutes about 15% of the total weight of high nitrogen maize grain, whereas dent maize of the usual composition has only about 11% of embryo. Zein appears to be the protein which is present in most variable amount, averaging 50.28% in high-nitrogen and only 31.85% in low-nitrogen maize. The protein of high-nitrogen "popcorn" is particularly rich in zein, averaging 57.24%. The total nitrogen content appears to determine the amounts of the various proteins.

The amino-nitrogen in the filtrate from the bases is found to be higher in the high-nitrogen maize than in that of low nitrogen content. The di-amino acids constitute approximately twice as

great a percentage of the total nitrogen in high-nitrogen as in low-nitrogen maize.

H. W.

Water-soluble Constituents of the Alfalfa Plant [Lucerne].

THOMAS B. OSBORNE, ALFRED J. WAKEMAN, and CHARLES S. LEAVENWORTH (*J. Biol. Chem.*, 1922, **53**, 411—429).—The investigation of the press-juice previously obtained (this vol., i, 99) has been continued. After removal of the colloid obtained by addition of 20% of alcohol, a second precipitate may be obtained by raising the alcohol content of the filtrate to 53%. This precipitate contains 8% of the original nitrogen, which is probably present as protein. The distribution of nitrogen, both before and after hydrolysis, has been determined in the two precipitates and also in the filtrate, and analyses have been made of the inorganic constituents of the three fractions. The filtrate appears to be suitable for investigating the water-soluble constituents of the juice; the present paper records preliminary experiments in this direction.

E. S.

Comber's Reaction for Acidity of Soils. J. HUDIG and

C. W. G. HETTERSCHIJ (*Chem. Weekblad*, 1922, **19**, 366—367).—The colour given by the reagent, an alcoholic solution of potassium thiocyanate, cannot be taken as a quantitative indication of acidity for sandy humus-bearing soils, since it does not indicate the same order as the hydrogen-ion determination. As Comber has pointed out, quantitative results are precluded, although for the same soil the test may indicate variations in acidity.

S. I. L.

Soil Reaction and Succession in Relation to Plant Covering.

E. J. SALISBURY (*Ann. Bot.*, 1922, **36**, 391—431).—An account of the soils of the dune, shingle, and salt marsh system of Blakeney Point (Norfolk). In the successive stages of dune formation the content of calcium carbonate diminishes owing to leaching, whilst the content of organic matter increases. Hydrogen-ion concentration shows a corresponding variation, the reaction of the older dunes being more acid than that of the younger dunes. A close relationship exists between organic matter and water content. Shingle banks show similar relationships. In salt marshes, however, tidal effects obscure other factors.

G. W. R.

Influence of Soil Colloids on Availability of Salts. NEIL E.

GORDON and E. B. STARKEY (*Soil Sci.*, 1922, **14**, 1—7).—Iron oxide and alumina gels have considerable adsorptive power for calcium acid phosphates, but the adsorption by silica gel is small. Within limits, adsorption increases with increasing concentration of the salt solutions. Adsorbed salts are only slowly released from the gel in contact with water. The hydrogen-ion concentration of the salt solution considerably affects the amount adsorbed. With silica gel the adsorption of calcium and potassium decreases, and of phosphate slightly increases, with decreasing p_H values. A. G. P.

Organic Chemistry.

The Action of Ozone on Hydrocarbons with Special Reference to the Production of Formaldehyde. I. The Action of Ozone on Methane. T. SHERLOCK WHEELER and E. W. BLAIR (*J. Soc. Chem. Ind.*, 1922, **41**, 331—332T).—Mixtures of methane and ozonised oxygen in proportions outside the explosive limits of 4% and 60% of methane were passed, with and without admixture with ammonia, through a tube which could be heated to any desired temperature in an electric furnace, at such a rate that the gas was heated for about two and a half minutes. At 15°, the reaction is very slow; it increases with the temperature until, at 100°, 53% of the ozone reacts in about two minutes, and 76% at 200°. Above 400° all the ozone decomposes. The first isolated product was formaldehyde, which is quickly further oxidised, but initially the oxidation rate does not increase so fast as that of methane and there is a slight increase in the amount isolated up to about 300°. The amount was not increased when ammonia was present, but the amount of formic acid isolated was much increased in these circumstances owing to formation of ammonium formate. In absence of ammonia only traces of formic acid remained unoxidised, and the greater portion of the methane oxidised was obtained as carbon dioxide and water formed from formic acid either by way of carbonic acid or by its decomposition into carbon dioxide and hydrogen, the latter being then oxidised to water. The non-stabilisation of formaldehyde by the ammonia is ascribed to the necessity of ten molecules interacting to form hexamethylenetetramine, which does not readily occur at such low concentrations. G. F. M.

The Absorption of Ethylene by Sulphuric Acid. Preparation of Ethyl Alcohol, Ethyl Sulphate, and Liquid Hydrocarbons. A. DAMIENS (*Compt. rend.*, 1922, **175**, 585—588; cf. A., 1913, ii, 349).—The effect of a catalyst on the speed of fixation of ethylene by sulphuric acid is considerable; cuprous oxide, which is transformed by the acid into cuprous sulphate, is the most efficient among the substances used. Whatever the nature of the final product may be, the reaction in the presence of the catalyst takes place in two stages: (1) the formation of a complex, $\text{Cu}_2\text{SO}_4 \cdot n\text{C}_2\text{H}_4$, partly soluble in sulphuric acid, (2) the action of the acid on this complex. The latter may yield either ethyl hydrogen sulphate and diethyl sulphate, or liquid hydrocarbons. The formation of the ethyl compounds occurs in the cold; the equilibrium $\text{H}_2\text{SO}_4 + \text{Et}_2\text{SO}_4 \rightleftharpoons 2\text{HEtSO}_4$ is displaced from left to right by elevation of temperature and by hydration of the acid. Formation of a mixture of saturated hydrocarbons of density 0.77 and b. p. 110° and upwards takes place when the catalyst is heated in contact with the acid, followed by absorption of the

gas at the ordinary temperature in presence of mercury or mercurous sulphate.

H. J. E.

Reactions of Combination with Conjugated Systems of Double Linkings. I. Bromination of Isoprene. A. G. BERGMANN (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 24—37).—Molecules composed of two similar atoms or groups of atoms unite with a conjugated system of double carbon linkings at the 1- and 4-positions, that is, at the ends of the system, an exception to this rule occurring in the combination of bromine with aromatic derivatives. As regards molecules consisting of dissimilar components, such as hydrogen bromide, few experimental data are available, but the union does not take place in accordance with Thiele's law.

Bromination of isoprene in chloroform solution cooled in ice yields: (1) A small quantity of the *monobromo*-compound, $\text{CH}_2\text{Br}\cdot\text{CMe}:\text{C}\cdot\text{CH}_2$ (?), b. p. $61.5\text{--}62.5^\circ/64\text{ mm.}$, d_4^{20} 1.3742. (2) The dibromide, $\text{C}_5\text{H}_8\text{Br}_2$, b. p. $62\text{--}64^\circ/10\text{ mm.}$, d_4^{20} 1.7431, which gives the dibromo-glycol, b. p. 126.5° , when oxidised by permanganate. (3) The isomeric dibromide, b. p. $88\text{--}92^\circ/10\text{ mm.}$, d_4^{20} 1.7880. This dibromide yields a viscous, oily ozonide, which is decomposed by boiling water, giving bromoacetone, bromoacetic acid, and a tarry mixture of bromoaldehydes, bromoketones, peroxides, etc. Oxidation of the dibromide by means of permanganate yields the dibromo-glycol, which is sparingly soluble in water, whilst treatment with chromic acid gives bromoacetone and bromoacetic acid (cf. Mokiewsky, A., 1899, i, 726; 1900, i, 509; *J. Russ. Phys. Chem. Soc.*, 1904, **36**, 912). With ammonia, the dibromide forms an amorphous, sometimes glue-like substance of high molecular weight, and with sodamide an amorphous, insoluble product containing 32.51—32.89% of bromine and 7.87—7.93% of nitrogen.

T. H. P.

Reactions of Combination with Conjugated Systems of Double Linkings. II. Combination of Hydrogen Bromide with Diisopropenyl [$\beta\gamma$ -Dimethyl- $\Delta^{\alpha\gamma}$ -butadiene]. A. G. BERGMANN (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 37—40).—The combination of hydrogen bromide with $\beta\gamma$ -dimethyl- $\Delta^{\alpha\gamma}$ -butadiene in glacial acetic acid solution takes place in the two stages: (1) $\text{CH}_2\cdot\text{CMe}\cdot\text{CMe}:\text{CH}_2 + \text{HBr} = \text{CMe}_2\text{Br}\cdot\text{CMe}:\text{CH}_2$, and (2) the latter $+ \text{HBr} = \text{CMe}_2\text{Br}\cdot\text{CMe}_2\text{Br}$ (30%) $+ \text{CMe}_2\text{Br}\cdot\text{CHMe}\cdot\text{CH}_2\text{Br}$ (70%).

γ -Bromo- $\beta\gamma$ -dimethyl- Δ^{α} -butene, $\text{C}_6\text{H}_{11}\text{Br}$, b. p. $84\text{--}86^\circ/100\text{ mm.}$, d_4^{20} 1.2201, yields dimethylisopropenylcarbinol when hydrolysed by means of aqueous potassium hydroxide.

$\beta\gamma$ -Dibromo- $\beta\gamma$ -dimethylbutane was described by Thiele (A., 1894, i, 217).

$\alpha\gamma$ -Dibromo- $\beta\gamma$ -dimethylbutane is a liquid, b. p. $88\text{--}89^\circ/16.5\text{ mm.}$, d_4^{20} 1.6065.

The product of the union of 1 mol. of hydrogen bromide with isoprene, namely, γ -bromo- γ -methyl- Δ^{α} -butene, combines with a second molecule of hydrogen bromide, apparently giving only $\beta\delta$ -dibromo- β -methylbutane.

T. H. P.

Formation of Acetylene and Ammonia during Incomplete Combustion. K. A. HOFMANN and ERICH WILL (*Ber.*, 1922, 55, [B], 3228—3233).—The gaseous products of an inverted air flame burning in the vapours of several organic substances have been investigated. The necessary apparatus is fully figured and described in the original text. The supply of air is so adjusted that the flame just burns continuously. The following quantities of acetylene (in grams) are obtained by the decomposition of 100 grams of the organic compound: benzene, 5; phenol, 4.4; aniline, 2.5; diphenylamine, 2.7; carbazole, 2.4; pyridine, 1.7; anthracene, 1.6; anthracene residues, 0.24; coal tar, 4; middle oil from Rositzer lignite tar, 1; benzoquinone, 1; hexane, 2. The formation of acetylene is partly due to thermal action, but oxidative degradation also plays a part, as is proved by the production of the gas from hexane. Hydrocyanic acid is also present in the gases (100 grams of aniline, carbazole, diphenylamine, and pyridine yield, respectively, up to 3, 1.5, and 5 grams and traces of hydrocyanic acid).

The possibility of the production of ammonia during the combustion of air charged with a number of catalysts in hydrogen or coal gas has also been investigated. The actual quantity formed is very small, but the effect of the catalyst is clearly perceptible. Arsenic trihydride, chromyl chloride, and silicon tetrachloride depress the formation of ammonia. Osmium tetroxide and the osmium formed therefrom and, in particular, nickel carbonyl are active catalysts. The action of the latter, by which metallic nickel is produced, appears to indicate that the effect is due to a catalytic hydrogenation of the nitrogen, and not to an influence of the flame ions. The carbon liberated from benzene vapour or coal gas favours the production of ammonia, possibly owing to intermediate formation of hydrogen cyanide. The yields of ammonia are not improved noticeably by bringing volatile salts, such as sodium or lithium carbonates, into the flame, by spreading the flame over a porous clay surface impregnated with various salts or by placing an inverted mantle over the orifice of the burner.

H. W.

Calcium Carbide. ERLING BOTOLFSEN (*Ann. Chim.*, 1922, 18, 5—48).—Pure calcium carbide is not obtained by heating calcium acetylide—acetylene—ammonia, $C_2Ca, C_2H_2, 4NH_3$ (cf. Moissan, A., 1899, i, 241; 1903, i, 545), as this substance, even when pure, yields an impure product containing free carbon, cyanamide, calcium cyanide, and probably calcium nitride and hydride. A diagrammatic representation of this decomposition is given, but it is pointed out that the series of reactions is more complex than the diagram indicates. A study of calcium—ammonia shows that its formation may take place at temperatures ranging from -15° to $+30^\circ$ (cf. Moissan, A., 1899, ii, 152); at the higher temperature, pressure is required, and if the calcium employed contains sodium as impurity, the product is pasty rather than crystalline. On being heated under reduced pressure, the substance decomposes

explosively; the temperature at which this occurs depends on the pressure. The author considers that the calcium-ammonium hitherto described is a mixture. The reaction between metallic calcium and free carbon is not appreciable at temperatures below the melting point of the metal. Above 800° , combination takes place more rapidly if the calcium is in the state of vapour. When the carbide is prepared in an iron tube, the product, even when practically pure, is black, the coloration being due, not to free carbon, but to iron, and on substituting alundum for iron a similar coloration is caused by aluminium which has been reduced by calcium. On heating calcium carbide, dissociation into its elements was observed without any intermediate formation of a sub-carbide. The progress of the dissociation is influenced by the presence of iron, iron oxide, and other substances. H. J. E.

The Oxidation of isoPropyl Alcohol with Potassium Permanganate. WILLIAM LLOYD EVANS and LILY BELL SEFTON (*J. Amer. Chem. Soc.*, 1922, **44**, 2271—2276; cf. A., 1912, i, 743; 1916, i, 362; 1919, i, 514).—When oxidised by potassium permanganate in the presence of potassium hydroxide, isopropyl alcohol yields carbon dioxide, oxalic acid, and acetic acid. In addition, a small amount of acetone is obtained if the temperature does not exceed 25° and the concentration of the alkali does not exceed 2.12 grams per litre. The amounts of oxalic and acetic acids produced increase and decrease respectively as the initial alkalinity increases from zero to 0.1—0.2 *N*. The general effect of temperature is to increase the amount of carbon oxidised to carbon dioxide to slightly more than one atom for each molecule of alcohol.

Oxalic acid is obtained in greater quantity from isopropyl alcohol in neutral solutions than from acetone, owing to the fact that in the first step of the reaction no acids are formed to neutralise the potassium hydroxide obtained from the potassium permanganate. Further, the course of the oxidation is such as to bring about a final concentration of alkali which is greater than in the oxidation of acetone alone. W. G.

A Simplified Method for the Resolution of Methyl-*n*-hexylcarbinol. JOSEPH KENYON (*T.*, 1922, **121**, 2540—2542).

Synthetic Experiments with Ethenylcarbinols. I. Conversion of γ -Methyl- Δ^{α} -butinen- γ -ol into γ -Methyl- Δ^{α} -butinene, β -Methylbutanolone, and its Condensation Products. HELMUT SCHEIBLER and ARTUR FISCHER (*Ber.*, 1922, **55**, [B], 2903—2923).—The preparation of γ -methylbutinenol, $\text{OH}\cdot\text{CMe}_2\cdot\text{C}\equiv\text{CH}$, and its conversion into isopropenylacetylene, $\text{CH}_2\cdot\text{CMe}\cdot\text{C}\equiv\text{CH}$, has been described by Farbenfabriken vorm. F. Bayer & Co. in a series of patents (cf. A., 1916, i, 113, 305). The preparation of the pure alcohol on a laboratory scale, and the applications of it for synthetic purposes are now described.

Finely divided sodamide is placed beneath ether which is cooled by ice and saturated with acetylene which has been purified by

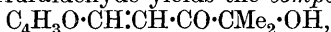
means of bleaching powder, copper nitrate solution acidified with nitric acid, concentrated sulphuric acid, and soda-lime. When saturation is complete, the subsequent current of acetylene is caused to pass through acetone heated at 30—40°, so that the sodium acetone as it is formed reacts immediately with the gas. The product thus obtained consists of a mixture of γ -methylbutinenol, mesityl oxide, and $\beta\epsilon$ -dimethyl- Δ^7 -hexinene- β -diol, $\text{OH}\cdot\text{CMe}_2\cdot\text{C}:\text{C}\cdot\text{CMe}_2\cdot\text{OH}$, m. p. 94°. Since γ -methylbutinenol and mesityl oxide can only be separated from one another incompletely by fractional distillation, the carbinol is purified by conversion into its *silver* derivative and subsequent decomposition of the latter by the theoretically necessary quantity of dilute hydrochloric acid. γ -Methylbutinenol, b. p. 103—104°, is a colourless, mobile liquid, with a characteristic odour, which mixes with water in all proportions and strongly reduces alkaline permanganate solution. It has d_4^{23} 0.8651, n_D^{23} 1.41867, $d_4^{15.8}$ 0.8678, $n_a^{15.8}$ 1.41536, $n_D^{15.8}$ 1.42446. With mercuric chloride, it gives a *compound*, decomp. above 240° without melting below 300°. Its *copper* and *potassium* derivatives are described. It is converted by acetic anhydride and sodium acetate into the corresponding *acetate*, a colourless liquid, b. p. 128—136°, which could not be obtained in a state of purity.

The conversion of γ -methylbutinenol into isopropenylacetylene by anhydrous magnesium sulphate at 250° is described in detail, and sketches are given of the necessary apparatus. The yields of the hydrocarbon are 15—18% of those theoretically possible; the unusual volatility of the product renders its complete condensation a matter of great difficulty. When freshly distilled, it is a colourless, mobile liquid with a very penetrating odour; it has b. p. 32—35°, d_4^{11} 0.6801, n_a^{11} 1.41666, n_D^{11} 1.43046. It gives a white *precipitate* with ammoniacal silver nitrate solution, and a highly characteristic, lemon-yellow *cuprous* derivative.

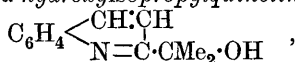
An ethereal solution of magnesium ethyl bromide reacts with isopropyleneacetylene (in the same manner as with acetylene) to yield ethane and magnesium isopropyleneacetylenyl bromide; the latter is converted by isobutyraldehyde into the secondary alcohol, $\text{CH}_2\cdot\text{CMe}\cdot\text{C}:\text{C}\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2$, but the product is not homogeneous, and when reduced by sodium and moist ether gives a mixture of substances, b. p. 75—90°/15 mm., and 110—125°/15 mm., respectively.

The mode of the addition of the elements of water to γ -methylbutinenol varies considerably with the catalyst employed. It is converted by dilute sulphuric acid in the presence of mercuric sulphate into a voluminous, white precipitate which disappears after a few minutes with formation of β -methylbutane- β -ol- γ -one (methyl α -hydroxyisopropyl ketone), $\text{OH}\cdot\text{CMe}_2\cdot\text{COMe}$, b. p. 140—141°, $d_4^{17.2}$ 0.9578, n_a 1.41425, n_D 1.42203 (semicarbazone, m. p. 164°; oxime, m. p. 86°; acetate, a colourless liquid with an odour resembling peppermint, b. p. 171—172°, $d_4^{17.4}$ 1.0064, $n_a^{17.4}$ 1.41485, $n_D^{17.4}$ 1.42302). It condenses with benzaldehyde in aqueous alcoholic solution in the presence of sodium hydroxide to form α -phenyl-

δ -methyl- Δ^{α} -pentene- δ -ol- γ -one (benzylidenemethyl α -hydroxyisopropyl ketone), $\text{CHPh}:\text{CH}\cdot\text{CO}\cdot\text{CMe}_2\cdot\text{OH}$, a greenish-yellow, very highly refractive liquid, b. p. $164\text{--}169^\circ/15\text{ mm.}$, m. p. $39\text{--}40^\circ$ (oxime, m. p. 136° ; acetate, m. p. 85°). α -3:4-Methylenedioxyphenyl- δ -methyl- Δ^{α} -pentene- δ -ol- γ -one (piperonylidenemethyl α -hydroxyisopropyl ketone) is prepared from β -methylbutanolone and piperonal, crystallises in lustrous, yellow leaflets, m. p. $105\text{--}106^\circ$; the corresponding acetate forms coarse, yellow crystals, m. p. 93° . α -Phenyl- ζ -methyl- Δ^{γ} -heptadiene- ζ -ol- ϵ -one (cinnamylidenemethyl α -hydroxyisopropyl ketone), pale yellow leaflets, m. p. $109\text{--}110^\circ$, and its acetate, almost colourless crystals, m. p. $58\text{--}59^\circ$, are described. In a similar manner, furfuraldehyde yields the compound,



a pale yellow, highly refractive, viscous liquid which rapidly darkens on exposure to air, b. p. $140\text{--}145^\circ/15\text{ mm.}$ (acetate, colourless, lustrous leaflets, m. p. 49°). β -Methylbutanolone and *o*-aminobenzaldehyde yield 2- α -hydroxyisopropylquinoline,



a colourless, crystalline powder, m. p. $64\text{--}65^\circ$.

In the absence of mercury salts, γ -methylbutinenol is transformed by boiling dilute sulphuric acid into isopropenylacetylene and probably also methyl isopropenyl ketone, $\text{CH}_2:\text{CMe}\cdot\text{COMe}$, whereas β -methylbutanolone is not produced. A solution of sulphuric acid in glacial acetic acid also converts γ -methylbutinenol into isopropenylacetylene and, ultimately, into an undistillable resinous condensation compound.

β -Methylbutan- β -ol- γ -one is converted by phosphoric oxide in the presence of light petroleum at the atmospheric temperature into a substance, $\text{C}_{10}\text{H}_{18}\text{O}_5$, a colourless liquid with an odour resembling camphor, b. p. $165\text{--}167^\circ$, $d_4^{17.6}$ 0.9702, $n_D^{17.6}$ 1.41696, $n_B^{17.6}$ 1.42456. It is stable towards permanganate, does not yield an oxime or semicarbazone, and does not react with acetic anhydride. Its physical constants point to the presence of three oxygen atoms in ether-like combination as indicated by the formula $\text{O}(\text{CMe}\begin{matrix} \diagup \text{CMe}_2 \\ \diagdown \text{O} \end{matrix})_2$.

Such a compound must have the properties of an acetal. This is found to be the case, since it is hydrolysed by concentrated hydrochloric acid to β -methylbutanolone, and is transformed by bromine into a dibromo-compound (?), $\text{O}(\text{C}(\text{CH}_2\text{Br})\begin{matrix} \diagup \text{CMe}_2 \\ \diagdown \text{O} \end{matrix})_2$, a colourless, crystalline powder, m. p. $64\text{--}65^\circ$.

H. W.

The Action of Boric Acid on Mannitol in Alkaline Solution. RENÉ DUBRISAY (*Compt. rend.*, 1922, 175, 762—764; cf. A., 1918, ii, 368; this vol., ii, 428).—The addition of increasing quantities of mannitol to a solution containing boric acid and sodium hydroxide, in the proportions of 1/10 mol. of each substance per litre, results in increase of the minimum temperature at which complete miscibility of the solution with phenol occurs. Measurement of the rotatory power of such solutions shows that it increases until the

molecular ratio of mannitol to boric acid is 1.2 to 1, and thence decreases with increase of the ratio. Similar results are obtained with a solution in which the concentrations of boric acid and sodium hydroxide are doubled. A series of observations on the surface tension of the two solutions is also recorded. H. J. E.

Derivatives of Behenic and Erucic Acids. YOSHIYUKI TOYAMA (*J. Chem. Ind. Japan*, 1922, 25, 1053—1055).—*Methyl behenate* separates from alcohol in lustrous scales, m. p. 54—54.5°, b. p. 224—225°/5 mm. Ethyl behenate forms fine, microcrystalline granules from alcohol, m. p. 50—50.5°, b. p. 230—231°/5 mm. Behenamide, fine needles, m. p. 111—112°. *Behenanilide*, fine needles, m. p. 101—102°.

Methyl erucate is a nearly colourless liquid, d^{15}_4 0.8735, d^{20}_4 0.8702, n^{15}_D 1.4577, n^{20}_D 1.4558, b. p. 221—222°/5 mm. Ethyl erucate is a nearly colourless liquid, d^{15}_4 0.8676, d^{20}_4 0.8648, n^{15}_D 1.4562, n^{20}_D 1.4543, b. p. 229—230°/5 mm. Erucamide forms fine needles, m. p. 82.5—83°. *Erucanilide* forms lustrous scales, m. p. 65.5—66°.

K. K.

Electro-synthesis of Azelaic and Thapsic Acids. MABEL CARMICHAEL (T., 1922, 121, 2545—2549).

Oxidation of some Sugar Acids. WILHELM GREINERT (*Annalen*, 1922, 429, 152—163).—An examination of the space formula of mucic acid shows that when this is oxidised in such a way as to eliminate two adjacent carbon atoms as oxalic acid, the residue should appear as racemic acid, but that if one carbon atom is removed from each end of the chain, the residue should be obtained as *i*-tartaric acid. Experiment shows that the tartaric acid obtained on oxidation by alkaline permanganate is racemic acid unaccompanied by any appreciable trace of *i*-tartaric acid.

Similarly, *d*-saccharic acid on oxidative fission could give oxalic acid and *i*-tartaric acid, oxalic acid and *d*-tartaric acid, or two molecules of carbon dioxide and *l*-tartaric acid. Experiment showed the presence of racemic acid mixed with *d*-tartaric acid, but no *i*-tartaric acid, in the oxidation product.

Mannosaccharic acid should give *i*-tartaric acid and oxalic acid, or *l*-tartaric acid and two molecules of carbon dioxide. Probably the reaction takes the former course, although no undoubted specimen of *i*-tartaric acid was isolated; for direct experiment shows that this acid is destroyed by permanganate more readily than *d*-tartaric acid, and that, under the conditions used in oxidising mannosaccharic acid, added *i*-tartaric acid could not be recovered from the product. C. K. I.

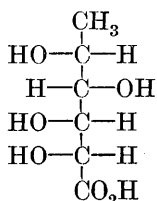
Chemistry of the Sugars. IV. H. KILIANI (*Ber.*, 1922, 55, [B], 2817—2826; cf. A., 1921, i, 304; this vol., i, 223, 321).—The technique of the oxidation of sugars and polyhydroxy-acids at the atmospheric temperature by nitric acid is improved further by removing any excess of nitric acid by agitating the solution, after dilution, if necessary, with five or six portions of ether (each one and

a half times the volume of the solution). The sixth extract is usually free from nitric acid. The aqueous solution may still contain nitric esters. It is allowed to remain exposed to the air for twelve to twenty-four hours to permit the dissolved ether to evaporate and is then concentrated, if necessary, in a vacuum over sulphuric acid. The nitric esters during this period become hydrolysed gradually, and the liberated nitric acid causes a fresh oxidation. For the sake of safety, the ethereal extracts are immediately transferred to a bottle containing sodium hydroxide solution (1 in 3). The efficiency of the process is illustrated by the identification of *l*-trihydroxyglutaric acid as a by-product of the preparation of ketorhamnonolactone and by the preparation of *r*-pentahydroxypimelic acid from α -glucoheptonic acid [*quinine pentahydroxypimelate* crystallises in long, lustrous needles ($+4\text{H}_2\text{O}$); the *brucine* salt ($+6\text{H}_2\text{O}$) forms microscopic rods].

The strongly reducing acid which has been isolated from the products of the oxidation of dextrose and *d*-gluconic acid with nitric acid (A., 1921, i, 304; this vol., i, 223) is identified as 5-keto-*d*-gluconic acid, which has been described previously by Boutroux and Bertrand (A., 1904, ii, 760). It is conveniently obtained as its calcium salt by precipitation of the strongly acetic acid solution with calcium chloride when it separates before the calcium saccharate. The identity of the acid with Bertrand's product is established by the crystallographical examination of the calcium and cadmium salts. 5-Keto-*d*-gluconic acid gives a *semicarbazone-semicarbazide*, $\text{C}_8\text{H}_{18}\text{O}_8\text{N}_6$, microscopic needles which become discoloured at about 170° , and often without actually melting at about 200° .

Constitution of Ketorhamnonic Acid.—This acid has been described previously (this vol., i, 223) as an α -keto-compound. The ease with which, in comparison with rhamnose, it yields iodoform suggests that the carbonyl and methyl groups are directly attached to one another, and that it is therefore a δ -keto-substance. This view is strengthened by the occurrence of *l*-trihydroxyglutaric acid among the products of its oxidation (see above), and confirmed by its behaviour when reduced with sodium amalgam, when, in place of *l*-isorhamnonic acid, which would be expected from an α -keto-compound, it yields a new acid, *l*-guleonic [δ -*epi-l*-rhamnonic] acid (annexed formula). *l*-Guleonolactone crystallises in rods or large plates with apparent rectangular bases, m. p. 152° . It has $[\alpha]_D -84.9^\circ$ or -87.7° initially in aqueous solution, which diminishes as the lactone becomes hydrated into the acid. The *calcium*, *sodium*, and *barium* salts are amorphous; the *brucine* salt ($+7\text{H}_2\text{O}$) crystallises in coarse plates. The *phenylhydrazide* forms coarse needles, m. p. 152° ; the *hydrazide*, m. p. 155 – 156° , has $[\alpha]_D +15.2^\circ$ in aqueous solution, the sign of the rotation in accordance with Hudson's rule proving definitely that *l*-isorhamnonic acid is not present.

Lævulosecarboxylic Acid.—The isolation of a lævorotatory *phenylhydrazide* of lævulosecarboxylic acid, m. p. 187° , $[\alpha]_D -29.5^\circ$



in aqueous solution, is directly contradictory to Nef's assumption with regard to the position of the α -hydroxy-group (A., 1910, i, 711). More recent observation renders it exceedingly improbable that the addition of hydrocyanic acid to lævulose is completely unsymmetrical; it is more probable that two acids are formed simultaneously. H. W.

A Highly Unsaturated Hydrocarbon, and some Higher Alcohols in a Commercial Illipé Fat. SHŪMEI KOBAYASHI (*J. Chem. Ind. Japan*, 1922, 25, 1188—1196).—A new, highly unsaturated hydrocarbon, *illipene*, $C_{32}H_{56}$, a light yellow solid with an aromatic odour, m. p. 64.5° , iodine value 382.5, was isolated from the unsaponifiable matter (8.55% of the fat) of a commercial illipé fat imported from India. It is optically inactive and boils at $315^\circ/2.5$ mm. The *hydrochloride* is a white powder, m. p. 115 — 116° . The unsaponifiable matter also contains four higher alcohols which were separated by repeated recrystallisation from acetone: (I) $C_{21}H_{38}O$, microscopic, silky needles, m. p. 196 — 197° , iodine value, 114.9 ; (II) $C_{31}H_{56}O$, silver-white crystals, m. p. 186 — 186.5° , iodine value, 100.2 ; (III) $C_{27}H_{48}O$, silver-white grains, m. p. 159 — 160° , iodine value 82.3 , and (IV) $C_{21}H_{36}O$, light yellow needles, m. p. 125 — 135° , iodine value 100.2 . The solid mixture of fatty acids of the fat is mainly composed of stearic acid. K. K.

The Drying of Fatty Oils. PAWEŁ ŚLANSKY (*Z. angew. Chem.*, 1922, 35, 389—391).—The drying of linseed oil is produced by oxidation and gelatinising processes, the latter being favoured by increase in temperature. The oxidation of linseed oil fatty acids proceeds more rapidly than that of linseed oil itself, and the oxidation of the oil is accelerated by the addition of linolic acid or linolenic acid. Gelatinisation of the oil is increased by the addition of oleic acid. The solid product, "linoxyn," obtained when linseed oil dries, is capable of absorbing 15% of its weight of water.

W. P. S.

Composition of the Fatty Acids of Rape Oil. YOSHIYUKI TOYAMA (*J. Chem. Ind. Japan*, 1922, 25, 1044—1053; cf. *J. Tokyo Chem. Soc.*, 1895, 16, 187).—The main constituent of the fatty acids of rape oil obtained from the seeds of *Brassica campestris*, L. (*B. chinensis*, L.), grown in the Shiga prefecture, was erucic acid (about 65%). The saturated acids (less than 2%) consisted of palmitic acid with seemingly stearic, behenic, lignoceric, and arachidic acids. The presence of linolenic, linolic, and oleic acids was proved from the bromination and oxidation of the liquid acids and their methyl esters. [Cf. *J. Soc. Chem. Ind.*, 1922, Dec.] K. K.

Stereochemical Studies. VI. Stereoisomeric Trithiocarbodilactic Acids. BROR HOLMBERG (*Arkiv Kem. Min. Geol.*, 1921—1922, 8, No. 8, 1—17).—The action of potassium trithiocarbonate on an α -bromopropionate yields two stereoisomeric trithiocarbodilactic acids (A., 1905, i, 323). That the isomeride with the higher melting point is the racemic modification is shown by unpublished work of the author and Ramberg, who, by using

q q*

highly active α -bromopropionic acid, obtained active trithiocarbodilactic acids. By means of *d*- and *l*- α -phenylethylamines (Lovén, A., 1905, i, 875), the author has now succeeded in resolving the racemic acid into its components. The inactive isomeride with the lower melting point represents the meso-form.

meso-Trithiocarbodilactic acid, $\text{CS}(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{H})_2$, forms crystals, m. p. 104—105°, its saturated aqueous solution containing 27.4 grams per litre at 25°; its crystalline barium salt (+5H₂O) was prepared. An attempt to prepare an aniline hydrogen salt yielded 3-phenyl-5-methylrhodanine (A., 1910, i, 361), and attempts to obtain *d*- α -phenylethylamine and *d*- α -phenylethylamine hydrogen salts resulted in the formation of *l*-di- α -phenylethylthiocarbamide, $\text{CS}(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na})_2 + \text{CHPhMe}\cdot\text{NH}_2 = \text{SH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na} + \text{CO}_2\text{Na}\cdot\text{CHMe}\cdot\text{S}\cdot\text{CS}\cdot\text{NH}\cdot\text{CHPhMe}$, and the latter + $\text{CHPhMe}\cdot\text{NH}_2 = \text{CO}_2\text{Na}\cdot\text{CHMe}\cdot\text{SH} + \text{CS}(\cdot\text{NH}\cdot\text{CHPhMe})_2$ (cf. Lovén and Ohlsson, A., 1914, i, 830); thiolactic acid is also formed, $\text{CS}(\text{S}\cdot\text{CHMe}\cdot\text{CO}_2\text{Na})_2 + 2\text{H}_2\text{O} = 2\text{CO}_2\text{Na}\cdot\text{CHMe}\cdot\text{SH} + \text{CO}_2 + \text{H}_2\text{S}$.

dl-Trithiocarbodilactic acid forms small, yellow prisms, m. p. 150—151° on slow, or 154—155° on rapid, heating; its saturated aqueous solution contains 3.04 grams per litre at 25°. Its readily soluble barium salt (+4H₂O); aniline hydrogen salt, $2\text{C}_7\text{H}_{10}\text{O}_4\text{S}_3\cdot\text{NH}_2\text{Ph}$, yellow, crystalline crust, m. p. 134—135°, and aniline salt, $\text{C}_{19}\text{H}_{24}\text{O}_4\text{N}_2\text{S}_3$, yellow, crystalline powder, m. p. 135° (gas evolution), were prepared.

d-Trithiocarbodilactic acid crystallises in small, yellow prisms, m. p. 136—136.5°, $[\alpha]_D^{20} +167.4^\circ$ in acetone, $+166.1^\circ$ in absolute alcohol, and $+187.9^\circ$ in ethyl acetate. As sodium hydrogen salt $[\alpha]_D^{25}$ for the acid is $+80.9^\circ$ and as sodium salt $+50.6^\circ$.

The *l*-isomeride shows the same melting point and solubility as the *d*-compound; $[\alpha]_D^{20} -167.8^\circ$ in acetone and -109° in water. When heated in aqueous solution, the acid gradually becomes inactive.

When heated with ammonia, *d*-trithiocarbodilactic acid yields a dextrorotatory thiolactic acid which is converted into a dextrorotatory dithiodilactic acid when oxidised (cf. Lovén, A., 1908, i, 714).
T. H. P.

The Properties of Dibenzoylcystine. CHARLES GEORGE LEWIS WOLF and ERIC KEIGHTLEY RIDEAL (*Biochem. J.*, 1922, **16**, 548—555).—Gels of dibenzoylcystine may be prepared by peptisation with hot water. The substance is a relatively strong acid with a dissociation constant of 1.49×10^{-3} . The gel structure appears to be fibrillary and relatively coarse. The sodium salt of the acid exhibits no gelatinising properties. The presence of acids greatly reduces the solubility of the compound. This was confirmed by observations on the water-retaining capacity and internal viscosity of the gel. Lyotropic salts, such as ammonium thiocyanate, reduce the water-retaining power of the gel, producing ultimate liquefaction. Kationic dyes are adsorbed and precipitated by the gel. Anionic dyes diffuse in a normal manner, whilst halogen dyes apparently react chemically with the sulphur group. Di-*m*-

nitrobenzoyl cystine has similar properties to the simple compound. A possible structure for the gel fibril based on the effect of chemical substitution on the gel formation is suggested. S. S. Z.

Preparation of Crotonaldehyde. CONSORTIUM FÜR ELEKTRO-CHEMISCHE INDUSTRIE G. M. B. H. (D.R.-P. 349915; from *Chem. Zentr.*, 1922, iv, 43).—Acetaldehyde vapour is passed over suitable catalysts at temperatures below 300°. The crotonaldehyde is removed at once from the seat of the reaction with the excess of unchanged acetaldehyde which is led back again into the reaction chamber, after separation from the crotonaldehyde. Charcoal coated with titanium oxide or moulds made of aluminium oxide or hydroxide, beryllium oxide, calcium hydroxide, bog iron ore, cement, or mixtures of these substances are used as catalysts.

G. W. R.

Synthesis of Substances resembling Disaccharides from Monohydroxyaldehydes. BURCKHARDT HELFERICH and RUDOLF WEIDENHAGEN (*Ber.*, 1922, 55, [B], 3348—3354).—In continuation of the examination of γ - and δ -hydroxyaldehydes which have been shown to exhibit a close analogy to the aldoses, it is found that they can be converted by boiling their ethereal solutions with dehydrated copper sulphate into products which are very similar to a disaccharide of the type of trehalose.

γ -Hydroxyvaleraldehyde is converted into *di- γ -hydroxyvaleraldehyde [bis-5-methyltetrahydro-2-furyl ether]*, $O\left(\text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CHMe} \end{array} \right)_2$, a colourless, mobile liquid, b. p. 86—92°/11 mm., d_4^{18} 1.0107, n_D^{18} 1.4409. It is sparingly soluble in water (1:55). It does not reduce boiling Fehling's solution or exhibit any reaction of a free aldehyde group. It does not evolve methane when treated with magnesium methyl iodide according to the method of Tschugaev and Zerewitinov. It is very smoothly hydrolysed by dilute acids with the production of two molecular proportions of γ -hydroxyvaleraldehyde.

γ -Hydroxy- γ -methylhexaldehyde is transformed in a similar manner into *di- γ -hydroxy- γ -methylhexaldehyde [bis-5-ethyl-5-methyltetrahydro-2-furyl ether]*, $O\left(\text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} - \text{CMeEt} \end{array} \right)_2$, a colourless liquid with a pleasant odour and bitter, resinous taste, b. p. 121—125°/11 mm., d_4^{18} 0.9678, n_D^{18} 1.4447. It is very sparingly soluble in water (1:100). In its chemical properties, it resembles its simpler homologue.

Di- δ -hydroxy-n-hexaldehyde, [*bis-6-methyltetrahydro-2- α -pyryl ether*] $O\left(\text{CH} \begin{array}{c} \text{CH}_2 \cdot \text{CH}_2 \\ \text{O} \cdot \text{CHMe} \end{array} \text{CH}_2 \right)_2$, is a colourless, fairly mobile liquid, b. p. 100—105°/11 mm., d_4^{18} 1.000, n_D^{18} 1.4480; one part of it dissolves in sixty parts of water. H. W.

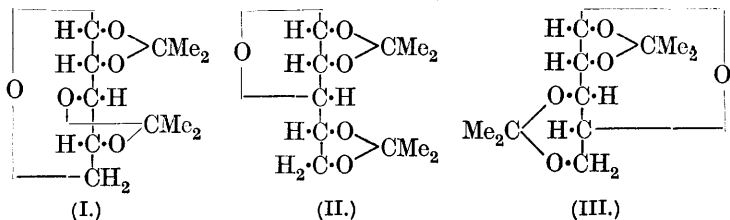
The Oxidation of Acetone with Potassium Permanganate. WILLIAM LLOYD EVANS and LILY BELL SEFTON (*J. Amer. Chem. Soc.*, 1922, 44, 2276—2283; cf. this vol., i, 1108).—By the oxidation
q q* 2

of acetone with neutral or alkaline potassium permanganate at 25°, 50°, and 75°, the sole products are oxalic and acetic acids and carbon dioxide. The yield of oxalic acid increases with increase both in the temperature and the concentration of the alkali, whilst that of acetic acid diminishes with decrease in the temperature and increase in the concentration of the alkali. The production of carbon dioxide increases with rise in temperature. Acetic acid and carbon dioxide arise from the oxidation of acetaldehyde and methylene, respectively. The production of oxalic acid in neutral solutions is due to the very slow oxidation of acetic acid and the oxidation of vinyl alcohol. The results indicate that in aqueous solution acetone must be in equilibrium with *iso*acetone, an increase in the alkalinity causing an increase in the formation of *iso*acetone. Confirmation of Witzemann's view as to the intermediate production of acetylcarbinol in the oxidation of acetone is given (cf. A., 1918, i, 58).
W. G.

Researches on Residual Affinity and Co-ordination. IX. Interaction of Selenium Tetrachloride and β -Diketones. GILBERT T. MORGAN, HARRY DUGALD KEITH DREW, and THOMAS VIPOND BARKER (T., 1922, **121**, 2432—2473).

Optical Rotations of the Sugars. I. The Aldohexoses and Aldopentoses. JOHN GWILLIAM MALTBY (T., 1922, **121**, 2608—2612).

Acetone Sugars. II. Diacetoneoxylose. KARL FREUDENBERG and OLAV SVANBERG (*Ber.*, 1922, **55**, [B], 3239—3242).—Diacetoneoxylose is of particular interest with regard to the relation of its existence to the structure of diacetoneglucose, since xylose has the same configuration as dextrose but lacks the carbon atom. The isolation of the compound therefore demonstrates that the carbon atoms in dextrose are in themselves capable of combining with two *isopropylidene* groups, and, although not in itself affording proof that this is actually the case, confirms the possibility that dextrosediacetone has position 6 unsubstituted (cf. Irvine and Hogg, T., 1914, **105**, 1386).



Diacetoneoxylose (formulae I, II, or III), a colourless, viscous liquid, b. p. 85—87°/0.5 mm., is prepared by the action of hydrogen chloride on a mixture of finely-divided xylose and anhydrous acetone. In freshly prepared aqueous solution it has $[\alpha]_D +13.8^\circ$, which, after a day, attains a constant value, -1.3° . A specimen which has been preserved for about ten days has an initial specific

rotation about half as great as that of the freshly prepared material under similar conditions. When prepared in this manner, a portion of the hydrogen chloride is retained in organic combination (but lost during the distillation); it appears to exist in an intermediate compound which could not be isolated. In the condensation, hydrogen chloride may be replaced by naphthalene- β -sulphonic acid, but the yields of the products are not quite so good.

H. W.

Carbohydrates. II. A New Anhydride ($\alpha\beta$) of Glucose.

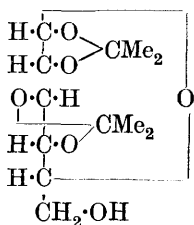
PERCY BRIGL (*Z. physiol. Chem.*, 1922, **122**, 245—262; cf. this vol., i, 225).—When α -chloro- $\gamma\epsilon\zeta$ -triacetylglucose is treated in benzene solution with ammonia, hydrogen chloride is removed with the formation of $\gamma\epsilon\zeta$ -triacetylglucose- $\alpha\beta$ -anhydride, white prisms, soluble in the usual organic solvents except light petroleum and carbon disulphide, m. p. 59.5°, $[\alpha]_D^{18} + 106.5^\circ$. The heat of combustion is 4595 cal. With acetic anhydride, it reacts readily, and from the product, (α)-penta-acetylglucose can be isolated, m. p. 115°. With water, it yields a mixture of the (α) and (β) forms of $\gamma\epsilon\zeta$ -triacetylglucose. (α)- $\gamma\epsilon\zeta$ -Triacetylglucose forms fine needles, m. p. 113—115°, $[\alpha]_D^{18} + 139.6^\circ$. With methyl alcohol, only $\gamma\epsilon\zeta$ -triacetyl- α -methylglucoside is formed, compact needles, m. p. 96—98°, $[\alpha]_{17} + 9.4$.

W. O. K.

Acetone Sugars. I. Transformations of Diacetoneglucose.

KARL FREUDENBERG and FRITZ BRAUNS (*Ber.*, 1922, **55**, [B], 3233—3238).—Toluene-*p*-sulphonyldextrosediactone (Freudenberg and Ivers, this vol., i, 523) is unusually stable towards alkalis, and is only slowly converted by boiling hydrazine into *hydrazinodiacetoneglucose*, $C_{12}H_{22}O_5N_2$, m. p. 96—97°, $[\alpha]_{H_g}^{17} \text{ yellow} + 83.4^\circ$ in water, $[\alpha]_{H_g}^{17} \text{ yellow} + 163.6^\circ$ in acetone. When oxidised, diacetoneglucose is re-formed from it in small amount, so that it appears that the carbonyl group of the sugar and the union of the isopropylidene groups have remained unchanged. It is, however, remarkable that the hydroxy-group of dextrosediactone after displacement by the hydrazine residue and re-formation by oxidation of the hydrazino-compound should return to its original spatial position in the molecule, and it is therefore tentatively suggested that the change would be more readily explicable if the hydroxy-group were regarded as attached to the 6-carbon atom and the annexed formula were ascribed to diacetoneglucose. Hydrazinodiacetoneglucose is converted by benzaldehyde in the presence of ether into the corresponding *benzylidene* compound, $C_{19}H_{26}O_5N_2$, prisms, m. p. 99—100°, $[\alpha]_{H_g}^{20} \text{ yellow} + 144.2^\circ$ in *s*-tetrachloroethane. The mother-liquors from the benzylidene derivative contain an unsaturated compound, *diacetoneglucoenose*, $C_{12}H_{18}O_5$, needles, m. p. 51° $[\alpha]_{H_g}^{17} \text{ yellow} + 21.56^\circ$ in absolute alcohol which is smoothly

reduced by hydrogen in the presence of methyl acetate and spongy platinum to *diacetonedeoxyglucose*, $C_{12}H_{20}O_5$, m. p. 80°, $[\alpha]_{H_g}^{26} \text{ yellow}$



—34·60° in absolute alcohol, $[\alpha]_{\text{Hg}}^{20}$ yellow —61·9° in aqueous solution. Toluene-*p*-sulphonyldiacetoneglucose is reduced by sodium amalgam and ethyl alcohol (80%) to diacetoneglucose and toluene-*p*-sulphinic acid.

H. W.

The Acetone [*iso*Propylidene] Compound of Anhydroenneaheptitol. The Acetone Compounds of Polyhydroxy-alcohols. C. MANNICH and W. BROSE (*Ber.*, 1922, 55, [B], 3155—3157).—Anhydroenneaheptitol, obtained by the condensation of acetone and formaldehyde in the presence of calcium

hydroxide, and to which the annexed formula is ascribed, readily yields a *diacetone* compound, $\text{C}_{15}\text{H}_{26}\text{O}_6$, leaflets, m. p. (indefinite) 229°. The substance still contains a free hydroxyl group, since it is converted by acetic anhydride and

sodium acetate into a *monoacetate*, highly refractive needles, m. p. 140° (corr.). The formation of an acetone derivative is the more remarkable since the parent substance is a 1:3-glycol; it has been assumed previously (cf. Fischer, A., 1920, i, 807; Fischer, Bergmann, and Bärwind, A., 1920, i, 805) that acetone derivatives are only obtainable from polyhydroxy-alcohols which have the hydroxy-groups attached to adjacent carbon atoms.

H. W.

Tetralævoglucosan and Tetraglucosan. HANS PRINGSHEIM and KARL SCHMALZ (*Ber.*, 1922, 55, [B], 3001—3007).—The polyamyloses, obtained by the fermentation of starch and glycogen with *Bacillus macerans*, are characterised by undergoing depolymerisation to their fundamental substances when acetylated by acetic anhydride in the presence of zinc chloride and by the impossibility of their complete methylation. These properties are not shown by polymeric anhydro-sugar, since tetralævoglucosan and tetraglucosan can be acetylated under similar conditions without undergoing depolymerisation, and are completely methylated with unexpected ease.

Lævoglucosan and tetralævoglucosan are prepared by a modification of the methods of Pictet and his co-workers (A., 1918, i, 59, 527; 1921, i, 766); the specific rotation of the latter substance could not be raised beyond +85°, whereas Pictet records +100°. Tetralævoglucosan is converted by acetic anhydride in the presence of a little zinc chloride into *tetralævoglucosan dodecaacetate*, $\text{C}_{48}\text{H}_{64}\text{O}_{32}$, an amorphous substance which is completely molten at 125° after softening at 108—109°; it has $[\alpha]_{\text{D}}^{20}$ +69·59° in glacial acetic acid solution. *Dodecamethyl tetralævoglucosan*, $\text{C}_{36}\text{H}_{64}\text{O}_{20}$, a pale yellow, viscous liquid, which does not reduce Fehling's solution, is readily prepared by two consecutive treatments of the parent substance with methyl sulphate and sodium hydroxide at 70°. It is hydrolysed by boiling dilute sulphuric acid (6%) to tetramethylglucose (identified as the anilide, m. p. 136—137°) and a dimethylglucose, whereby it is established that in the polymerisation of lævoglucosan, the rupture of the 1:6-oxygen bridge with formation of a free 6-hydroxy-group has occurred in two of the four molecules of the parent substance

Tetraglucosan dodeca-acetate is an amorphous, hygroscopic substance, $[\alpha]_D^{20} + 70.82^\circ$ when dissolved in glacial acetic acid. *Dodecamethyltetraglucosan* is hydrolysed to tetramethylglucose, and two products which are characterised by solubility in anhydrous ether in the one case and in acetone in the other case.

Tetraglucosan octa-acetate has m. p. $84-86^\circ$, in agreement with the observations of Pictet (*loc. cit.*). H. W.

Polysaccharides. XVI. P. KARRER [with W. FIORONI] (*Ber.*, 1922, **55**, [B], 2854—2863; cf. this vol., i, 435).—The heats of combustion of the amyloses have been redetermined with the following results expressed in calories per gram of substance: diamylose (4285), α -tetra-amylose (4196), α -octa-amylose (4620), β -hexa-amylose (4166), lævoglucosan (4181), triamylose (identical with β -hexa-amylose) (4162.5). Polymerisation proceeds exothermally from diamylose to α -tetra-amylose and then strongly endothermally to octa-amylose. In further examination of the possibility of calculating the heat of combustion of a sugar of the general formula $(C_6H_{12}O_6)_n - (n-1)H_2O$, the values have been determined experimentally for cellobiose (3944) (calculated from the observed value for a specimen containing 2.2% of water), sucrose (3945), lactose (3953), and maltose (3949); within the limits of experimental error, these disaccharides, $C_{12}H_{22}O_{11}$, have identical heats of combustion. This is also true of maltose octa-acetate (4468) and cellobiose octa-acetate (4471). The observed and calculated values for the trisaccharide, raffinose, have been shown to be in harmony, and similar observations are recorded for the tetrasaccharide, stachyose (observed 4065; calculated, 4058).

The dependence of the heat of combustion on the degree of polymerisation is illustrated in the case of the α -amyloses. A comparison of the heats of combustion of acetyl-cellulose, -starch, and -inulin on the one hand and the non-acetylated polysaccharides on the other should therefore give valuable information as to the possibility of acetylation being accompanied by depolymerisation. The observed values are as follows: inulin (4190), starch (4182), cellulose (4185), starch hexa-acetate (4499), cellulose hexa-acetate (4496), inulin triacetate (4522). The heats of combustion of the acetates are calculated from those of the parent substances on the assumption that the heat of esterification (known to be small) can be neglected. The observed and calculated values agree so closely that there is no reason to suppose that an alteration of the degree of polymerisation of the carbohydrate occurs during acetylation.

The author has shown that hexa-amylose is identical with triamylose and his observations have been confirmed by the crystallographical measurements of Miggle and Johnson. The individuality of the substances has, however, been maintained by Pringsheim (this vol., i, 633), to whose arguments a critical reply is now given. Pringsheim's doubt as to the identity of the maltose hepta-acetate obtained by the action of acetyl bromide on triamylose is unjustified since it is a well-defined, crystalline substance. Attempts

to repeat the preparation of triamylose sodium hydroxide according to Pringsheim's method gave a product which contains sodium ethoxide. Contrary to Pringsheim's observations, the solubilities of triamylose and hexa-amylose in water are identical, and the observed discrepancies are due to the inadequacy of Pringsheim's method of experiment. With regard to Pringsheim's observation that the molecular weight of acetylated hexa-amylose is identical with that required for an acetylated triamylose, the author points out that acetylated anhydro-sugars are not in general suitable for determinations of molecular weight; incidentally, the molecular weight of acetylated hexa-amylose as determined by Rast's method (this vol., ii, 421) is about 1950 (or exactly double that found by Pringsheim). Doubts are cast on the individuality of Pringsheim's trifructose.

H. W.

The Absorption of Iodine by Starch. H. VON EULER and KARL MYRBÄCK (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 9, 1—29; cf. this vol., i, 527).—Measurements have been made of the distribution of iodine between benzene and a solution of starch. Evidence is found of the existence of two compounds of iodine and potato starch, to which the formulæ $(C_6H_{10}O_5)_{18}I_2$ and $(C_6H_{10}O_5)_{18}I_4$ are given. Soluble starch has less affinity for iodine than potato starch, and there is more iodine in the benzene layer. There is evidence that hydrogen iodide is not necessary for the formation of the blue colour and that the compound of Mylius containing hydrogen iodide or potassium iodide is a further additive compound.

W. O. K.

Oxidation of Amylodextrin. WIKTOR SYNIEWSKI (*Roczniki Chem.*, 1922, 2, 83—94).—When amylodextrin (soluble starch) is oxidised by means of bromine in the presence of barium carbonate (to prevent the hydrolysis of the molecule), amyloextrinic acid, $C_{216}H_{348}O_{198}$, is obtained as a white, non-crystalline substance. It has an acid reaction, $[\alpha]_D^{20} + 191.09^\circ$, and its reducing power is 23.24% of that of maltose. In solution, it reduces alkaline silver solution and gives the "Molisch" reaction with α -naphthol, but the colour is not violet as with starch and the sugars, but carmine-red. In concentrated solution, it gives a red colour on warming with hydroxylamine hydrochloride and potassium hydroxide. The author assumes that amyloextrin has the formula $C_{216}H_{372}O_{186}$ and contains twelve maltose residues connected together by the carbonyl groups, and that the $CH_2\cdot OH$ groups alone undergo oxidation to carboxyl groups.

W. T.

Some Physical Properties of Cotton Cellulose and its Modifications. A Summary of Existing Data. GEO. E. COLLINS (*Trans. Text. Inst.*, 1922, 13, 204—213).—The following subjects are dealt with: specific gravity, elasticity, specific inductive capacity, electrification, mechanical absorption of liquids, thermal effects accompanying water adsorption, changes resulting from the action of heat and cold, thermal conductivity, specific heat, heat of combustion, heat of reaction, refractive index, double

refraction and appearance in polarised light, action of ultra-violet light, optical activity of sols, ultra-microscopy, evidence of X-rays on structure. Data dealing with the swelling of cellulose and the adsorption of vapour by cellulose will be summarised in future reports, but it may be taken that little or nothing has been published about properties not included in the above list. J. C. W.

The Viscosity of Cellulose. II. The Lowering of the Viscosity of Cellulose by Various Reagents. REGINALD ARTHUR JOYNER (T., 1922, 121, 2395—2409).

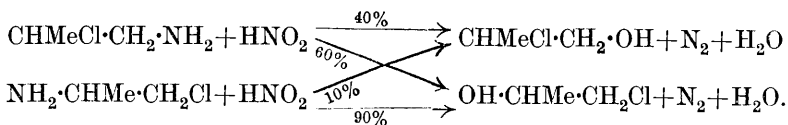
"Oxycellulose:" its Formation and Reactions. PERCY HERBERT CLIFFORD and ROBERT GEORGE FARGHER (*Trans. Text. Inst.*, 1922, 13, 189—204).—A review of the various methods of oxidation of cellulose, and the reactions of, and tests for, "oxycellulose," together with a bibliography. J. C. W.

Ligninsulphonic Acids. R. H. MCKEE and GEO. BARSKY (*Paper Trade J.*, 1922, 74, 46—48).—An attempt to separate the various acids by precipitation with calcium chloride. Three litres of sulphite waste liquor were concentrated to 800 c.c., filtered, and neutralised with calcium hydroxide. Calcium chloride was then added in quantities of 50 grams, the mixture being heated on the water-bath for two hours to induce coagulation; the precipitate was collected after each addition. Each fraction was then reprecipitated with calcium chloride from its solution in twice its weight of water. Analysis of the corresponding barium salts of the final fractions gave C 59.7—55.1%, H 6.4—5.9%. The ratio of carbon to hydrogen thus varies from 8.6 to 10.1, whilst the ratio for cellulose is 7. It is therefore considered that the substance contains several compounds of varying composition. CHEMICAL ABSTRACTS.

The Decomposition of Amines in the Vapour Stage. FRED W. UPSON and LILA SANDS (*J. Amer. Chem. Soc.*, 1922, 44, 2306—2310).—When ethylamine vapour is passed over kaolin at 700° the chief products are ammonia, hydrogen cyanide, and a substance which is probably acetonitrile, together with smaller quantities of hydrogen and nitrogen. At 500°, no hydrogen cyanide is produced, a larger amount of ammonia is formed, and the gaseous products contain relatively larger amounts of unsaturated hydrocarbons. At 1000°, the nitrogen appears exclusively as free nitrogen, and much of the hydrogen as free hydrogen. The hydrocarbons are almost entirely saturated and to a large extent consist of butane. The decomposition of propylamine under similar conditions at 700° proceeds in a manner similar to that of ethylamine. The results may be explained on Nef's theory of methylenic dissociation (cf. *Annalen*, 1899, 309, 126; 1901, 318, 37). W. G.

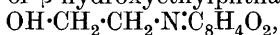
Kinetic Determinations of the Constitutions of Hydroxy- and Amino-chloropropanes. L. SMITH and B. PLATON (*Ber.*, 1922, 55, [B], 3143—3155).—The preparation of β -chloro-*n*-propylamine (cf. Gabriel and Ohle, A., 1917, i, 562) and α -chloro- β -amino-

propane and their reactions with nitrous acid have been investigated. The latter changes are represented in the scheme :



It is therefore shown that a definite transformation can accompany the conversion of an amino- into a hydroxy-compound by means of nitrous acid even when the operation is conducted at a low temperature. The tendency towards transformation is most marked with the α -amino-compound. The reaction of an aliphatic amino-compound with nitrous acid should not therefore be used as a general method for the elucidation of constitution. The optically active " β -propylene chlorohydrin" described by Abderhalden and Eichwald (A., 1919, i, 2) must be regarded as a mixture of approximately equal quantities of the α - and β -compounds, the former of which is inactive; the corresponding propylene oxide and propylene glycol must also be partly inactive. The synthesis of $\alpha\beta$ -diglycerides from acylated γ -aminopropylene glycols (Bergmann, Brand, and Dreyer, A., 1921, i, 444) does not appear to rest on a firm theoretical basis.

The preparation of β -chloro-*n*-propylamine is effected according to the method of Gabriel and Ohle (*loc. cit.*); (the melting points observed for the various intermediate compounds by these chemists are recorded in brackets). Propylene oxide is converted by phthalimide into a mixture of β -hydroxyethylphthalimide,



lustrous leaflets, m. p. 129.5° (corr.), and β -hydroxy-*n*-propylphthalimide, prisms, m. p. 88° (corr.) [$90-91^\circ$, $88-89^\circ$]. The latter substance is converted into the corresponding chloride, b. p. $183-184^\circ/10$ mm., m. p. $97.5-98^\circ$ (corr.) [$100-102^\circ$], which is hydrolysed by glacial acetic and fuming hydrochloric acids to β -chloro-*n*-propylamine hydrochloride, m. p. 179° (corr.) [$183.5-186^\circ$]. The substance is, however, prepared more conveniently in quantity by the method of Abderhalden and Eichwald (*loc. cit.*). It is diazotised in faintly acid solution either as hydrochloride or tartrate; the chlorohydrin which is formed has b. p. $128-129.5^\circ$ and $128-129^\circ$, respectively, and is colourless, neutral, and free from aldehyde.

The preparation of α -chloro- β -aminopropane is effected by converting β -chloro-*n*-propylamine hydrochloride by means of sodium hydroxide into the imine, $\text{CHMe} < \begin{smallmatrix} \text{CH}_2 \\ \text{NH} \end{smallmatrix}$, which is trans-

formed by concentrated hydrochloric acid into α -chloro- β -aminopropane hydrochloride; since the latter substance is hygroscopic and difficult to preserve, it is converted into the corresponding picrate, m. p. 146° , which is re-converted into the hydrochloride immediately before use. It is diazotised at $40-50^\circ$, giving a colourless, neutral chlorohydrin, b. p. 126° .

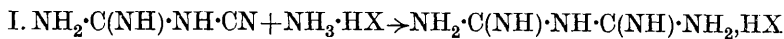
The composition of the mixture of chlorohydrins is established from measurements of its rate of decomposition by barium hydroxide. The bimolecular velocity coefficient for α -chloro- β -hydroxypropane for $t=0$ is $k_0=14.3$, whereas the corresponding constant for β -chloro- α -hydroxypropane is about 4. The coefficients of the mixtures lie intermediate between these values and decrease markedly as decomposition proceeds. The composition of the mixtures is calculated on the assumption that for a definite mixture the velocity coefficient at any instant is only dependent on the ratio of quantities of isomerides actually present at that instant.

The constitution of the chloropropylamines is established similarly by studying the rate of decomposition by barium hydroxide. The picrates are used, and the velocity of the change is determined by estimation of the chlorine by Volhard's method. α -Chloro- β -propylamine has $k=0.50$ at 25° , whereas the corresponding value for β -chloro- n -propylamine is 0.067. Since the action of chloroamines towards alkali hydroxide is similar to that of chlorohydrins, it is valid to assume that the compound which is most readily decomposed contains the halogen in the α -position. H. W.

The Action of Sodammonium on Hexamethylenetetramine, Tetramethyldiaminomethane, and Ethylidene-ethylamine.

M. PICON (*Compt. rend.*, 1922, **175**, 695—698; cf. Lebeau and Picon, this vol., i, 801).—Sodammonium is the only hydrogenating substance that is without action on hexamethylenetetramine, and it has no action on saturated aliphatic compounds which contain nitrogen. Its action on unsaturated aliphatic nitrogen compounds results in the formation of condensation products in which two molecules of the original substance are linked by the carbon atoms which were previously unsaturated. This reaction furnishes a new method of preparing secondary diamines. The inference is drawn that the inertness of sodammonium with respect to hexamethylenetetramine is due to the fact that the latter has no double bond which links carbon to nitrogen; this tends to support the constitutional formula suggested by Duden and Scharff (A., 1896, i, 122). H. J. E.

Mechanism of Guanidine Formation in Fused Mixtures of Dicyanodiamide and Ammonium Salts. J. S. BLAIR and J. M. BRAHAM (*J. Amer. Chem. Soc.*, 1922, **44**, 2342—2352; cf. Davis, this vol., i, 117, 118; Werner and Bell, T., 1920, **117**, 1133).—Experimental evidence is given in support of the view that the mechanism of guanidine formation in fused mixtures of dicyanodiamide and an ammonium salt consists first in the formation of the diguanide salt by the addition of the ammonium salt to the nitrile group of dicyanodiamide, and the subsequent addition of a second molecule of the ammonium salt to form two molecules of the guanidine salt.



When dicyanodiamide is fused with ammonium thiocyanate, the amount of diguanide thiocyanate in the fused mass increases at first with the time of fusion, then reaches a maximum, and slowly diminishes. On the other hand, guanidine thiocyanate does not make its appearance until the diguanide thiocyanate has nearly reached its maximum concentration.

When diguanide nitrate is fused with ammonium nitrate there is a decided formation of guanidine nitrate and the statement that diguanide salts are formed by the reverse of reaction II above is shown to be very doubtful.

The authors consider that the experimental results support the cyanoguanidine structure for dicyanodiamide. W. G.

Mutarotation and Pseudo-mutarotation of Glucosamine and its Derivatives. JAMES COLQUHOUN IRVINE and JOHN CAMPBELL EARL (T., 1922, 121, 2370—2376).

Salicylidene Derivatives of *d*-Glucosamine. JAMES COLQUHOUN IRVINE and JOHN CAMPBELL EARL (T., 1922, 121, 2376—2381).

The Influence of Position and of Temperature on the Reaction of Aliphatic Amino-nitrogen with Nitrous Acid. MAX S. DUNN and CARL L. A. SCHMIDT (*J. Biol. Chem.*, 1922, 53, 401—410).—The rate at which nitrous acid deaminises aliphatic amino-acids depends on the position of the amino-group; the greater the distance of this from the carboxyl the more slowly the reaction proceeds. In all cases, a decrease in temperature causes a diminution in the rate, but, contrary to the statement of Sure and Hart (A., 1917, ii, 551) the deamination of the ϵ -amino-group of lysine is not completely inhibited at 1°. Casein is deaminised more slowly than lysine at the ordinary temperature. E. S.

The Synthesis of Glycine from Formaldehyde. ARTHUR ROBERT LING and DINSHAW RATTONJI NANJI (*Biochem. J.*, 1922, 16, 702—703).—Methyleneaminoacetonitrile is prepared by Klages' method by condensing two molecules of formaldehyde with one molecule of ammonium cyanide. The nitrile is then hydrolysed with a boiling 40% solution of barium hydroxide and the methylene derivative of glycine formed is boiled until no more formaldehyde is given off. The yield of glycine from aldehyde by this method is 54% of the theoretical—the highest yield of glycine yet recorded as a result of its direct synthesis from formaldehyde.

S. S. Z.

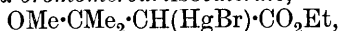
Hydrolysis of Glycylglycine by Hydrochloric Acid. IV. S. JAITSCHNIKOV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 147—150).—Both at 10° and at 100°, the hydrolysis of glycylglycine by means of hydrochloric acid proceeds, for about one-third of its course, in accordance with the equation for a reaction of the first order (cf. Euler, A., 1907, i, 574).

T. H. P.

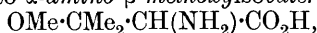
The Preparation of α -Amino- β -hydroxy-acids from Olefine Carboxylic Acids. WALTHER SCHRAUTH and HANNS GELLER (*Ber.*, 1922, 55, [B], 2783—2796).—The possible general applicability of a synthesis of α -amino- β -hydroxy-acids from ethylene-carboxylic acids on the following lines has been investigated: ester of olefinecarboxylic acid $\xrightarrow[\text{methyl alcohol}]{\text{mercury acetate}}$ β -methoxy- α -acetato-

mercuri-ester $\xrightarrow{\text{KBr}}$ β -methoxy- α -bromomercuri-ester $\xrightarrow{\text{bromine}}$ α -bromo- β -methoxy-ester $\xrightarrow{\text{hydrolysis}}$ α -bromo- β -methoxy-acid $\xrightarrow{\text{ammonia}}$ α -amino- β -methoxy-acid $\xrightarrow{\text{HBr}}$ α -amino- β -hydroxy-acid. The synthesis appears likely to be valuable in the purely aliphatic series, but complications follow when aromatic radicles are present.

Ethyl β -methoxy- α -bromomercuriisovalerate,



colourless plates, m. p. 51° , is prepared by treating ethyl $\beta\beta$ -dimethylacrylate with a solution of mercuric acetate in methyl alcohol during three days at the atmospheric pressure and subsequently adding an aqueous solution of potassium bromide to the mixture. It is slowly transformed by a solution of bromine in chloroform into *ethyl α -bromo- β -methoxyisovalerate*, a colourless liquid which is hydrolysed by $N/2$ -aqueous sodium hydroxide to *α -bromo- β -methoxyisovaleric acid*, $\text{OMe}\cdot\text{CMe}_2\cdot\text{CHBr}\cdot\text{CO}_2\text{H}$, m. p. 77° . When the latter is heated with aqueous ammonia (25%) at 100° , it is transformed into *α -amino- β -methoxyisovaleric acid*,



colourless, lustrous plates, decomp. 250 — 260° , from which *α -amino- β -hydroxyisovaleric acid*, $\text{OH}\cdot\text{CMe}_2\cdot\text{CH}(\text{NH})\cdot\text{CO}_2\text{H}$, m. p. 218° (decomp.), is prepared by means of boiling hydrobromic acid (d 1.47). The latter acid is converted by phenylcarbimide into the compound, $\text{C}_{12}\text{H}_{16}\text{O}_4\text{N}_2$, m. p. 162° (decomp.); it gives a naphthalene- β -sulphonyl derivative, $\text{C}_{15}\text{H}_{17}\text{O}_5\text{NS}$, small, colourless needles, m. p. 261° .

Difficulties are encountered when the series of reactions is applied to methyl cinnamate (cf. Schrauth, Schoeller, and Struensee, A., 1910, i, 347). The preparation of methyl β -methoxy- α -bromomercuri- β -phenylpropionate, $\text{OMe}\cdot\text{CHPh}\cdot\text{CH}(\text{HgBr})\cdot\text{CO}_2\text{Me}$, is effected in good yield, but the replacement of the mercury complex by bromine occurs slowly in the presence of chloroform with simultaneous production of methyl $\alpha\beta$ -dibromo- β -phenylpropionate, but rapidly in the presence of ethyl acetate, with formation of *methyl α -bromo- β -methoxy- β -phenylpropionate*. The hydrolysis of the latter is not very satisfactory, since considerable quantities of halogen-free products are obtained when sodium hydroxide is used, whereas $\alpha\beta$ -dibromo- β -phenylpropionic acid is formed when hydrobromic acid is employed. Attempts are made to overcome the difficulties attendant on hydrolysis by the use of cinnamic acid as initial material. The latter is converted successively into *β -methoxy- α -bromomercuri- β -phenylpropionic acid*, m. p. 160 — 166° (decomp.), *α -bromo- β -methoxy- β -phenylpropionic acid*, m. p. (indefinite) 170° after softening at 165° (which appears to be a stereoisomeride of the acid obtained in the above series, starting from methyl cin-

namate) and α -amino- β -methoxy- β -phenylpropionic acid, plates, m. p. 236° (decomp.) [corresponding compound from phenylcarbimide, colourless plates, m. p. 161° (decomp.); β -naphthalenesulphonyl derivative, prisms, m. p. 157°]. Replacement of the methoxy by the hydroxy-group in the latter acid could not be effected by hydrobromic or hydriodic acids, bromohydrocinnamic and cinnamic acids being formed. α -Bromo- β -methoxy- β -phenylpropionic acid, prepared by the hydrolysis of methyl α -bromo- β -methoxy- β -phenylpropionate, crystallises in colourless needles, m. p. $126-127^\circ$.

Ethyl p -methoxycinnamate is converted in the usual manner into ethyl β -methoxy- α -bromomercuri- β - p -methoxyphenylpropionate, prismatic plates, m. p. 107° . The elimination of the mercury complex by bromine does not, however, follow a completely normal course, since bromination of the phenyl group occurs simultaneously, as is shown by the ultimate isolation of α -amino- β -methoxy- β - p -methoxybromophenylpropionic acid, pale yellow plates, m. p. 224° (decomp.) (the corresponding derivative from phenylcarbimide is described). On the other hand, ethyl β -methoxy- α -iodomercuri- β - p -methoxyphenylpropionate, m. p. 117° , is very slowly converted by iodine in ethereal solution into ethyl α -iodo- β -methoxy- β - p -methoxyphenylpropionate, a pale yellow liquid, which is hydrolysed by $N/2$ -sodium hydroxide solution to α -iodo- β -methoxy- β - p -methoxyphenylpropionic acid, $C_{11}H_{13}O_4I \cdot 2H_2O$, lustrous needles, m. p. $89-90^\circ$, in which, however, the iodine could not be replaced by the amino-group; all experiments with aqueous or liquid ammonia led to the formation of p -methoxycinnamic acid or the corresponding styrene. In one instance, however, the desired α -amino- β -methoxy- β - p -methoxyphenylpropionic acid, long plates, m. p. 233° (decomp.), was obtained in very small yield, but the experiment could not be repeated. H. W.

Synthesis of Aminohydroxy-acids and the Amino-acid from cycloPropyl Methyl Ketone (Acetyltrimethylene). N. D. ZELINSKY and E. F. DENGIN (*Ber.*, 1922, **55**, [B], 3354—3361).—The synthesis of a series of hydroxyamino-acids from keto-alcohols by the cyanohydrin method is recorded (cf. Zelinsky and Stadnikoff, *A.*, 1906, i, 425).

α -Amino- β -hydroxy- α -methylpropionic acid (α -methylserine), $OH \cdot CH_2 \cdot CMe(NH_2) \cdot CO_2H$, transparent platelets, m. p. 243° (decomp. in a sealed capillary), is prepared by the addition of acetylcarbinyl acetate (cf. Perkin, *T.*, 1891, **59**, 786) to an aqueous solution of potassium cyanide and ammonium chloride and treatment of the product of the reaction with hydrochloric acid; the yield is 12.6% of that theoretically possible. Better yields (41%) are obtained when acetylcarbinol is substituted for the acetate. The copper salt of α -methylserine, $(C_4H_8O_3N)_2Cu \cdot 2H_2O$, crystallises in small, blue needles.

Hydroacetylacetone, potassium cyanide, and ammonium chloride give α -amino- γ -hydroxy- α -methyl- n -valeric acid (α - β' -hydroxy- n -propylalanine), $CH_3 \cdot CH(OH) \cdot CH_2 \cdot CMe(NH_2) \cdot CO_2H$, small needles,

m. p. 232—233° (the crystalline, *copper salt*, $(C_6H_{12}O_3N)_2Cu, 2H_2O$, is described).

α-Amino-δ-hydroxy-α-methyl-n-valeric acid (α-γ'-hydroxy-n-propyl-alanine), $OH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CMe(NH_2) \cdot CO_2H$, small needles, m. p. 198—200°, is similarly prepared from acetopropyl alcohol (a modified method for the preparation of this substance is described in detail); the corresponding *copper salt* is described.

α-Amino-ε-hydroxy-α-methyl-n-hexoic acid (α-δ-hydroxy-n-butylalanine), $OH \cdot CH_2 \cdot [CH_2]_3 \cdot CMe(NH_2) \cdot CO_2H$, prepared from δ-aceto-n-butylalcohol, crystallises in small platelets, m. p. 224—226°; the *copper salt*, $(C_7H_{14}O_3N)_2Cu, 2H_2O$, is a blue, crystalline powder.

α-Amino-α-cyclopropylpropionic acid (α-cyclopropylalanine), $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > CH \cdot CMe(NH_2) \cdot CO_2H$, prepared from acetylcyclopropane, crystallises in needles, m. p. 273—275°, in a closed capillary; it sublimes readily at about 125°. The corresponding *hydrochloride* and *copper salt*, $(C_6H_{10}O_2N)_2Cu, 2H_2O$, bluish-violet plates, are described.

H. W.

Catalysis of the Formation and Hydrolysis of Acetamide by Acetic Acid. WILLIAM A. NOYES and WALTER F. GOEBEL (*J. Amer. Chem. Soc.*, 1922, **44**, 2286—2295).—Acetic acid acts as a catalyst both for the formation of acetamide from ammonium acetate and for the hydrolysis of acetamide by water. The hydrolysis of acetamide by water is autocatalytic, probably because the acetic acid from the dissociation of the ammonium acetate formed catalyses the subsequent reaction.

The formation of acetamide from ammonium acetate with or without the addition of 0.1 mol. of acetic acid is essentially a bimolecular reaction between ammonia and acetic acid. In all probability an intermediate compound, $CH_3 \cdot C(OH)_2 \cdot NH_2$, is formed as a passing phase in the reaction. The formation and hydrolysis of acetamide in the presence of 1.5 mols. of acetic acid is chiefly a bimolecular reaction with one of the constituents, hydrogen-ion or acetic acid, constant. The other constituents limiting the speed of the reaction must be ammonia on one side, and acetamide on the other.

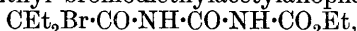
In the preparation of acetamide a practically quantitative yield is obtained if equimolecular proportions of ammonium acetate and glacial acetic acid are heated together at just below the boiling point of the mixture for thirty to fifty minutes and then the mixture is slowly distilled through a good fractionating column the temperature at the top of which is not allowed to exceed 103—104°. In this way a residue of acetamide, b. p. 215—217°, is obtained.

W. G.

The Compounds of Carbamide and Benzoic Acid. YUKICHI OSAKA and KINJI ANDO (*Mem. Coll. Sci. Kyōtō*, 1922, **5**, 169—172).—The solubility of mixtures of carbamide and benzoic acid in alcohol have been determined at 0°, 25°, and 40°, and no evidence was found for the existence of any compound of the two.

W. E. G.

Ethyl Bromodiethylacetylallophanate. J. CALLSEN (U.S. Pat. 1424236).—Ethyl bromodiethylacetylallophanate,



colourless crystals, m. p. 62—63°, is obtained by heating bromodiethylacetylcarbimide with urethane and crystallising the product from light petroleum.

CHEMICAL ABSTRACTS.

Preparation of Hydrocyanic Acid in Large Quantities in the Laboratory. E. FRITZMANN (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 227—234).—For preparing hydrocyanic acid from potassium ferrocyanide, sulphuric acid, and water, less of the last two ingredients than is usually recommended may be employed, the yield of the acid and the velocity of the reaction remaining unimpaired if the three reagents are taken in the proportions 10 : 5 : 8. The apparatus used is described.

T. H. P.

The X-Ray Structure of Potassium Cyanide. P. A. COOPER (*Nature*, 1922, 110, 544).—Polemical (cf. *ibid.*, 1921, 107, 745; Bozworth, this vol., i, 441).

A. A. E.

Preparation of Cyanuric Triazide. ERWIN OTT (D.R.-P. 355926; from *Chem. Zentr.*, 1922, iv, 550; cf. Ott and Ohse, A., 1921, i, 231).—In the preparation of cyanuric triazide from cyanuric trihydrazide, $\text{C}_3\text{H}_9\text{N}_9$, and nitrites (Swiss Pat. 89718), the following occur as intermediate products depending on the amount of nitrite used and the duration of the reaction. *Cyanuric dihydrazidomonoazide*, $\text{C}_3\text{H}_6\text{N}_{10}$, crystalline, m. p. 85—87°; and *cyanuric monohydrazidodiazide*, $\text{C}_3\text{H}_3\text{N}_{11}$, crystalline, m. p. 87—88°. These compounds are less sensitive to percussion than the pure cyanuric triazide, C_3N_{12} .

G. W. R.

Electrolysis of Organo-magnesium Compounds. N. V. KONDYREV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 17—24).—Experiments with magnesium ethyl bromide, magnesium propyl bromide, and magnesium phenyl bromide show that, when dissolved in dry ether, these compounds function as electrolytes. When a current is passed through the ethereal solution by means of a platinum cathode and a zinc or aluminium anode, and a copper voltameter is included in the circuit, the amount of zinc or aluminium which passes into solution corresponds exactly with the amount of copper deposited in the voltameter, aluminium behaving as a trivalent metal; a deposit of magnesium is formed at the same time on the platinum cathode. When, however, the anode consists of copper, the latter passes into solution only in traces. There is little doubt that organo-zinc and organo-aluminium compounds are formed in this way when corresponding metals are used as the anode and it may be possible to prepare these compounds by such means.

T. H. P.

Magnesium Compounds of the Olefines. I, II, and III. VL. KRESTINSKI (*Ber.*, 1922, 55, [B], 2754—2762, 2762—2770, 2770—2774; *J. Russ. Phys. Chem. Soc.*, 1920, 52, 63—74, 75—84, 85—90).—I. Alkenyl haloids in which the halogen atom is

attached to the carbon atom from which the double bond proceeds have been but little used in the formation of Grignard's reagents possibly on account of Grignard's supposition that such haloids would either not react with the metal at all or only in an abnormal manner. The only cases previously investigated appear to be the action of magnesium on ω -bromostyrene and the application of vinyl haloids to the production of erythrene (Austerweil, A., 1912, i, 525). The behaviour of β -methyl- Δ^{α} -propenyl bromide (*isocrotyl* bromide), $\text{CMe}_2\text{:CHBr}$, has now been investigated in a series of researches of which this communication gives the first account.

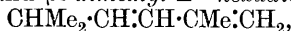
A solution of *isocrotyl* bromide in anhydrous ether does not react with magnesium under the usual conditions and only does so slowly and incompletely when the mixture is warmed or iodine is added. In the presence of Baeyer's pre-activated magnesium an energetic action occurs which can only be regulated with difficulty, since undue rise of temperature causes the Grignard reagent to decompose with the copious evolution of gas, whereas action soon ceases when the mixture is cooled. The course of the action can be most easily regulated when the ethereal solution of the haloid is added gradually to the mechanically-stirred mixture of the other components; it is not possible, however, to cause the whole of the magnesium to enter into reaction. The gas evolved is mainly *isobutylene*, which is converted by bromine into a mixture of $\alpha\beta$ -dibromoisobutane, $\text{CMe}_2\text{Br}\cdot\text{CH}_2\text{Br}$, b. p. $54\text{--}56^\circ/24\text{ mm.}$, $d_4^{20}\text{ }1.7827$, $n_D^{15}\text{ }1.51406$, $n_D^{20}\text{ }1.51186$, and a tribromoisobutane, b. p. $107\text{--}109^\circ/19\text{ mm.}$ The course of the action is represented most simply by the schemes $\text{CMe}_2\text{:CH}\cdot\text{MgBr} \rightarrow \text{CMe}_2\text{:C} < [\text{or } \cdot\text{CH}_2\cdot\text{CMe}\text{:CH-}] + \text{H}\cdot\text{MgBr}$ and $\text{CMe}_2\text{:CHBr} + \text{H}\cdot\text{MgBr} = \text{CMe}_2\text{:CH}_2 + \text{MgBr}_2$. The fate of the radicle $\text{CMe}_2\text{:C} <$ or $-\text{CH}_2\cdot\text{CMe}\text{:CH-}$ remains undecided. An examination of the products of the action of water on the Grignard solution only led to the isolation of ill-defined products containing oxygen.

Magnesium and *isocrotyl* bromide react with acetaldehyde in ethereal solution to yield ethyl alcohol, *methylisocrotylcarbinol*, $\text{CMe}_2\text{:CH}\cdot\text{CHMe}\cdot\text{OH}$, and two fractions, b. p. $80\text{--}87^\circ/15\text{ mm.}$, $d_4^{20}\text{ }0.8596$, $n_D^{20}\text{ }1.45534$, and b. p. $87\text{--}97^\circ/15\text{ mm.}$, $d_4^{20}\text{ }0.8763$, $n_D^{20}\text{ }1.45854$, which appear to be a mixture of isomeric alcohols, $\text{C}_{10}\text{H}_{18}\text{O}$; a fourth fraction, b. p. $228\text{--}232^\circ$, has not been investigated further. *Methylisocrotylcarbinol* has b. p. $136\text{--}138^\circ$, $d_4^{20}\text{ }0.8384$, $n_D^{20}\text{ }1.43159$, $n_D^{20}\text{ }1.43430$, $n_D^{20}\text{ }1.44098$, $n_D^{20}\text{ }1.44721$. It is transformed by acetic anhydride at 100° into a mixture of δ -methyl- $\Delta^{\alpha\gamma}$ -pentadiene, $\text{CMe}_2\text{:CH}\cdot\text{CH}\text{:CH}_2$, b. p. $75.5\text{--}76^\circ$, $d_4^{20}\text{ }0.72155$, $n_D^{20}\text{ }1.44664$, and *methylisocrotylcarbinyl acetate*, $\text{OAc}\cdot\text{CHMe}\cdot\text{CH}\text{:CMe}_2$, b. p. $140\text{--}146^\circ$.

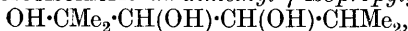
II. The action of magnesium *isocrotyl* bromide on *isobutaldehyde* has been examined.

isoCrotyl bromide, magnesium, and *isobutaldehyde* are caused to react in the presence of ether, and the product is submitted to fractional distillation whereby *isobutyl* alcohol, *isopropylisocrotylcarbinol*, $\text{CHMe}_2\cdot\text{CH}(\text{OH})\cdot\text{CH}\text{:CMe}_2$, and fractions of higher boiling

point from which homogeneous products could not be separated are obtained. *iso*Propylisocrotylcarbinol has b. p. 161—163°, d_4^{20} 0.8444, n_D^{20} 1.44493. It is converted by acetic anhydride at 100° into *isopropylisocrotylcarbinyl acetate*, b. p. 177—180°, d_4^{20} 0.8270, n_D^{20} 1.43288, and $\beta\epsilon$ -dimethyl- $\Delta^{\alpha\gamma}$ -hexadiene,



b. p. 116—118°, d_4^{20} 0.7412, n_D^{20} 1.45024. The constitution of the hydrocarbon is deduced from its oxidation by potassium permanganate to formic, acetic, and *isobutyric* acids. The production of a hydrocarbon of this constitution from *isopropylisocrotylcarbinol* is difficult to explain unless it is assumed that the substance not only is acetylated by acetic anhydride, but also simultaneously unites with a molecule of acetic acid which is eliminated subsequently in a different direction, thus: $\text{CMe}_2\cdot\text{CH}\cdot\text{CH}(\text{OH})\cdot\text{CHMe}_2 \rightarrow \text{OAc}\cdot\text{CMe}_2\cdot\text{CH}_2\cdot\text{CH}(\text{OAc})\cdot\text{CHMe}_2 \rightarrow \text{CH}_2\cdot\text{CMe}\cdot\text{CH}:\text{CH}\cdot\text{CHMe}_2$. The constitution assigned to *isopropylisocrotylcarbinol* is established by the observation that it is oxidised by potassium permanganate to acetone, two stereoisomeric $\alpha\alpha$ -dimethyl- γ -isopropylglycerols,



sparingly soluble crystals, m. p. 159—160°, and a very hygroscopic substance, m. p. 73—75°, respectively, formic, acetic, and *isobutyric* acids, and a non-crystalline acid, $\text{CHMe}_2\cdot\text{CO}\cdot\text{CO}_2\text{H}$, which is analysed in the form of its *calcium* salt, $(\text{C}_5\text{H}_7\text{O}_3)_2\text{Ca}\cdot\text{H}_2\text{O}$, and characterised further by the formation of a crystalline *semicarbazone*. Re-examination of the action of acetic anhydride on *isopropylisocrotylcarbinol* shows that two isomeric *acetates*, $\text{C}_{10}\text{H}_{18}\text{O}_2$, are actually produced which have b. p. 167—170°, d_4^{20} 0.88676, n_D^{20} 1.43739, and b. p. 174—176°, d_4^{20} 0.88226, n_D^{20} 1.43238, respectively. When hydrolysed with barium hydroxide solution two *alcohols*, $\text{C}_8\text{H}_{16}\text{O}$, b. p. 158—161°, d_4^{20} 0.8449, n_D^{20} 1.43679, and b. p. 160—165°, d_4^{20} 0.8455, n_D^{20} 1.43789, respectively, are obtained, but on account of lack of substance it has not yet been found possible to elucidate their constitution.

*iso*Propylisocrotylcarbinol is converted by aluminium oxide at an incipient red heat mainly into *disocrotyl*, $\text{CMe}_2\cdot\text{CH}:\text{CH}:\text{CMe}_2$, b. p. 132—138° (which is transformed by hydrogen bromide into the hydrobromide, m. p. 65°), and (?) $\beta\epsilon$ -dimethyl- $\Delta^{\beta\gamma}$ -hexadiene, $\text{CMe}_2\cdot\text{C}:\text{CH}:\text{CHMe}_2$, b. p. 119—123°, d_4^{20} 0.7637, n_D^{20} 1.45054.

III. *Phenylisocrotylcarbinol*, $\text{CMe}_2\cdot\text{CH}:\text{CHPh}\cdot\text{OH}$, a colourless liquid, b. p. 122—125°/7 mm., d_4^{20} 0.9861, n_D^{20} 1.53516, is prepared by the action of magnesium *isocrotyl* bromide on benzaldehyde.

The observations have been extended to α -methylisocrotyl bromide [γ -bromo- β -methyl- Δ^{β} -butylene], $\text{CMe}_2\cdot\text{CBrMe}$. The substance reacts with magnesium in much the same manner as, but with rather more difficulty than, its simpler homologue. Trimethylethylene [β -methyl- Δ^{β} -butylene] is evolved in large quantity and is identified by converting it into dibromopentane and *tert.*-amyl iodide; it appears to be the sole gaseous product of the change. Decomposition of the Grignard reagent with water leads to the further evolution of large volumes of trimethylethylene. The non-volatile products are unsaturated compounds which con-

tain oxygen; their nature has not been established definitely. The action of magnesium α -methylisocrotyl bromide on acetaldehyde appears to lead to the formation of *methyl- $\alpha\beta$ -dimethyl- α -propenylcarbinol*, $\text{CMe}_2\cdot\text{CMe}\cdot\text{CHMe}\cdot\text{OH}$, which, however, has not been investigated closely.

The action of an ethereal solution of vinyl bromide on activated magnesium commences very rapidly and proceeds with the evolution of a mixture of acetylene and ethylene. H. W.

Derivatives of Methylstannonic Acid. Their Bearing upon its Constitution. HERBERT LAMBOURNE (T., 1922, **121**, 2533—2540).

The Dinitro-derivatives of *p*-Dichlorobenzene. ANNIE LOUISE MACLEOD, MARION C. PFUND, and MARY L. KILPATRICK (*J. Amer. Chem. Soc.*, 1922, **44**, 2260—2271).—The product, m. p. 81° , obtained as one of the products of nitration of *p*-dichlorobenzene (cf. Nason, A., 1919, i, 10) is shown to be a molecular compound of 2:5-dichloro-1:4-dinitro- and 2:5-dichloro-1:3-dinitro-benzene, the proportions approximating to two molecules of the former to three of the latter. When this substance was reduced by tin and hydrochloric acid a mixture of the corresponding diamines was obtained.

From a study of the action of alcoholic ammonia on the isomeric dichlorodinitrobenzenes, it is shown that the *m*-dinitro-derivative is converted entirely into chlorodinitroaniline, the chlorine atom in the ortho-position to the two nitro-groups being replaced by an amino-group. With the *o*- and *p*-dinitro-derivatives, the main reaction results in the replacement of one nitro-group by an amino-group, but at the same time a comparatively small amount of the corresponding dinitro-*p*-phenylenediamine is produced.

On reduction by tin and hydrochloric acid, 3:6-dichloro-1:2-dinitrobenzene yields 3:6-dichloro-*o*-phenylenediamine, m. p. 98° , which condensed with benzil to give 1:4-dichlorodiphenylquinoline, m. p. 214° . W. G.

Aromatic Sulphonyl Chlorides. JESSIE STEWART (T., 1922, **121**, 2555—2561).

Preparation of Aryl Sulphonic Esters of Halogenated Aliphatic Alcohols. GEORG VON KERESZTY and EMIL WOLF (D.R.-P. 353195; from *Chem. Zentr.*, 1922, iv, 156).—An arylsulphonyl chloride mixed with a halogenated aliphatic alcohol is shaken at low temperatures with concentrated alkali hydroxide solution until an alkaline reaction persists. The ester formed is rapidly hydrolysed. *Chloroethyl benzenesulphonate*, from benzenesulphonyl chloride and glycol chlorohydrin, has b. p. $184^\circ/8$ — 11 mm. *Bromoethyl benzenesulphonate*, similarly prepared, has b. p. $192^\circ/20$ mm. *Dichloropropyl benzenesulphonate*, from $\alpha\alpha$ -dichlorohydrin and benzenesulphonyl chloride, has b. p. $205^\circ/20$ mm. and m. p. 50° . G. W. R.

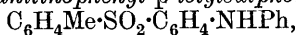
The Labile Nature of the Halogen Atom in Organic Compounds. VI. The Action of Titanous Chloride and of Ammonia on Representative Halogen Compounds. IAN ARMSTRONG BLACK, EDMUND LANGLEY HIRST, and ALEXANDER KILLEN MACBETH (T., 1922, 121, 2527—2533).

Thermal Analysis of the System o-:p-Toluenesulphonamides. A. F. DOBRJANSKI (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 139—144).—Thermal analysis of this system yields a melting-point curve composed of two branches intersecting at the eutectic point about 108°, which corresponds with 42.5% and 57.5% of the ortho- and para-isomerides, respectively. This eutectic point is identical with the melting point of the non-separable mixture of the two amides obtained in practice when the mixture of the corresponding ortho- and para-chlorides is treated with ammonia. Separation of the para-amide from this mixture by fractional precipitation should hence be, and is found experimentally to be, impossible. The acicular crystals, m. p. 120°, mentioned by Fahlberg, correspond with a mixture in equal parts of the two isomerides, but no indication is obtained of the formation of a molecular compound and no distectic point is observed; such crystals are readily resolved into their components under the microscope.

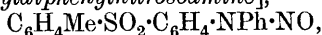
T. H. P.

Transformation of the Diphenyl-, Phenyl-p'-tolyl-, and Di-p₁-tolyl-amides of Toluene-p-sulphonic Acid. J. HALBERKANN (*Ber.*, 1922, 55, [B], 3074—3095; cf. A., 1921, i, 660, 779).—In continuation of previous work, the behaviour of diarylamides of toluene-p-sulphonic acids has been investigated and transformations similar to those recorded for the mixed aromatic amides (*loc. cit.*) have been observed.

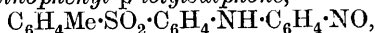
p-Toluenesulphondiphenylamide, $C_6H_4Me \cdot SO_2 \cdot NPh_2$, m. p. 142°, prepared by heating diphenylamine with toluene-p-sulphonyl chloride in the presence of pyridine, is almost quantitatively hydrolysed when heated with sulphuric acid (*d* 1.74). Its behaviour towards concentrated sulphuric acid depends greatly on the temperature used; at 100°, sulphonation occurs to a considerable extent and the remainder of the amide is partly hydrolysed and partly isomerised. The most favourable temperature for transformation is 20°, under which conditions 75% of the amide is converted into o-anilinophenyl-p-tolylsulphone,



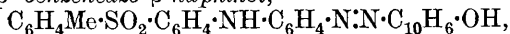
colourless, prismatic rods, m. p. 96—97°. The latter substance is converted by hydrochloric acid and sodium nitrite in the presence of aqueous acetone into o'-phenylnitrosoaminophenyl-p-tolylsulphone [*o'*-p-toluenesulphonyldiphenylnitrosoamine],



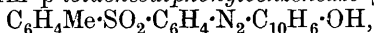
colourless crystals, m. p. 126—127°. Treatment of a concentrated ethereal solution of the nitrosoamine with a saturated solution of hydrogen chloride in ethyl alcohol brings about its isomerisation to 2-p-nitrosoanilinophenyl-p-tolylsulphone,



large, steel-blue crystals which appear green by reflected light and give a dark green powder, m. p. 150—151° [the *hydrochloride*, an ochre-coloured powder, m. p. 197° (complete decomp.) after darkening above 150°, is described], which is reduced by sodium hyposulphite in alkaline solution to 2-*p*-aminoanilinophenyl-*p*-tolylsulphone, $C_6H_4Me \cdot SO_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4 \cdot NH_2$, colourless, prismatic crystals, m. p. 134—135°; the amine can be diazotised and then couples normally with β -naphthol to yield *p*-toluenesulphonyl-*o*'-anilino-*p*'-benzeneazo- β -naphthol,



small, red needles, m. p. 172°. 2-*p*-Nitrosoanilinophenyl-*p*-tolylsulphone is converted by protracted treatment with aqueous sodium hydroxide solution into *o*'-aminophenyl-*p*-tolylsulphone, $C_6H_4Me \cdot SO_2 \cdot C_6H_4 \cdot NH_2$, colourless, prismatic rods which readily become red, m. p. 120—121°, which is diazotised and coupled with β -naphthol to form *p*-toluenesulphonylbenzeneazo- β -naphthol,

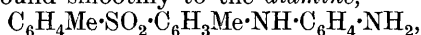


brownish-red, lustrous needles, m. p. 208°.

The proof that the amino-group in aminophenyl-*p*-tolylsulphone, m. p. 120—121°, occupies the ortho-position is obtained in two ways. On the one hand, *p*'-aminophenyl-*p*-tolylsulphone, groups of colourless, four-sided rods, m. p. 181°, is synthesised from *N*-acetyl-*p*-sulphanilic chloride and toluene by the Friedel-Crafts' reaction and subsequent hydrolysis of the product with hydrochloric acid. On the other, if wandering normally occurs towards the ortho-position even when the para-position is free, the compound m. p. 120—121° should be obtainable in the following manner (this is the case). *p*-Toluenesulphonanilide is quantitatively transformed by ethyl toluene-*p*-sulphonate or ethyl sulphate into the corresponding *N*-ethyl compound, m. p. 87—88°, which is partly hydrolysed and partly isomerised by concentrated sulphuric acid to *o*'-ethylaminophenyl-*p*-tolylsulphone, $C_6H_4Me \cdot SO_2 \cdot C_6H_4 \cdot NH_2$, coarse, colourless prisms, m. p. 90—91° [acetyl derivative, hexagonal needles or plates, m. p. 141° (cf. Witt, A., 1913, i, 360)]. De-ethylation of the compounds is effected with considerable difficulty by heating it at 270—275° in a current of dry hydrogen chloride. The small amount of *o*'-aminophenyl-*p*-tolylsulphone which is produced is isolated by diazotising the crude product, coupling the diazo-solution with resorcinol, filtering the solution, precipitating the dye by addition of acid, and subsequently reducing it to the amine by means of sodium hyposulphite. The product has m. p. 120°.

Toluene-p-sulphonphenyl-p'-tolylamide, $C_6H_4Me \cdot SO_2 \cdot NPh \cdot C_6H_4Me$, colourless, four-sided needles, m. p. 122—123°, is prepared by heating toluene-*p*-sulphonyl chloride with phenyl-*p*-tolylamine in the presence of pyridine. It is converted by concentrated sulphuric acid into a mixture of the two possible sulphones, the reaction being accompanied by very little hydrolysis. 2-*p*-Toluidinophenyl-*p*-tolylsulphone, $C_6H_4Me \cdot SO_2 \cdot C_6H_4 \cdot NH \cdot C_6H_4Me$, almost colourless, coarse prisms or four-sided prismatic rods, m. p. 147°, is readily isolated from the product by reason of its sparing solubility in

alcohol. It gives an *N*-acetyl derivative, colourless, prismatic rods, m. p. 164—165°, and an *N*-nitroso-compound, aggregates of pale yellow needles, m. p. 168° (decomp.); the latter regenerates the parent compound when treated with hydrogen chloride in the presence of alcohol and ether and does not become isomerised to the nuclear nitroso-compound although the para-position in the benzene nucleus is not occupied. The second sulphone is isolated by converting the mixture obtained as above into the corresponding nitroso-derivatives, which are separated mechanically from one another and subsequently reduced by phenylhydrazine. *p*-Tolyl-1-anilino-*m*-tolylsulphone, $C_6H_4Me \cdot SO_2 \cdot C_6H_3Me \cdot NHPh$, forms coarse, colourless crystals, m. p. 124°. The corresponding nitrosoamine crystallises in brown, hexagonal plates or large rhombs, m. p. 132° (decomp.); it is reduced by zinc dust and acetic acid in the presence of acetone and alcohol to the corresponding hydrazine, $C_{20}H_{20}O_2N_2S$, coarse, colourless prisms, m. p. 169—170° (benzylidene compound, $C_{27}H_{24}O_2N_2S$, pale yellow prisms, m. p. 195°). The nitrosoamine is isomerised by hydrogen chloride in the presence of alcohol and ether to the corresponding *p*-nitrosophenyl compound, $C_6H_4Me \cdot SO_2 \cdot C_6H_3Me \cdot NH \cdot C_6H_4 \cdot NO$, greenish-yellow, prismatic needles, m. p. 174—175° (apparent decomp.) [the hydrochloride, brownish-red prisms, m. p. 178—179° (decomp.) after darkening at about 160° is described]. Ammonium sulphide reduces the *p*-nitroso-compound smoothly to the diamine,



colourless crystals, m. p. 148—149° (hydrochloride, colourless needles or plates), whereas with sodium hyposulphite or zinc dust as reducing agent an azo-compound, $C_{40}H_{36}O_4N_4S_2$, m. p. 267—268°, is also formed (the latter is produced also by heating molecular quantities of the *p*-nitroso- and *p*-amino-compounds dissolved in glacial acetic acid). When heated with sodium hydroxide solution (10%) at 140°, the *p*-nitroso-compound is converted into *p*-tolyl-6-amino-*m*-tolylsulphone, $C_6H_4Me \cdot SO_2 \cdot C_6H_3Me \cdot NH_2$, m. p. 168—169°. The transformation of toluene-*p*-sulphonphenyl-*p'*-tolylamide is always accompanied by a greater or less amount of sulphonation. The free sulphonic acid, $C_6H_4Me \cdot SO_2 \cdot C_6H_3Me \cdot NH \cdot C_6H_4 \cdot SO_3H$, crystallises in colourless, slender needles (+2H₂O), m. p. 146° (decomp.); the corresponding barium salt has m. p. 269—270° (a mono- and a di-hydrate are described).

Toluene-*p*-sulphondi-*p*-tolylamide, $C_6H_4Me \cdot SO_2 \cdot N(C_6H_4Me)_2$, colourless, rhombic plates, m. p. 144°, is isomerised quantitatively by concentrated sulphuric acid at 60° into the corresponding sulphone, $C_6H_4Me \cdot SO_2 \cdot C_6H_3Me \cdot NH \cdot C_6H_4Me$, long, colourless needles, m. p. 110—111°. The latter yields an *N*-nitroso-derivative, $C_{21}H_{20}O_3N_2S$, pale yellow, hexagonal platelets, m. p. 148—149°, which is reconverted into the sulphone when treated with hydrogen chloride in the presence of alcohol and ether. H. W.

Union of Hydrogen with Acetylene Derivatives. XIV. Hydrogenation of Phenylacetylene. J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 191—198).—The velocity of hydro-

genation of phenylacetylene in presence of colloidal platinum increases to a maximum after combination of the first two atoms of hydrogen and subsequently diminishes. The reaction proceeds, but extremely slowly, after four atoms of hydrogen have been combined; characteristic of this late stage of the hydrogenation is the fact that it proceeds more rapidly with low than with high concentrations of the catalyst. Further, hydrogenation of the triple to the double linking takes place more slowly than that of the double to the single linking.

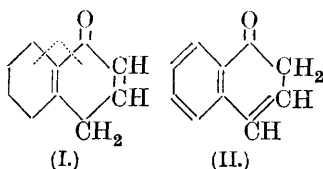
The results of experiments with styrene indicate that, in the nascent state, this compound is more readily hydrogenated than when ready-formed. Here, too, the hydrogenation does not cease when the side-chain is converted into the ethyl group, but is continued at the expense of the double linkings of the nucleus. It seems possible, indeed, that the initial stage of the reaction proceeds in two different directions, yielding, not merely ethylbenzene, but also 5-methyl- $\Delta^{1,3}$ -cyclohexadiene.

T. H. P.

The Action of Bromine Water on Indene. JOHN READ and ERIC HURST (T., 1922, **121**, 2550—2554).

Chemistry of Naphthalene and its Derivatives : Chemical Peculiarities of the Naphthalene Nucleus. N. N. VOROSHOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 125—151).—The author discusses the four principal structural formulæ which have been proposed for the naphthalene molecule: (1) That proposed by Erlenmeyer (*Annalen*, 1866, **137**, 346) and Graebe (*Ber.*, 1868, **1**, 36) and expounded by Marckwald (A., 1894, i, 474; 1895, i, 244) and composed of two benzene rings having two common carbon atoms; (2) Bamberger's formula (A., 1890, 1299); (3) Thiele's formula (A., 1899, i, 534), and (4) the formula proposed by Harries (A., 1906, i, 225) and Willstätter and King (A., 1913, i, 353). The identity of the two six-membered rings in naphthalene appears certain, in the absence of evidence that isomeric mono-substituted naphthalenes exist with the substituents in the same position. Besides being unsymmetrical, Willstätter's formula rests on inadequate foundations. Thiele's formula appears the most probable, as it brings out the special reactivity of the α -position. The different behaviour shown towards reagents by benzene and by octatetrene cannot be advanced as an argument against Thiele's theory, as it may be explained by differences between six- and eight-membered rings.

In the monohydroxy- and monoamino-derivatives of naphthalene, however, the naphthalene nucleus exhibits other relations. The results of the author's investigations on the action of sodium hydrogen sulphite on naphthalene derivatives (A., 1916, i, 293) do not agree with Bucherer's statements (A., 1904, i, 309; 1905, i, 48), and show that the naphthols are not esterified by sulphurous acid or sulphites, but first yield additive compounds, which are regarded as formed from the ketones isomeric with the naphthols. In view of the marked analogy in reaction relationships between



the hydrogen atom in the 4-position of α -naphthol and that in the 1-position of β -naphthol, the constitution I is favoured for the keto-form of α -naphthol, although the structure II is not excluded. Thiele's theory of conjugated double linkings renders it probable that the keto-forms of the naphthols are but slightly unsaturated.

The divergent behaviour shown by benzene and naphthalene derivatives evidenced in the alkylation of the naphthols in acid solution, in the amination of the hydroxy-group and hydrolysis of the amino-group, and in the reaction with sulphites, is readily explainable on the assumption that the hydroxy- and amino-derivatives of the naphthalene series more readily undergo keto-enolic transformations than the corresponding compounds of the benzene series. Thus, hydroxy-derivatives of naphthalene are true enols, whereas the hydroxyl of the monohydroxyl derivatives of the benzene series functions as aromatically combined hydroxyl; this conclusion is not in accord with the views of Meyer (A., 1913, i, 704), but is supported by various reactions of naphthalene derivatives. Application of the sulphite reaction to the naphthylene-1 : 5- and -1 : 8-diamines results in the formation of the additive compound first in one of the substituted rings, the second ring remaining intact as a typically aromatic ring. If then the sulphurous acid additive compound is destroyed, the amino-group of the second ring reacts on subsequent treatment with sulphurous acid; in this case the second ring exhibits aliphatically-unsaturated, and the first aromatic behaviour. The various stages of the reaction are in agreement with the author's views. T. H. P.

Preparation of Symmetrical Octahydroanthracenes. GEORG SCHROETER and TETRALIN G. M. B. H. (D.R.-P. 352721; from *Chem. Zentr.*, 1922, iv, 159).—Purified anthracene, melted or in solution, is treated with hydrogen under pressure in the presence of catalysts. For example, purified anthracene, m. p. 214° , is dissolved in tetrahydronaphthalene and in the presence of a catalyst, prepared by precipitation of reduced nickel on fuller's earth, treated with hydrogen at 180 – 200° under a pressure of 10–15 atmospheres until a quantity equivalent to four molecules is absorbed. The product is fractionated under reduced pressure.

s-Octahydroanthracene, $C_6H_8 \begin{smallmatrix} <CH \\ >CH \end{smallmatrix} C_6H_8$, forms crystals, m. p. 72 – 73° , b. p. 160 – $162^{\circ}/11$ mm. It forms a *monosulphonic acid*, $C_6H_8 \begin{smallmatrix} <CH \\ >C(SO_3H) \end{smallmatrix} C_6H_8$. With chlorine and bromine crystalline halogen substitution products are formed. By oxidation with chromium trioxide, 4-*keto-s*-octahydroanthracene is obtained. The symmetrical constitution of the octahydroanthracene is shown by the following synthesis. Tetrahydronaphthalene gives with chloroacetyl chloride in the presence of phosphoric oxide α - and β -*tetra*-

hydronaphthoylacetyl chlorides, $C_{10}H_{11} \cdot CO \cdot CH_2 \cdot COCl$; the latter give with ethyl sodiomalonate *ethyl α - and β -tetrahydronaphthoylacetylmalonates*, $C_{10}H_{11} \cdot CO \cdot CH_2 \cdot CH(CO_2Et)_2$, which by hydrolysis give α - and β -tetrahydronaphthoylpropionic acids,



By reduction, these acids yield α - and β -tetrahydronaphthylbutyric acids. From the chlorides of these acids cyclic ketones are obtained by inner condensation. From β -tetrahydronaphthylbutyryl chloride, 4-keto-*s*-octahydroanthracene and 4-keto-*s*-octahydrophenanthrene are obtained and may be separated by means of their semicarbazones. 4-Keto-*s*-octahydroanthracene yields, on reduction, *s*-octahydroanthracene, m. p. 72–73°, identical with that prepared by the catalytic process. Similarly, catalytic *s*-octahydroanthracene gives on oxidation with chromium trioxide 4-keto-*s*-octahydroanthracene identical with the compound obtained in the above synthesis.

G. W. R.

Preparation of Symmetrical Octahydrophenanthrenes.

GEORG SCHROETER and TETRALIN G. M. B. H. (D.R.-P. 352719; from *Chem. Zentr.*, 1922, iv, 159–160).—Purified phenanthrene, melted or in solution, is hydrogenated in the presence of catalysts. For example, phenanthrene, purified by treatment with readily fusible or finely divided metals such as sodium, potassium, copper, iron, or nickel, or other metallic compounds such as sodamide or calcium carbide, is treated with hydrogen at 180–220° at 15 atmospheres pressure in the presence of a catalyst prepared by precipitating nickel on fuller's earth. The product, b. p. 160–170°/13 mm., is purified by way of its *sulphonic acid* (I) which by treatment with hydrochloric acid (I.) $\begin{matrix} C_6H_8 \cdot C \cdot SO_3H \\ | \\ C_6H_8 \cdot CH \end{matrix}$ (II.) $\begin{matrix} C_6H_8 \cdot CH \\ | \\ C_6H_8 \cdot CH \end{matrix}$ gives *s*-octahydrophenanthrene (II). The latter compound forms crystals, m. p. 16.7°, b. p. 167.5°/13 mm., d^{20}_D 1.026. Its constitution is demonstrated in the same way as that of the *s*-octahydroanthracene (see preceding abstract). *s*-Octahydrophenanthrenemonosulphonic acid gives a stable *chloride* which with dilute aniline solution yields a crystalline *anilide*.

G. W. R.

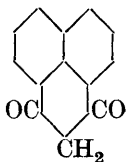
Diphenylene-ethylene. HEINRICH WIELAND, FRITZ REINDEL, and JUAN FERRER (*Ber.*, 1922, 55, [B], 3313–3317).—The preparation of diphenylene-ethylene [dibenzofulvene], $\begin{matrix} C_6H_4 \\ \diagup \\ C_6H_4 \end{matrix} > C : CH_2$,

by leading the vapours of fluorene over heated lead oxide has been described by Manchot and Krische (A., 1905, i, 142) and by Sieglitz and Jassoy (A., 1921, i, 791); repetition of their work shows that the product is a mixture of fluorene and bidiphenylene-ethylene. For the preparation of the hydrocarbon, 9-methylfluorenol (Daufresne, A., 1908, i, 164) is mixed with dry aluminium phosphate and distilled under diminished pressure; the monomeric substance is obtained in only very small yield on account of the unusual readiness with which it polymerises at a high temperature. The isolated polymeride can be depolymerised by a second heating, but the isolation of the monomeride is not possible even by dis-

tillation in a high vacuum. The product is therefore converted into the crystalline *dibromide*, broad, lustrous needles, m. p. 143° (decomp.), which is debrominated by treating its solution in alcohol with zinc dust and acetic acid; the operation must be performed in artificial light. *Diphenylene-ethylene* crystallises in lustrous, pointed prisms, m. p. 53° . It may be preserved unchanged for a few hours if shielded from daylight, but is rapidly polymerised when exposed even to diffused daylight or the rays from a mercury lamp. In solution, it is considerably more stable; thus, the ethereal solution is unchanged after being illuminated during twenty minutes by the mercury lamp. Polymerisation is not accelerated by ethereal hydrogen chloride. It instantly combines with bromine with re-formation of the dibromide. It is readily reduced by hydrogen in ethereal solution in the presence of palladium black to 9-methylfluorene, m. p. $45-46^{\circ}$. The *polymeride*, $(C_{14}H_{10})_n$, is a chalky, amorphous, colourless powder, which commences to soften at about 270° , whereby incipient depolymerisation begins. H. W.

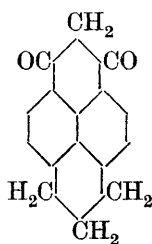
Synthesis of Pyrene. KARL FLEISCHER and EWALD RETZE (*Ber.*, 1922, **55**, [B], 3280—3290).—A direct synthesis of pyrene from naphthalene has been effected by condensing the latter with malonyl bromide, reducing the product, again condensing the reduction product with malonyl bromide, and submitting the compound so produced to a final reduction.

A solution of malonyl bromide and naphthalene in carbon disulphide is converted by aluminium chloride into *peri-naphth-indanedione* (annexed formula), decomp. about 265° after darkening at 250° , which is identical with the product obtained by Errera (A., 1911, i, 465) by the action of naphthalic anhydride on ethyl malonate in the presence of zinc chloride; malonyl chloride may be substituted for the bromide with equally good results. A suspension of the dione in benzene is converted by phosphorus pentachloride into 3 : 3-dichloro-1-ketoperinaphthindane, red-



dish-brown crystals, m. p. about 340° (decomp.). Reduction of the dione to the corresponding hydrocarbon can be effected only with great difficulty. It is either not affected or converted into amorphous products, which retain the property of solubility in alkali hydroxide, by amalgamated zinc and hydrochloric acid, zinc or magnesium, and glacial acetic acid, zinc dust in alkaline solution, sodium amalgam, sodium and amyl alcohol or cyclohexanol. Treatment with hydriodic acid (d 1.7) and red phosphorus under pressure converts the keto- into methylene groups, but the product also suffers hydrogenation in the nucleus; since the conditions of the reaction cannot be precisely governed, a mixture of hydrogenated hydrocarbons is produced. The product can, however, be dehydrogenated by passage over freshly-reduced copper at 500° thereby yielding *peritrimethylenenaphthalene* (*perinaphthindane*), m. p. $68-69^{\circ}$, identical with the product isolated by Langstein (A., 1910, i, 726) by the degradation of pyrene. It is very sensitive towards air. The corresponding *picrate* crystallises

in red needles, m. p. 134—135° after becoming discoloured at 124°, whereas the additive compound with 1:3:5-trinitrobenzene forms yellow needles, m. p. 159—160° after becoming discoloured at 130°.



*peri*Naphthindane reacts with malonyl bromide in the presence of carbon disulphide and aluminium chloride to give 1:3-diketo-1:2:3:4:5:6-hexahydropyrene (annexed formula), a pale yellow, amorphous substance which does not melt below 280°. It is converted by distillation with zinc dust in a slow current of hydrogen into pyrene, the identity of which is established by converting it into the picrate, long, red needles, m. p. 215°. H. W.

Amine Oxidation. VI. Radicles as Intermediate Stages in Chemical Reactions. STEFAN GOLDSCHMIDT and BERNARD WURZSCHMITT (*Ber.*, 1922, 55, [B], 3216—3220).—A characteristic property of organic radicles is their ability to combine with the radicles of other elements to form relatively stable additive compounds. This behaviour may be used in the detection of the transitory existence of radicles during the course of a chemical reaction provided that the second radicle is not itself changed under the experimental conditions used, and that the velocity of addition of the radicles is greater than that of the polymerisation of the intermediate radicle. From this point of view, the oxidation of aniline, *p*-toluidine, and *o*-toluidine dissolved in ether by lead peroxide in the presence of ignited sodium sulphate and hexaphenylethane has been investigated; anilinothriphenylmethane, colourless, hexagonal prisms, m. p. 148—149°, *p*-toluidinothriphenylmethane, m. p. 176°, and *o*-toluidinothriphenylmethane, m. p. 142°, respectively, are thereby obtained in good yield, thus showing that the radicle $R\cdot NH_2$ is intermediately produced (which probably becomes transformed into $R\cdot N:$ and $R\cdot NH_2$). Under similar conditions, diphenylamine yields solely tetraphenylhydrazine; diphenylaminotriphenylmethane cannot be obtained even by considerable variation of the experimental conditions. The rate of polymerisation of diphenylnitrogen appears to be much greater than its velocity of combination with triphenylmethyl.

The thermal decomposition of hydrazobenzene into azobenzene and aniline has been interpreted by Stieglitz and Curme (*A.*, 1913, ii, 398) as taking place in accordance with the scheme: $NHPh\cdot NHPh \rightarrow PhN: + PhNH_2$, whereas Wieland (1915, i, 850) has considered it to occur thus: $NHPh\cdot NHPh = NPh:NPh + 2H$. Conclusive evidence in favour of the latter view is deduced from the observation that azobenzene and triphenylmethane are almost quantitatively produced when a solution of hydrazobenzene in toluene is boiled with triphenylmethyl in an atmosphere of carbon dioxide; the radicle thus acts as acceptor of the activated hydrogen. H. W.

Amine Oxidation. VII. The Oxidation of Aniline. STEFAN GOLDSCHMIDT and BERNARD WURZSCHMITT (*Ber.*, 1922, 55, [B], 3220—3227; cf. *A.*, 1920, i, 226).—It has been suggested

previously that the formation of the different complex products of the oxidation of aniline may be due to the intermediate formation of benzoquinonephenyldi-imine or to the production and subsequent polymerisation of the radicle $\text{PhN}\cdot$. It is now found that it is explicable by the great reactivity of the former, which finds its expression in very differing directions. The second suggestion is therefore considered to be less probable and is relegated to the background.

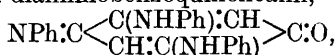
Benzoquinonephenyldi-imine is polymerised by glacial acetic or a small quantity of hydrochloric acid in the presence of ether almost quantitatively to the trimeride, $\text{NPh}\cdot\text{C}_6\text{H}_2(\text{NH}\cdot\text{C}_6\text{H}_4\cdot\text{NPh})_2\cdot\text{NH}$ (cf. Willstätter and Kubli, A., 1909, i, 976). It depends essentially on the nature and quantity of the added acid whether the di-imine is polymerised to emeraldine or to Willstätter's compound.

The oxidation of solutions of aniline salts by lead peroxide (cf. Börnstein, A., 1901, i, 375; Majima and Aoki, A., 1911, i, 216, 992) leads to the formation of the compound $\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{CH}\cdot\text{C}(\text{NPh}) \\ \text{C}(\text{NPh})\cdot\text{CH} \end{smallmatrix}\text{C}\cdot\text{NH}$

or $\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{C}(\text{NPh})-\text{CH} \\ \text{CH}\cdot\text{C}(\text{NPh}) \end{smallmatrix}\text{C}\cdot\text{NH}_2$. It is found that benzoquinonephenyldi-imine reacts readily with aniline to form this substance under the conditions selected by Börnstein, and that, in addition, Willstätter's trimeride is produced; the latter is not isolated in the oxidative experiments, since it undergoes further change.

According to Börnstein, azophenine, $\text{NPh}\cdot\text{C}\begin{smallmatrix} \text{C}(\text{NPh})\cdot\text{CH} \\ \text{CH}\cdot\text{C}(\text{NPh}) \end{smallmatrix}\text{C}\cdot\text{NPh}$, is a further product of the oxidation of aniline; it is obtained when aniline is mixed with dianilinobenzoquinonephenyldi-imine in ethereal solution in the presence of a little glacial acetic acid.

The formation of dianilinobenzoquinoneanil,

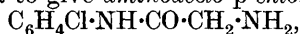


by the oxidation of aniline in acetic acid solution by hydrogen peroxide has been observed by Schunk and Marchlewski. Since benzoquinonephenyldi-imine is readily hydrolysed with loss of ammonia to benzoquinonephenylimine, $\text{NPh}\cdot\text{C}_6\text{H}_4\cdot\text{O}$, it appears probable that the anil is produced by condensation of this substance with aniline in dilute acid solution. Such condensation is shown to take place readily and at the atmospheric temperature in ethereal solution in the presence of a little acetic acid. A second possible mode for its formation consists in the hydrolysis of Börnstein's anil; dianilinobenzoquinoneanil is actually formed from this compound by the prolonged action of dilute hydrochloric acid, but not by acetic acid, so that its preparation in this manner during oxidative experiments in dilute acetic acid solution appears improbable.

H. W.

Formation and Properties of Dithioketones ($\text{R}_2\text{C}\cdot\text{S}\cdot\text{S}$) and Dithio-ethers ($\text{R}_2\text{S}\cdot\text{S}$). III. KUVIRJI GOSAI NAIK and MAHADEO DATTATRAYA AVASARE (T., 1922, 121, 2592—2595).

Thiocyanates and Thiocarbimides. XV. The Nature of the Intramolecular Rearrangement of Thiocarbimidoacetanilides. ARTHUR J. HILL and ERWIN B. KELSEY (*J. Amer. Chem. Soc.*, 1922, **44**, 2357—2369; cf. A., 1920, i, 681; Beckurts and Frerichs, A., 1915, i, 798, 799).—Using the method previously described (*loc. cit.*), the authors have converted the chloroanilides used by Beckurts and Frerichs (*loc. cit.*) successively into the corresponding primary amines, dithiocarbamates, carbethoxydithiocarbamates, and finally the thiocarbimides. The latter are so unstable that they rearrange immediately into normal 2-thiohydantoin. That these were normal thiohydantoin was shown by their conversion into the corresponding oxyhydantoin, which latter were also synthesised from the urethanes of the general formula $\text{NHR}\cdot\text{CO}\cdot\text{CH}_2\cdot\text{NH}\cdot\text{CO}_2\text{Et}$. Further, it is shown that their melting points differ from those of the ψ -hydantoin described by Beckurts and Frerichs. Chloroaceto-*p*-chloroanilide reacts with alcoholic ammonia to give *aminoaceto-p-chloroanilide*,



m. p. 64° ; and the *di-p-chlorophenylamide* of diglycolamidic acid, $(\text{C}_6\text{H}_4\text{Cl}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_2)_2\text{NH}$, m. p. $170\text{--}171^\circ$, according to the conditions. The first-named anilide by the action of ethyl chloroformate is converted into the *carbethoxy*-derivative, m. p. 198° , and by the action of benzoyl chloride into *benzoylaminoaceto-p-chloroanilide*, m. p. $217\text{--}218^\circ$. Aminoaceto-*p*-chloroanilide reacts with carbon disulphide in alcoholic solution to give its *dithiocarbamate*, m. p. 155° , and the carbethoxy-derivative gives a *dithiocarbamate* which is unstable and on distillation is converted into 2-thio-1-*p-chlorophenylhydantoin*, m. p. $225\text{--}227^\circ$ (decomp.), which is also prepared by the action of mercuric chloride on aminoaceto-*p*-chloroanilide dithiocarbamate. This hydantoin gives 2-thio-1-*p-chlorophenyl-4-benzylidenehydantoin*, m. p. 257° , and 2-benzylthiol-1-*p-chlorophenyl-4-benzylidenehydantoin*, m. p. $176\cdot5^\circ$. 1-*p-Chlorophenylhydantoin*, m. p. 174° , was obtained either by the action of chloroacetic acid on the corresponding thiohydantoin or by the action of alcoholic potassium hydroxide on carbethoxyaminoaceto-*p*-chloroanilide and yielded 1-*p-chlorophenyl-4-benzylidenehydantoin*, m. p. 274° .

A similar series of compounds has been prepared from chloroaceto-*p*-aniside and from chloroaceto-*m*-toluidide, as follows. Aminoaceto-*p*-aniside, m. p. $98\text{--}99^\circ$; the *di-p-anisylamide* of diglycolamidic acid, m. p. 143° ; the *tri-p-anisylamide* of triglycolamidic acid, m. p. $192\text{--}193^\circ$; carbethoxyaminoaceto-*p*-aniside, m. p. 154° ; aminoaceto-*p*-aniside dithiocarbamate, m. p. $140\text{--}145^\circ$ (decomp.), and its carbethoxy-derivative; 2-thio-1-*p-anisylhydantoin*, m. p. $207\text{--}209^\circ$; 1-*p-anisylhydantoin*, m. p. 208° ; 2-thio-1-*p-anisyl-4-benzylidenehydantoin*, m. p. 203° ; 2-benzylthiol-1-*p-anisyl-4-benzylidenehydantoin*, m. p. 174° ; 1-*p-anisyl-4-benzylidenehydantoin*, m. p. 238° .

Aminoaceto-*m*-toluidide, m. p. $54\text{--}55^\circ$; the *di-m-tolylamide* of diglycolamidic acid, m. p. 136° ; benzoylaminoaceto-*m*-toluidide, m. p. 186° ; carbethoxyaminoaceto-*m*-toluidide, m. p. 103° ; aminoaceto-*m*-

toluidide dithiocarbamate, m. p. 138° (decomp.), and its *carbethoxy*-derivative, m. p. 113° (decomp.); 2-*thio*-1-*m*-tolylhydantoin, m. p. 187° (decomp.); 1-*m*-tolylhydantoin, m. p. 123°; 2-*thio*-1-*m*-tolyl-4-benzylidenehydantoin, m. p. 183°; 2-benzylthiol-1-*m*-tolyl-4-benzylidenehydantoin, m. p. 145°; 1-*m*-tolyl-4-benzylidenehydantoin, m. p. 214°.

The di-*p*-chlorophenylamide of diglycolamidic acid when warmed in acetone solution deposits a crystalline compound, m. p. 250—251°, which is apparently produced by the combination of two mol. of the secondary amine and one mol. of acetone. The diphenylamide of diglycolamidic acid gave a similar compound, m. p. 166—167°. W. G.

The Mobility of Symmetrical Triad Systems. I. The Conditions Relating to Systems Terminated by Phenyl Groups. CHRISTOPHER KELK INGOLD and HENRY ALFRED PIGGOTT (T., 1922, 121, 2381—2389).

5-Aminoacenaphthene. KARL FLEISCHER and KARL SCHRANZ (*Ber.*, 1922, 55, [B], 3253—3280).—An account is given of an extensive series of derivatives of 5-aminoacenaphthene.

Reduction of 5-aminoacenaphthene in aqueous alcoholic solution by means of sodium hyposulphite leads to the formation of a mixture of 5-aminoacenaphthene, m. p. 108° (20%), *sodium acenaphthylsulphamate*, $C_{12}H_9 \cdot NH \cdot SO_3Na$ (about 50%), and 5-aminoacenaphthene-4-sulphonic acid, colourless needles which darken without melting at 270° (4%). The production of the sulphamate appears to take place in accordance with the equations: $C_{12}H_9 \cdot NO_2 + 2Na_2S_2O_4 + 3H_2O = C_{12}H_9 \cdot NH \cdot OH + 4NaHSO_3$ and $C_{12}H_9 \cdot NH \cdot OH + H \cdot SO_3Na = C_{12}H_9 \cdot NH \cdot SO_3Na + H_2O$. It forms aggregates of colourless crystals, decomp. above 235° after darkening at 200°. *Acenaphthyl-5-sulphamic acid*, $C_{12}H_9 \cdot NH \cdot SO_3H$, crystallises in slender, colourless needles, which do not melt below 270°; it is hydrolysed by boiling hydrochloric acid to 5-aminoacenaphthene and sulphuric acid. For the preparation of 5-aminoacenaphthene by the reduction of the 5-nitro-compound the procedure of Sachs and Mosebach (*A.*, 1910, i, 726; 1911, i, 960) is modified in that the crude product of the reaction after removal of alcohol is boiled with hydrochloric acid and the base is subsequently liberated by addition of ammonia to the solution; the yield is 71% of that theoretically possible.

5-Aminoacenaphthene is converted by concentrated sulphuric acid at 100° into a mixture of di- and tri-sulphonic acids; a more dilute acid (80%), under similar conditions, converts it into 5-aminoacenaphthene-(?)6-sulphonic acid, almost colourless needles (the product is frequently amorphous) which become blackened, without melting, at 300°. It couples with diazotised *m*-nitroaniline to yield the compound, $NH_2 \cdot C_{12}H_7(SO_3Na) \cdot N \cdot N \cdot C_6H_4 \cdot NO_2$, a brownish-red powder with a metallic lustre. It is conveniently diazotised by the addition of hydrochloric acid to an aqueous solution of its sodium salt and sodium nitrite, and the dark green

diazonium compound couples with β -naphthol to the *dye*, $\text{SO}_3\text{Na}\cdot\text{C}_{12}\text{H}_8\cdot\text{N}\cdot\text{N}\cdot\text{C}_{10}\text{H}_6\cdot\text{OH}$, a brownish-red, metallic powder.

5-Aminoacenaphthene reacts with aldehydes in boiling alcoholic solution to give normal azomethines, of which the following are described: 5-benzylideneaminoacenaphthene, $\text{C}_{12}\text{H}_9\cdot\text{N}\cdot\text{CHPh}$, pale yellow plates, m. p. 67—68°; 5-o-nitrobenzylideneaminoacenaphthene, oblique, brownish-yellow prisms, m. p. 135°; 5-m-nitrobenzylideneaminoacenaphthene, lemon-yellow needles, m. p. 156° after softening at 147°; 3-p-nitrobenzylideneaminoacenaphthene, cinnabar-red prisms, m. p. 226°; 5-o-chlorobenzylideneaminoacenaphthene, yellow needles, m. p. 112—114°; 5-p-chlorobenzylideneaminoacenaphthene, yellow, rectangular plates, m. p. 126—128°; 5-o-hydroxybenzylideneaminoacenaphthene, ochre-yellow, rectangular platelets, m. p. 92—93°; 5-p-hydroxybenzylideneaminoacenaphthene, yellow, rhombic platelets, m. p. 194—196°; 5-p-methoxybenzylideneaminoacenaphthene, yellow, oblique prisms, m. p. 85—86°; 5-3':4'-dimethoxy-2'-styrylbenzylideneaminoacenaphthene, $\text{C}_{12}\text{H}_9\cdot\text{N}\cdot\text{CH}\cdot\text{C}_6\text{H}_2(\text{OMe})_2\cdot\text{CH}\cdot\text{CHPh}$, slender, pale yellow needles, m. p. 132—134°; 5- α -furylideneaminoacenaphthene, minute, brownish-yellow crystals, m. p. 106—108°.

The condensation of 5-aminoacenaphthene with the chlorides of dibasic acids gives symmetrical diacenaphthyl derivatives of the acid amides. The following are described: di-5-acenaphthylcarbamide, $\text{CO}(\text{NH}\cdot\text{C}_{12}\text{H}_9)_2$, slender, pale brown rods, m. p. 301° (decomp.) after darkening at 295°, prepared from the amine and carbonyl chloride in the presence of benzene; oxalodi-5-acenaphthylamide, colourless, slender rodlets, m. p. 274—275° after previous darkening; malonodi-5-acenaphthylamide, pale brown, rectangular plates, m. p. 222—223° after slight previous softening; diethylmalonodi-5-acenaphthylamide, $\text{CEt}_2(\text{CO}\cdot\text{NH}\cdot\text{C}_{12}\text{H}_9)_2$, slender, colourless needles, m. p. 218—220°; succinodi-5-acenaphthylamide, needles, m. p. 288—289° after previous darkening.

5-Dimethylaminoacenaphthene is conveniently prepared by the action of methyl sulphate on 5-aminoacenaphthene in the presence of concentrated aqueous sodium acetate solution and removal of simultaneously formed monomethyl derivatives by treatment of the crude product of the reaction with benzenesulphonyl chloride; it crystallises in colourless, rhombic platelets, m. p. 45—46°. It gives a *picrate*, canary-yellow crystals, m. p. 172—174°, and a stable *methiodide*, long, colourless needles, m. p. 177°; it could not be caused to react with ethyl bromide. 5-Diethylaminoacenaphthene, colourless leaflets, m. p. 41—42°, is prepared similarly by the use of ethyl sulphate. The corresponding *picrate*, lemon-yellow crystals, m. p. 181—184° after previous softening (decomp. 186°), and the unstable *methiodide*, m. p. 165—167° (decomp.), are described. The base is not affected by ethyl bromide at 100°.

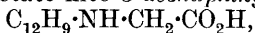
5-Aminoacenaphthene exhibits a marked tendency to form diacyl derivatives under conditions which in general lead only to the production of the mono-compounds. Thus, with benzenesulphonyl chloride in the presence of potassium hydroxide solution it gives a mixture of 5-benzenesulphonylaminoacenaphthene, colourless, rhombic platelets, m. p. 198—199° after darkening at 195°,

and 5-dibenzenesulphonylaminoacenaphthene, aggregates of colourless prisms, m. p. 220° after previous darkening. The latter substance is unaffected by concentrated, aqueous solutions of alkali hydroxides, but is converted by sodium ethoxide dissolved in alcohol into the monobenzenesulphonyl compound. Similarly, toluene-*p*-sulphonyl chloride yields a mixture of 5-toluene-*p*-sulphonylaminoacenaphthene, pale yellow rodlets, m. p. $194-195^{\circ}$, and 5-ditoluene-*p*-sulphonylaminoacenaphthene, small, colourless pyramids, m. p. $215-217^{\circ}$, to a dark liquid. 5-Acetylmethylaminoacenaphthene has m. p. $124-125^{\circ}$.

The phenylation of the base could not be accomplished smoothly by treatment of it with bromobenzene and copper powder. On the other hand, it reacts with chloro-2:4-dinitrobenzene in boiling alcoholic solution to give 5-2':4'-dinitroanilinoacenaphthene, cinnamon-red needles, m. p. $177-178^{\circ}$, after previous softening and with picryl chloride to yield 5-2':4':6'-trinitroanilinoacenaphthene, dark red needles which soften at 230° and decompose at a higher temperature.

A diazotised solution of 5-aminoacenaphthene couples with sodium β -naphthol-3:6-disulphonate with the formation of a reddish-violet dye and with sodium α -naphthol-4-sulphonate to yield an unstable compound. Reddish-violet dyes are also obtained from diazotised 5-aminoacenaphthene-6(?)sulphonic acid and *R*-salt or sodium α -naphthol-4-sulphonate, but the shades are not sufficiently pure to render them technically valuable.

5-Aminoacenaphthene is converted by chloroacetic acid in the presence of sodium acetate into 5-acenaphthylglycine,



plates, m. p. $210-212^{\circ}$ (decomp.). The corresponding potassium salt becomes carbonised when treated with molten sodamide.

H. W.

The Preparation of cycloHexanol. ANDRÉ BROCHET (*Compt. rend.*, 1922, **175**, 583—585; cf. A., 1914, i, 645).—Certain aspects of the reaction between hydrogen and phenol in presence of reduced nickel are dealt with. Values of the specific activity of nickel are given for a temperature range of 90° . The reaction should be carried out under pressure. No trace of a substance intermediate between phenol and cyclohexanol was found. The mechanism of the reaction does not depend on the method of hydrogenation, which may be effected in either the liquid or vapour phase; in the latter case, formation of cyclohexene, cyclohexane, and cyclohexanone may occur, but this is avoided by working at as low a temperature as possible. It is advisable to work with at least 5% of the catalyst, as repeated use causes the nickel to decrease considerably in activity, although such used nickel may be shown to be of almost full activity if used for hydrogenation of sodium cinnamate.

H. J. E.

The Action of Bromine on Nitrophenol-sulphonic and -sulphocarboxylic Acids. EUKLID SAKELLARIOS (*Ber.*, 1922, **55**, [B], 2846—2853).—A series of instances has been examined

in which the sulphonic or carboxylic groups of substituted nitrophenyl are displaced smoothly by bromine.

Potassium *o*-nitrophenol-4 : 6-disulphonate, $\text{NO}_2 \cdot \text{C}_6\text{H}_2(\text{OH})(\text{SO}_3\text{K})_2 \cdot \text{H}_2\text{O}$ (cf. Charnot and Pratt, A., 1909, i, 641), is obtained conveniently by dissolving phenol in fuming sulphuric acid (20%), nitrating the product with nitric acid (85%) and sulphuric acid (96%), diluting the mixture with water, and precipitating the salt directly by the addition of potassium chloride solution. It is reduced by zinc and hydrochloric acid or by concentrated sodium hydrogen sulphite solution to *potassium hydrogen o-aminophenol-4 : 6-disulphonate*, $\text{NH}_2 \cdot \text{C}_6\text{H}_2(\text{OH}) \cdot (\text{SO}_3\text{H})(\text{SO}_3\text{K}) \cdot \text{H}_2\text{O}$. An aqueous solution of the potassium salt of the nitro-acid is converted by bromine dissolved in glacial acetic acid into *potassium 2-bromo-6-nitrophenol-4-sulphonate* and 4 : 6-dibromo-*o*-nitrophenol, m. p. 117·5°. The constitution of the potassium salt is established by the observations that it is transformed by further bromination into 4 : 6-dibromo-*o*-nitrophenol and by nitric acid into 2 : 4-dinitro-*o*-bromophenol, m. p. 118·5°.

According to Datta (A., 1921, i, 331), the bromination of *o*-nitrophenol-4-sulphonic acid yields 4 : 6-dibromo-*o*-nitrophenol; if, however, only one molecular proportion of bromine is used, 6-nitro-*o*-bromophenol-4-sulphonic acid is obtained. The latter acid is reduced by zinc dust and hydrochloric acid to 2-bromo-6-aminophenol-4-sulphonic acid, colourless crystals.

Potassium 2 : 6-dinitrophenol-4-sulphonate is converted by bromination into 4-bromo-2 : 6-dinitrophenol, m. p. 78° (the m. p. 85·6° recorded in Richter's Lexicon is incorrect).

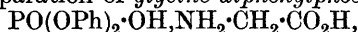
Potassium hydrogen 3-nitro-5-sulphosalicylate is converted by bromine in a similar manner into 4 : 6-dibromo-2-nitrophenol, m. p. 117·5°, and potassium 6-bromo-*o*-nitrophenol-4-sulphonate, the constitution of which is established by its further conversion into 4 : 6-dibromo-*o*-nitrophenol and 6-bromo-2 : 4-dinitrophenol. The nitrosulphosalicylic acid is therefore shown to be 3-nitro-5-sulpho-*o*-hydroxybenzoic acid.

H. W.

Preparation of Di- and Poly-halogen Substitution Products of Monohydric Phenols. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 349794; from *Chem. Zentr.*, 1922, iv, 45; cf. *Chemische Werke Ichendorf*, A., 1915, i, 674; *Holleman*, A., 1918, i, 216; 1921, i, 102).—Tri- and poly-halogen substitution products of aromatic hydrocarbons are heated at high temperatures under pressure with alkali hydroxides and methyl alcohol, or its homologues, with or without addition of other solvents. For example, 1 : 2 : 4 : 5-tetrachlorobenzene is heated with sodium hydroxide and methyl alcohol, with or without addition of pyridine, for about seven hours at 160° under pressure, or with potassium hydroxide and alcohol for about ten hours at 200°, or with potassium hydroxide and amyl alcohol for sixteen hours at 200° under pressure; whereby 2 : 4 : 5-trichlorophenol is obtained; it forms lustrous needles, m. p. 64—65°. 2 : 4 : 5-Tribromophenol is similarly prepared. 2 : 5-Dichlorophenol, from 1 : 2 : 4-trichlorobenzene, sodium

hydroxide, and methyl alcohol, has b. p. 211° , m. p. 58° . A mixture of polybromonaphthols may be prepared from mixed polybromonaphthalenes by similar means. G. W. R.

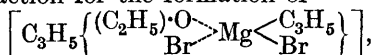
Diphenylphosphoric Acid [Diphenyl Hydrogen Phosphate], a Reagent for the Amino-group. A. BERNTON (*Ber.*, 1922, 55, [B], 3361—3365).—Attempts to cause diphenylphosphoric chloride to react with copper glycine suspended in benzene were unsuccessful, but the addition of a little water to the mixture resulted in the separation of *glycine diphenylphosphate*,



large, quadratic plates, m. p. 177 — 178° . The acid reacts with other amino-acids in aqueous solution, giving salts which crystallise in matted needles resembling cotton wool. The following are described: *alanine diphenylphosphate*, m. p. 193° ; *leucine diphenylphosphate*, m. p. 217° ; *glutamine diphenylphosphate*, m. p. 137° ; *glycylglycine diphenylphosphate*, m. p. 178° . *Methylamine diphenylphosphate* crystallises in thin, transparent plates, m. p. 78 — 79° , *ethylamine diphenylphosphate* forms small, colourless crystals, m. p. 126° , whereas *ammonium diphenylphosphate* has m. p. 130° . The acid, according to observations with acetamide and benzamide, does not appear to react with amides.

Diphenylphosphoric acid (+2 aq.) is most conveniently prepared by gradually adding diphenylphosphoric chloride to an aqueous solution of sodium hydroxide and subsequently warming the mixture on the water-bath, whereby the sodium salt (+5H₂O), thick plates which melt at 70° in their water of crystallisation, is obtained; the free acid is precipitated by the addition of hydrochloric acid to an aqueous solution of the sodium salt. Silver diphenylphosphate has m. p. 213° . H. W.

The Auxiliary Valency of the Hydroxyl Group. I. HANS REIHLEN (*Z. anorg. Chem.*, 1922, 123, 173—195).—The author reinvestigated the complex salts of pyrocatechol and its derivatives. He finds that the co-ordinated complex contains a water molecule, and that the reactions are only explained by assuming the co-ordination number to be four, and not six as suggested by Weinland (*A.*, 1914, i, 553). Thus the complex with iron as central metal is given the formula $[\text{Fe}(\text{H}_2\text{O})(\text{O} \cdot \text{C}_6\text{H}_4 \cdot \text{O})_3]'''$. Besides the two spheres (inner and outer, non-ionic and ionic), the author suggests a sphere between the two—non-ionic, but at the same time not under the full influence of the central atom. For example, in Grignard's reaction for the formation of



the allyl group is only loosely held but is non-ionic. Co-ordination is shown to depend, not only on the central atom, but also on the character of the negative groups. It is also shown that a hydroxyl group attached to the benzene nucleus loses its power of exerting auxiliary valency if its hydrogen atom receives ionic properties. W. T.

The Auxiliary Valency of the Hydroxyl Group. The Complex Salts of Substituted Pyrocatechol. HANS REIHLEN and ADOLF SAPPER (*Z. anorg. Chem.*, 1922, **124**, 275—288).—Several complex salts with catechol and its derivatives are prepared; in these the author holds that the co-ordination number is four irrespective of the nature of the central atom. To explain the formation of the compound, the author assumes that the four groups are arranged at the corners of a tetrahedron around the central atom. The preparation and the properties of the following compounds are described, $[\text{Cu}_2(\text{C}_7\text{H}_4\text{O}_3)_4(\text{H}_2\text{O})_2]\text{Na}_4, 7\text{H}_2\text{O}$.
 $[\text{Zn}_2(\text{C}_7\text{H}_4\text{O}_3)_4(\text{H}_2\text{O})_2]\text{Na}_4, 18\text{H}_2\text{O}$. $[\text{Ni}(\text{C}_7\text{H}_3\text{O}_4)_2(\text{H}_2\text{O})_2]\text{Na}_4, 18\text{H}_2\text{O}$.
 $[\text{Ni}_2(\text{O}\cdot\text{C}_6\text{H}_3\text{O}\cdot\text{CO}_2\text{Et})_4(\text{H}_2\text{O})_2]\text{Na}_4, 25\text{H}_2\text{O}$.
 $[\text{Ni}_5(\text{C}_7\text{H}_4\text{O}_3)_{10}(\text{C}_7\text{H}_4\text{O}_2\cdot\text{OH})\text{H}_2\text{O}]\text{Na}_{11}, 45\text{H}_2\text{O}$.
 $[\text{Ni}_5(\text{C}_7\text{H}_4\text{O}_3)_{10}(\text{C}_7\text{H}_4\text{O}_2\cdot\text{OH})(\text{OH})_4]\text{Na}_{12}, 50\text{H}_2\text{O}$.
 $[\text{Cd}_6(\text{C}_7\text{H}_4\text{O}_3)_{12}(\text{C}_7\text{H}_4\text{O}_2\cdot\text{OH})]\text{Na}_{13}, 54\text{H}_2\text{O}$.
This cadmium compound is given a cyclic structure. W. T.

The Constitution of Resorcinol and some of its Derivatives. RENÉ FABRE (*Ann. Chim.*, 1922, **18**, 49—116).—The ketonic character of resorcinol, shown by Herzig and Zeisel from a study of ethylresorcinols (A., 1891, 75), was confirmed from the molecular refraction of the tetraethyl derivative. Ethylation of 4-chlororesorcinol results in the formation of a mixture of diethyl and triethyl derivatives, and in the latter (4-chloro-2:2-diethylresorcinol ethyl ether) only one of the ethyl groups is present as an ethoxy-group, the resorcinol behaving partly as a phenol and partly as a ketone. An isomeride of this substance is obtained by the action of sulphuryl chloride on triethylresorcinol. Attempts were made to obtain other derivatives in which resorcinol functions as a ketone (cf. Fuchs and Eisner, A., 1920, i, 545); these were unsuccessful. A study of nitrosoresorcinols showed that the nitroso-group enters in the 2-position if the 4-position is already substituted. Sodium resorcinoxide combines directly with carbon dioxide, giving, under a pressure of six atmospheres at 115—120°, 85% of the theoretical yield of sodium β -resorcylate (cf. Kostanecky, A., 1886, 242). Similar attempts at fixation of carbon dioxide with 4-chlororesorcinol showed that, as with the nitroso-derivatives, the fixation occurs in the 2-position if the 4-position is already substituted. The condensation of resorcinol with benzaldehyde was effected in acetic acid solution, yielding a crystalline product, benzylideneresorcinol, which is soluble in alcohols of high boiling point. The substance gives an acetyl derivative of the formula $(\text{C}_{17}\text{H}_{14}\text{O}_4)_2$, and the inference is drawn that its formula is $\text{C}_{26}\text{H}_{20}\text{O}_4$; a study of analogous condensation products previously obtained (Liebermann, Lindenbaum, and Glave, A., 1904, i, 443; Pope and Howard, T., 1910, **97**, 78) shows it to be similar to these, although a crystalline product had not been prepared. Structural formulae for this and the analogous substances obtained are suggested. Benzaldehyde does not react with tetraethylresorcinol, but with the triethyl derivative condensation occurs; this appears to indicate that the aldehyde is linked in the para-position with

respect to one of the hydroxyl groups. Condensation products obtained from resorcinol with xanthyrol confirm the conclusion that the most easily replaceable hydrogen atom is that which occupies the 4-position, and thus is in the *para*-position with respect to hydroxyl; di-substitution takes place in the 2- and 4-positions. Although in some cases resorcinol behaves as a ketone, in the majority of instances it reacts as a phenol; the former type of reaction occurs in the case of condensations effected in presence of sodium methoxide, and the replaceable hydrogen is then that which is linked to the carbon atom situated between the two carbonyl groups.

The following substances do not appear to have been previously described. 4-Chloro-2 : 2-diethylresorcinol 3-ethyl ether, colourless needles, m. p. 25°. 4-Chloro-2-nitrosoresorcinol, yellow plates. 3-Chloro-2 : 4-dihydroxybenzoic acid, colourless needles, m. p. 203°. 3-Chloro-2 : 6-dihydroxybenzoic acid, colourless crystals, m. p. 215—216°. 2 : 4-Dihydroxy-3-xanthylbenzoic acid, colourless crystals, turning red and softening without melting at 200°. Acetylbenzylideneresorcinol, colourless, prismatic needles, m. p. 364—366°. 4-Benzylidene-1 : 2 : 3-triethylresorcinol, colourless needles, decompose on heating. Vanillideneresorcinol, pale rose crystals, from acetic acid, colourless needles, from benzyl alcohol, decompose on heating; acetyl derivative, m. p. 323°. Piperonylideneresorcinol, needles turning pink on exposure to light, resinify on heating; acetyl derivative, m. p. above 370°. 4-Xanthylresorcinol, colourless needles, m. p. 178—179°; diacetyl derivative, m. p. 242—243°. 2 : 4-Dixanthylresorcinol, colourless needles, m. p. 255—257°; diacetyl derivative, m. p. 262—263°. 4-Xanthyl-1 : 2-diethylresorcinol 3-ethyl ether, colourless crystals, m. p. 201—202°. 4-Nitroso-2-xanthylresorcinol, bright, dark red crystals, m. p. 212°. 2-Nitroso-4-xanthylresorcinol, golden-yellow, hexagonal crystals, m. p. 295—296°. 4-Chloro-2-xanthylresorcinol, colourless crystals, m. p. 215°. Xanthylquinol, pale greenish-yellow crystals, m. p. 215—216°. 2 : 3-Dixanthylquinol, colourless crystals, m. p. 231—232°. 3-Chloro-2-xanthylquinol, colourless crystals, m. p. 236—237°. Xanthylpyrocatechol, yellow crystals, m. p. 205—206°. 4 : 5-Dixanthylpyrocatechol, colourless crystals, m. p. 235—236°. 4-Chloro-3-xanthylpyrocatechol, colourless crystals, m. p. 224°.

H. J. E.

Univalent Oxygen. I. STEFAN GOLDSCHMIDT (*Ber.*, 1922, 55, [B], 3194—3197).—If a solution of guaiacol in ether is treated during a few minutes with a large excess of lead peroxide at a low temperature, a very unstable green or bluish-green solution is obtained which exhibits the properties to be expected of a radicle with univalent oxygen. It is completely insensitive towards oxygen. It is immediately decolorised by quinol, phenylhydrazine, or a solution of triphenylmethyl in benzene. It does not react with nitric oxide. When cooled to -80° , the solution becomes much lighter in colour. The further investigation of the solutions and the isolation of any radicle which may be present is rendered exceedingly difficult by its great instability. Quan-

titative oxidation with phenylhydrazine shows that only a small fraction of the guaiacol has been oxidised in the direction indicated.

Similar observations are made during the oxidation of quinol monomethyl ether. The solutions are pure blue in colour and extraordinarily unstable. The change of colour with alteration in temperature is more pronounced than with guaiacol solutions. Under similar conditions, *o*-cresol gives a blood-red, α -naphthol a blue-red, and β -naphthol a pale green solution.

It appears reasonable to assume that the blue oxidation products of guaiacol and quinol methyl ether are formed by the removal of the hydrogen atom of the hydroxyl group, thus $\text{MeO}\cdot\text{C}_6\text{H}_4\cdot\text{O}\cdot$. This view, however, does not appear to be tenable, since the reduction product of oxidised guaiacol, after removal of guaiacol, can be re-oxidised to the blue substance. The constitution of the compound is still under investigation. H. W.

Univalent Oxygen. II. Phenanthroxyls. STEFAN GOLDSCHMIDT and WALTER SCHMIDT (*Ber.*, 1922, 55, [B], 3197—3215; cf. preceding abstract).—Phenanthraquinol monomethyl and monoethyl ethers are readily oxidised to colourless substances which are insoluble in alkali hydroxide and are distinguished from the parent material by containing one atom of hydrogen less in their molecule. They form greenish-yellow solutions which gradually darken when preserved. The occurrence of radicle dissociation is established by the failure of the solutions to obey Beer's law and by the dependence of molecular weight on dilution. The present cases of dissociation are distinguished by the long period which is necessary for the establishment of equilibrium which can be followed by periodical determination of molecular weight; constancy of the latter and of the colour of the solutions is attained simultaneously. The process is complete in about two and a half hours and in *N*/100-solution at the atmospheric temperature about 37% of the methyl and 62% of the ethyl compound is dissociated into radicles. The constitution of the compounds is discussed in detail, and the authors draw the conclusion that the bimolecular products are to be regarded as 9-alkoxy(acyloxy)-10-phenanthryl peroxides, $\text{C}_6\text{H}_4\cdot\text{C}\text{---}\text{OR}$ $\text{RO}\text{---}\text{C}\cdot\text{C}_6\text{H}_4$, and the unimolecular substances as $\text{C}_6\text{H}_4\cdot\text{C}\text{---}\text{O}\text{---}\text{O}\text{---}\text{C}\cdot\text{C}_6\text{H}_4$, 9-alkoxy(acyloxy)-10-phenanthroxyls, $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{OR}$ $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{O}\text{---}$.

Phenanthraquinol monomethyl ether, $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{OMe}$ $\text{C}_6\text{H}_4\cdot\text{C}\cdot\text{OH}$, colourless aggregates of small needles, m. p. 103° after darkening at 92°, is obtained in small yield by the action of methyl sulphate and potassium hydroxide on phenanthraquinol in the complete absence of air. The corresponding monoethyl ether (+ EtOH) is prepared conveniently by the addition of finely divided phenanthraquinone to an ethereal solution of zinc ethyl. The preparation of the mono-methyl compound by a corresponding alteration of this method

does not appear to be practicable; the course of the change is not very obvious, but the ultimate product is *phenanthraquinol dimethyl ether*, needles, m. p. 87° . Phenanthraquinol monoacetate, colourless needles, m. p. 170° (decomp.), is obtained conveniently by short treatment of the quinol with hot acetic anhydride.

Oxidation of the monomethyl ether dissolved in aqueous potassium hydroxide solution by means of potassium ferricyanide gives *9-methoxy-10-phenanthryl peroxide*, almost colourless crystals, m. p. 165° (decomp.), to a pale brown mass. The substance combines with triphenylmethyl in benzene solution, but the additive compound shows little tendency to crystallise, and is identified by hydrolysing it with dilute sodium hydroxide solution to triphenylcarbinol and the original ether. It is reduced by the action of zinc dust and glacial acetic acid on its solution in ether to phenanthraquinol monomethyl ether, m. p. $102\text{--}103^{\circ}$, and converted slowly by oxygen in the presence of benzene to phenanthraquinone. It does not react with nitric oxide.

Phenanthraquinol monoethyl ether is converted by potassium ferricyanide in the presence of aqueous potassium hydroxide solution or by lead peroxide in the presence of ether and anhydrous potassium carbonate into *9-ethoxy-10-phenanthryl peroxide*, almost colourless aggregates of needles ($+2\text{C}_6\text{H}_6$), m. p. 138° (decomp.). It unites with triphenylmethyl, and the additive compound is hydrolysed (as in the case of the methyl compound) to triphenylcarbinol and phenanthraquinol monomethyl ether. It is reduced by zinc dust and glacial acetic acid, phenylhydrazine, quinol, or hydriodic acid to phenanthraquinol monoethyl ether; with the reagent last-mentioned, the reduction is practically quantitative. The radicle, when dissolved in benzene, is slowly converted by oxygen into phenanthraquinone and ultimately into diphenic acid. It does not react with nitric oxide. It immediately decolorises a solution of bromine in chloroform, by which it is converted into phenanthraquinone. It does not react smoothly with potassium in the presence of benzene, since the metal is only superficially attacked. With potassium phenyl diphenyl ketone the green solution is rapidly decolorised with formation of the *potassium* salt which is decomposed with production of the pure ethyl ether.

Phenanthraquinyl monoacetate, suspended in anhydrous ether, is oxidised by lead peroxide to a compound, $\text{C}_{32}\text{H}_{22}\text{O}_6$, colourless, rhombic crystals, m. p. $208\text{--}209^{\circ}$ (decomp.). Its solutions in all solvents are colourless, even when warmed. In boiling ethyl benzoate a yellow colour is observed which is due to decomposition. The substance does not react with phenylhydrazine in the presence of chloroform.

H. W.

Chlorination of Benzoyl Chloride. I. EDWARD HOPE and GEORGE CLIFFORD RILEY (T., 1922, 121, 2510—2527).

Dealkylation of Mixed Secondary Bases by Phosphorus Chloride. JULIUS VON BRAUN and JOSEF WEISMANTEL (Ber., 1922, 55, [B], 3165—3170).—The relative affinity of the alkyl groups for nitrogen has been determined for the reaction:

$\text{NHR}^1\text{R}^2 \rightarrow \text{NR}^1\text{R}^2\cdot\text{COPh} \xrightarrow{+\text{PCl}_5} \text{NR}^1\text{R}^2\cdot\text{CCl}_2\text{Ph} \rightarrow \text{R}^1\text{Cl} + \text{NR}^2\cdot\text{CClPh} \rightarrow \text{R}^1\text{Cl} + \text{NH}_2\text{R}^2$. The series may be arranged in the sequence: benzyl, methyl, ethyl, propyl, *n*-butyl; so, for example, benzylmethylamine yields methylamine. It is remarkable that the order is precisely the same as in the cyanogen bromide reaction which is effected at 0° , whereas the present change is carried out at about 140° .

Benzomethylbenzylamide, m. p. 44° (cf. Lander, P., 1903, **19**, 45), is converted by phosphorus pentachloride at 110° and subsequent treatment with water into benzyl chloride and benzomethylamide, b. p. $164\text{--}165^\circ/15$ mm., m. p. 80° . Benzomethyl-ethylamide, b. p. $163\text{--}165^\circ/27$ mm. (cf. Titherley, T., 1901, **79**, 407) at 140° yields methyl chloride and benzoethylamide, m. p. 68° . *Benzoethylpropylamide*, b. p. $158\text{--}160^\circ/12$ mm., gives ethyl chloride and benzopropylamide.

When propylamine is treated with benzenesulphonyl chloride, the resulting amide is converted by *n*-butyl bromide into *benzenesulphonpropyl-n-butylamide*, $\text{SO}_2\text{Ph}\cdot\text{NPr}\cdot\text{C}_4\text{H}_9$, a colourless liquid, b. p. $202\text{--}204^\circ/12$ mm.; this is transformed in the usual manner into *propyl-n-butylamine*, b. p. $134\text{--}135^\circ$ (*hydrochloride*, m. p. 255°). *Benzopropyl-n-butylamide* is converted by phosphorus pentachloride at 150° into propyl chloride and benzo-*n*-butylamide.

H. W.

Preparation of a Basic Aluminium Salicylate. SOCIÉTÉ CHIMIQUE DES USINES DU RHÔNE (D.R.-P. 354698; from *Chem. Zentr.*, 1922, iv, 377).—A basic aluminium salicylate of the formula $\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{CO}_2\cdot\text{Al}(\text{OH})_2$ is obtained by mixing aluminium hydroxide with salicylic acid, if necessary, with the application of heat. The product is a colourless or slightly red powder. It is distinguished from the normal salt by its stability in the presence of water and dilute acids and on warming.

G. W. R.

Derivatives of Dulcin. PAUL HERMANN (*Annalen*, 1922, **429**, 163—174).—3-*Carbamido-6-methoxybenzoic acid* has m. p. $187\text{--}193^\circ$, and is soluble in 125 parts of hot [$? \text{boiling}$] water or 400 parts of water at 15° ; the solution has a sour taste. The *ethyl ester* melts at $191\text{--}192^\circ$. 3-*Thiocarbamido-6-methoxybenzoic acid*, m. p. $205\text{--}206^\circ$, is insoluble in cold water, and has a faintly sour taste. 3-*Carbamido-6-ethoxybenzoic acid* forms colourless, small needles, m. p. $195\text{--}196^\circ$, soluble in 40 parts of hot water and in 660 parts of water at 15° , and has a faintly sour taste. Its *ethyl ester*, m. p. $179\cdot5\text{--}180\cdot5^\circ$, has a bitter taste. 3-*Thiocarbamido-6-ethoxybenzoic acid* forms needles, m. p. $182\text{--}183^\circ$, and is soluble in 90 parts of boiling water; it has a feebly sour taste. 4-*Carbamido-1-ethoxynaphthalene* forms small needles which sinter at $205\text{--}207^\circ$, m. p. $264\text{--}265^\circ$ (decomp.); it has a bitter taste. 4-*Thiocarbamido-1-ethoxynaphthalene* has m. p. $210\cdot5\text{--}211\cdot5^\circ$, and has a very bitter taste in alcoholic solution. These substances are all formed by the action of potassium cyanate or ammonium thiocyanate on the appropriate amine. 3 : 3-*Carbamidebis-6-methoxy-*

benzoic acid is obtained when methoxyaminobenzoic acid is heated with carbamide. It has m. p. 243° (decomp.). C. K. I.

Anhydrides of *N*-Carboxylic Acids. FRIEDRICH FUCHS (*Ber.*, 1922, **55**, [B], 2943).—In connexion with the recent observations of Curtius and Sieber (this vol., i, 721), it is pointed out that phenylglycine anhydride, $\text{NPh} \begin{smallmatrix} \text{CH}_2 \cdot \text{CO} \\ \text{CO} - \text{O} \end{smallmatrix}$, can be obtained in good yield

by the action of carbonyl chloride on a cold, alkaline solution of phenylglycine. With aniline and alcohols, it gives the anilide and esters of phenylglycine. The *N*-carboxylic anhydride derived from *p*-tolylglycine is more stable and better adapted to further investigation than the lower homologue. H. W.

The Resin Acids of the *Coniferae*. V. The Nitrosochloride, Nitrosite, and Nitrosate of Pinabietic Acid and Abietic Acid [Levy]. Constitution of Abietic Acid and Abietine. OSSIAN ASCHAN [with NILS FONTELL and P. E. SIMOLA (*Ber.*, 1922, **55**, [B], 2944—2959; cf. this vol., i, 221, and previous abstracts).—Pinabietic acid has been isolated from pine oil and characterised as a homogeneous substance by Aschan and his co-workers (A., 1921, i, 669); its constitution has been established except for certain details by Virtanen (A., 1921, i, 669). The acid is very similar to the abietic acid of Levy (A., 1907, i, 947; 1910, i, 11) and Johansson (A., 1920, i, 232). The two acids give nitrosochlorides, nitrosites, and nitrosates which are most probably identical, and also the same colour changes in Liebermann's cholesterol reaction. It is therefore most probable that the acids are structurally identical. Certain differences are, however, apparent in their optical properties (as will be shown later) so that the possibility of stereoisomerism is not excluded. The strongest argument against the structural identity of the acids lay in the observation of Levy (*loc. cit.*) that abietic acid is converted by cold potassium permanganate into a well-defined tetrahydroxy-acid, $\text{C}_{19}\text{H}_{29}(\text{OH})_4 \cdot \text{CO}_2\text{H}$, of high melting point, whereas the similarly prepared product from pinabietic acid is a crystalline, apparently saturated, monocarboxylic acid of low melting point (the details of which will be given later). Repetition of Levy's experiments has failed to yield the tetrahydroxy-acid, which is presumed to have owed its origin to associated silvic acid. Levy's abietene and Virtanen's pinabietene must also be regarded as structurally identical 7 : 13-dimethyl-2-isopropyl-5 : 6 : 7 : 8 : 9 : 10 : 13 : 14-octahydrophenanthrene. For the parent hydrocarbon the name *phenoctalin* is proposed, on account of its similarity to tetralin [tetrahydronaphthalene].

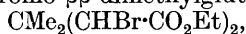
[With NILS FONTELL and P. E. SIMOLA.]—*Pinabietic acid nitrosochloride*, $\text{HO} \cdot \text{N} : \text{C}_{19}\text{H}_{28}\text{Cl} \cdot \text{CO}_2\text{H}$, is prepared by passing hydrogen chloride into a solution of pinabietic acid and ethyl or amyl nitrite in glacial acetic acid. It crystallises in lustrous, very voluminous needles, m. p. 144 — 145° . (The *sodium* salt is described.) It is converted by a boiling solution of sodium in ethyl alcohol (90%) into *oximinopinabietic acid*, $\text{HO} \cdot \text{N} : \text{C}_{19}\text{H}_{27} \cdot \text{CO}_2\text{H}$, a brownish-yellow

powder, decomp. about 130° after incipient softening at 120° . The nitrosite of pinabietic acid, $\text{OH}\cdot\text{N}\begin{smallmatrix} \nearrow \\ \searrow \end{smallmatrix} \text{C}_{19}\text{H}_{28}\cdot\text{CO}_2\text{H}$, is obtained by the gradual addition of concentrated hydrochloric acid to a solution of pinabietic acid in benzene which is floating on an aqueous solution of sodium nitrite; it is a colourless, voluminous, crystalline powder which softens at about $75\text{--}76^{\circ}$ and is generally completely molten at about $120\text{--}130^{\circ}$. Pinabietic acid nitrosate, a voluminous, yellow powder, decomp. $72\text{--}73^{\circ}$, is prepared by the gradual addition of concentrated nitric acid (*d* 1.4) to a well-cooled solution of pinabietic acid and amyl nitrite in glacial acetic acid.

The following compounds are prepared from abietic acid obtained from American colophony by Levy's method; the specimen used was not quite homogeneous, having m. p. $167\text{--}170^{\circ}$ instead of $181\text{--}183^{\circ}$. Nitrosochloride, m. p. 140° ; nitrosite, which softens and evolves gas at 76° ; nitrosate, a yellow powder which softens at 72° . The melting or decomposing points of these substances are unchanged by admixture with the respective corresponding compounds derived from pinabietic acid.

Further work (as yet unpublished) makes it probable that pinabietic and abietic acids are completely identical. H. W.

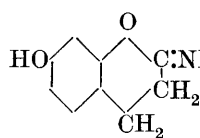
Attempted Synthesis of Norpinic Acid. KANAI LAL GANGULY (*J. Indian Inst. Sci.*, 1922, 5, 23—28).—Verification of the structure of norpinic acid by synthesis is of importance on account of its close relationship to pinene and the products derived therefrom. An attempt was made to synthesise norpinic acid by condensing ethyl $\alpha\gamma$ -dibromo- $\beta\beta$ -dimethylglutarate,



with methylene bromide or iodide by means of sodium in benzene. A very small amount of crystalline product, m. p. 172° , which might have been *cis*-norpinic acid, was obtained, but the experiment cannot be regarded as successful. E. H. R.

Condensation of certain Nitriles and Various Polyhydroxyphenols to form Phenolic Acids. WILSON D. LANGLEY and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, 44, 2320—2330).—

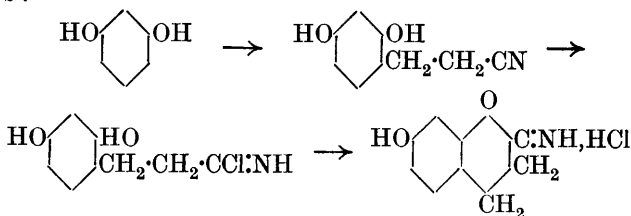
Unlike chloroacetonitrile (cf. Sonn, A., 1918, i, 31), β -chloropropionitrile does not condense normally with resorcinol. In dry ether in the presence of anhydrous zinc chloride and hydrogen chloride, β -chloropropionitrile and resorcinol give first a white solid, which probably has the annexed constitution. This reacts with



water, giving β -2:4-dihydroxyphenylpropionolactone, m. p. $132\text{--}133^{\circ}$, which on further heating with water was converted into the acid, m. p. 165° (Hlasiwetz, *Annalen*, 1866, 139, 102, gives m. p. 110° , decomp.). If the acid is boiled with excess of

acetic anhydride, β -2-hydroxy-4-acetoxyphenylpropionolactone, m. p. 112° , is obtained. Acrylonitrile may be used instead of β -chloropropionitrile in the above condensation. β -2:4-Dimethoxyphenylpropionic acid, m. p. $102.5\text{--}103.5^{\circ}$, was obtained by the direct methyl-

ation of the dihydroxy-acid, and by the action of butyl nitrite the dihydroxy-acid gave β -5-nitroso-2:4-dihydroxyphenylpropionolactone, m. p. 147.5—148°. Resorcinol monomethyl ether and β -chloropropionitrile gave β -2-hydroxy-4-methoxyphenylpropionic acid, m. p. 138—139.5°, together with the lactone, and the nitrile, m. p. 126.5—127.5°, as intermediate products. The suggested mechanism of the condensation of resorcinol and of β -chloropropionitrile is as follows:



Under similar conditions, orcinol gives with β -chloropropionitrile or acrylonitrile β -3:5-dihydroxy-o-tolylpropionolactone, m. p. 140—141.5°. Similarly, phloroglucinol gives β -2:4:6-trihydroxyphenylpropionolactone, a viscous oil.

Resorcinol and γ -chlorobutyronitrile react in dry ether in the presence of zinc chloride and hydrogen chloride to give γ -2:4-dihydroxyphenylbutyric acid, m. p. 118.5—119°, and in this case the lactone could not be obtained.

W. G.

Preparation of Sodium and Potassium Phthalimide.

DALZIEL LLEWELLYN HAMMICK and GEORGE HAZLEWOOD LOCKET (T., 1922, 121, 2362—2363).

Derivatives of Amino-aldehydes. ERICH RADDE (*Ber.*, 1922, 55, [B], 3174—3179).—A number of attempts are recorded to prepare amino-aldehydes of the aliphatic series by the reduction of amino-acids in which the basic group is protected by the presence of the phthalyl radicle; complete success, however, has not been attained.

Phthalimino- α -hydroxy-propionic and -butyric acids lose carbon dioxide when heated with sulphuric acid, but an aldehydo-compound cannot be isolated from the resinous substances which are produced (Gabriel, A., 1907, i, 625; Gabriel and Colman, A., 1908, i, 274); the use of phosphoric acid, thionyl chloride, or hydrochloric acid in place of sulphuric acid does not lead to improved results.

Phthalylglycylanilide, $\text{C}_8\text{H}_4\text{O}_2\text{:N}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NHPh}$, aggregates of needles, m. p. 227°, is converted by phosphorus pentachloride in the presence of benzene into the corresponding chloro-compound, $\text{C}_8\text{H}_4\text{O}_2\text{:N}\cdot\text{CH}_2\cdot\text{CCl:NPh}$, needles, m. p. about 90°; reduction of the imino-chloride with stannous chloride according to the method of Sonn and Müller (A., 1920, i, 58) does not give an aldehydo-compound.

The action of hydrocyanic acid and pyridine on a solution of phthalylglycyl chloride in anhydrous ether gives the compound,

$C_8H_4O_2:N \cdot CH(CO \cdot CN) \cdot CO \cdot CH_2 \cdot N:C_8H_4O_2$, needles, m. p. 203·5—205·5° (decomp.), instead of the expected phthalylglycyl cyanide.

Attempts to convert phthalylglycylanilide chloride into the corresponding amidine or to reduce phthalylglycyl esters to aldehydes by sodium amalgam in acid solution were unsuccessful.

Phthalylglycylamide, $C_8H_4O_2:N \cdot CH_2 \cdot CO \cdot NH_2$, needles, m. p. 257°, is converted by thionyl chloride or, preferably, by distillation with phosphoric oxide into *phthalylglycylonitrile*, $C_8H_4O_2:N \cdot CH_2 \cdot CN$, four-sided plates, m. p. 124—126°, which can also be prepared from chloroacetonitrile and potassium phthalimide at 120°. The nitrile could not be converted into the corresponding imino-ether, from which it might have been reduced to the aldehyde according to the method of Heale (A., 1905, i, 490).

A solution of phthalylglycyl chloride in toluene is reduced by hydrogen in the presence of palladised barium sulphate and "sulphured" quinoline in accordance with the procedure of Rosenmund and Zetzsche to *phthalimidoacetaldehyde*, $C_8H_4O_2:N \cdot CH_2 \cdot CHO$, needles, m. p. 113—114·5° (*phenylhydrazone*, yellow needles, m. p. 163—165°; *oxime*, clusters of needles, m. p. 166—168°; *semicarbazone*, needles, m. p. 233—244°). The hydrolysis of phthalimidoacetaldehyde is invariably accompanied by the liberation of ammonia. α -Phthalimidopropionyl chloride is similarly reduced to α -*phthalimidopropaldehyde*, $C_8H_4O_2:N \cdot CHMe \cdot CHO$, needles, m. p. 108·5—111° (*semicarbazone*, needles, m. p. 225·5—226·5°), which also yields ammonia when hydrolysed by hydrochloric acid. Similar unsuccessful results are obtained with compounds containing the phthalimido-residue in the β -, γ -, or δ -position. The following observations are incidentally recorded. Ethyl β -phthalimidoethylmalonate, $C_8H_4O_2:N \cdot CH_2 \cdot CH_2 \cdot CH(CO_2Et)_2$, is transformed by hydrobromic acid (*d* 1·49) into β -*phthalimidoethylmalonic acid*, needles, m. p. 168° (decomp.) (the *ammonium* salt and the *methyl* ester, m. p. 64—65°, are described); the decomposition of the acid by heat gives a convenient method for the preparation of γ -phthalimido-*n*-butyric acid. δ -Phthalimido-*n*-valeric acid is similarly prepared from γ -phthalimido-*n*-propylmalonic esters; γ -*phthalimido-*n*-propylmalonic acid*, $C_8H_4O_2:N \cdot [CH_2]_3 \cdot CH(CO_2H)_2$, has m. p. 165° (decomp.).

Phthalylglycylonitrile is converted by a boiling solution of sodium methoxide and subsequent treatment with ammonium chloride into the *ammonium* salt, $NH_4 \cdot CO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot CH_2 \cdot CN$, prisms, m. p. about 240° (decomp.) [the corresponding *silver* salt, needles, and free *acid*, needles, m. p. 138—139° (decomp.) are described]; sodium ethoxide behaves similarly, but yields a less pure product. The action of the alkali consists essentially in the opening of the ring and does not lead to the production of an *iso*-quinoline derivative, as would be expected from the observations of Gabriel and Colman (*loc. cit.*) on the behaviour of phthalylglycyl esters under similar conditions. *Phthalyl- α -alanylamine*, $C_8H_4O_2:N \cdot CHMe \cdot CO \cdot NH_2$, m. p. 211—212° (prepared from the corresponding chloride and gaseous ammonia in the presence of benzene), is converted by distillation with phosphoric oxide into

the *nitrile*, $C_8H_4O_2 \cdot N \cdot CHMe \cdot CN$, four-sided plates, m. p. 139—140°. The latter is transformed by sodium ethoxide into the sparingly soluble *ammonium* salt, $NH_4 \cdot CO_2 \cdot C_6H_4 \cdot CO \cdot NH \cdot CHMe \cdot CN$, which is reconverted into the original material when treated with hydrochloric acid.

H. W.

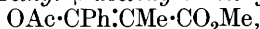
Dyes Derived from "Saccharin." The Sulphamphthaleins. SIKHIBHUSHAN DUTT (T., 1922, 121, 2389—2394).

The Relationship between the Dimeric Ketens and cyclo-Butane-1 : 3-dione and its Derivatives. W. DIECKMANN and ADOLF WITTMANN (*Ber.*, 1922, 55, [B], 3331—3347).—The dimeric alkylketencarboxylic esters and a series of other dimeric ketens have been regarded by Schroeter (A., 1917, i, 145; 1920, i, 852) as "polymolecules" in which the monomeric components are not united by main or subsidiary atomic valencies, but by molecular valencies. This conception has been criticised adversely by Staudinger (A., 1920, i, 517). An extended examination of the question leads the author to the conclusion that Schroeter's views are untenable.

Schroeter's conclusions are based on the established difference in properties between the products obtained by the action of chloroformic esters on dialkylcyclobutanedionemonocarboxylic esters and those derived by the polymerisation of monomeric alkylketencarboxylic esters. He regards the conception of the former as O-derivatives, $CMe \begin{smallmatrix} \text{C}(\text{O} \cdot \text{CO}_2\text{R}) \\ \text{CO} \end{smallmatrix} > CMe \cdot \text{CO}_2\text{R}$, as erroneous. A consideration of analogous cases leads the author to consider it as probable, but conclusive evidence in favour of this view is afforded by the observation that *methyl 2-ethylcarbonato-1 : 3-dimethylcyclobutene-4-one-3-carboxylate*, $CMe \begin{smallmatrix} \text{C}(\text{O} \cdot \text{CO}_2\text{Et}) \\ \text{CO} \end{smallmatrix} > CMe \cdot \text{CO}_2\text{Me}$, colourless crystals, m. p. 66—68°, b. p. 173—175°/11 mm. (obtained from ethyl chloroformate and methyl dimethylcyclobutanedionecarboxylate) differs from *ethyl 2-methylcarbonato-1 : 3-dimethylcyclobutene-4-one-3-carboxylate*, $CMe \begin{smallmatrix} \text{C}(\text{O} \cdot \text{CO}_2\text{Me}) \\ \text{CO} \end{smallmatrix} > CMe \cdot \text{CO}_2\text{Et}$, a colourless liquid, b. p. 173—175°/11 mm., which does not solidify (prepared from methyl chloroformate and ethyl dimethylcyclobutanedionecarboxylate), whereas if, according to Schroeter, the new group had become attached to a carbon atom, the compounds must be identical, thus $\text{CO}_2\text{Me} \cdot CMe \begin{smallmatrix} \text{CO} \\ \text{CO} \end{smallmatrix} > CMe \cdot \text{CO}_2\text{Et}$. The esters when treated with sodium alkoxide re-form methyl and ethyl 2 : 4-dimethylcyclobutanedionecarboxylates, respectively. The difference of these esters from the dimeric alkylketencarboxylic esters cannot be regarded as an argument against the conception of the latter as unitary dialkylcyclobutanedionecarboxylic esters. A further argument in favour of the "polymolecular" structure of the dimeric alkylketencarboxylic esters has been based by Schroeter (*loc. cit.*) on their catalytic decomposition in alcoholic solution by a trace of sodium alkoxide whereby two molecules of

alkylmalonic esters are produced. The same property is, however, observed in the acyclic analogues of the dialkylcyclobutanedione-carboxylic esters, for example, acetylalkylmalonic ester and α -diaryl- α -methylacetic esters, which are beyond doubt unitary compounds containing the group $\begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} > \text{CR} \cdot \text{CO}_2\text{R}$. All these compounds

resemble the dimeric alkylketencarboxylic esters in that they are stable towards boiling alcohol but are catalytically decomposed with evolution of heat when a trace of sodium alkoxide is added to the alcoholic solution. Contrary to Schroeter's assumption, fusion invariably occurs in such a manner that an acyl and not an alkylcarbonato-group is eliminated. The following examples are quoted: *Methyl α -benzoyl- α -methylacetoacetate*, $\text{CH}_3 \cdot \text{CO} \cdot \text{CMeBz} \cdot \text{CO}_2\text{Me}$, colourless crystals, m. p. 79–80°, b. p. 173–174°/10 mm., prepared by the action of a solution of benzoyl chloride in ether on an ethereal suspension of methyl methylsodioacetoacetate, is transformed by methyl alcohol and sodium methoxide into methyl acetate and methyl α -benzoylpropionate, b. p. 141–142°/10 mm. *Methyl β -acetoxy- α -methylcinnamate*,



b. p. 161°/10 mm., prepared by the action of acetyl chloride on methyl α -methylsodiobenzoylacetate in the presence of ether, is converted in a similar manner into methyl α -methylbenzoylacetate, b. p. 143–144°/10 mm. Methyl acetylmethylacetoacetate $(\text{CH}_3 \cdot \text{CO})_2\text{CMe} \cdot \text{CO}_2\text{Me}$ or $\text{CH}_3 \cdot \text{C}(\text{OAc}) \cdot \text{CMe} \cdot \text{CO}_2\text{Me}$, b. p. 108°/13 mm., gives methyl methylacetoacetate. Ethyl acetylethylmalonate, $\text{CH}_3 \cdot \text{CO} \cdot \text{CEt}(\text{CO}_2\text{Et})_2$, yields ethyl ethylmalonate, whilst methyl acetylmethylmalonate is converted into methyl methylmalonate.

Methyl dimethylacetoacetate is converted by contact with a solution of an approximately equivalent quantity of sodium ethoxide in ethyl alcohol during about an hour at the atmospheric temperature into ethyl dimethylacetoacetate; after a few days it is transformed into ethyl isobutyrate. Ethyl diethylacetoacetate is unchanged by the short action of sodium methoxide in methyl alcohol, but after five days it is transformed into methyl diethylacetoacetate; fission does not appear to occur. The esters of benzoic, succinic, and phthalic acid suffer transformation in the course of a few hours.

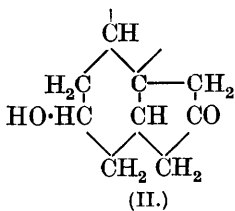
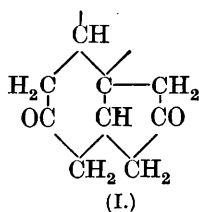
The behaviour of the dimeric alkylketencarboxylic esters towards aniline has not yet been fully explained, and appears to require further examination.

Against the conception of the dimeric ketens as ketonic forms, $\text{R} \cdot \text{HC} < \begin{smallmatrix} \text{CO} \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} > \text{CHR}$, and the acidic isomerides as enolic varieties, $\text{R} \cdot \text{HC} < \begin{smallmatrix} \text{C}(\text{OH}) \\ \diagup \diagdown \\ \text{CO} \end{smallmatrix} > \text{C} \cdot \text{R}$, of the dialkylcyclobutanediones, it has been urged by Schroeter that the latter are indifferent towards the alkali metals in inactive solvents. This argument does not appear to be valid, since, on the one hand, compounds poor in or free from the enolic forms such as alkyl- β -ketocarboxylic esters and malonic or alkylmalonic esters react relatively readily with sodium,

whereas undoubted enols, for example, phenylhydroresorcinol and succinylosuccinic esters, can exhibit the same inactivity towards the metal as is observed by Schroeter in the case of the acidic forms of the dialkylcyclobutanediones. As further evidence in favour of the enolic form, it is shown that the acid dimethylcyclobutanedionecarboxylic ester and the acid diphenylcyclobutanedione behave as mono-enols when titrated with bromine in alcoholic solution, and are stable as such when dissolved in alcohol. The behaviour of dimeric phenylketen is in harmony with the conception that it is the ketonic form of diphenylcyclobutanedione. Its slow conversion into the acid form in indifferent solvents in the absence of catalysts and rapid transformation in the presence of alkali are precisely similar to the phenomena frequently observed in cases of keto-enolic desmotropy. Its conversion by ammonia into diphenylacetoacetamide and the acidic diphenylcyclobutanedione is readily explained by the assumption of simultaneous enolisation and ring fission.

H. W.

The Constitution of the Bile Acids. IV. Reductodehydrocholic Acid. W. BORSCHÉ and F. HALLWASS (*Ber.*, 1922, 55, [B], 3318—3323).—Reductodehydrocholic acid, $C_{24}H_{36}O_5$, a hydroxy-diketonic acid of the cholic acid series, has been obtained previously by the action of sodium amalgam on dehydrocholic acid or by electrolytic reduction of the latter at a lead cathode. It is now prepared by the catalytic hydrogenation of dehydrocholic acid dissolved in glacial acetic acid in the presence of palladium black; it crystallises in colourless, slender needles which soften at 112° owing to loss of water of crystallisation (the *monohydrate* is described) and have m. p. 186 — 187° . Reductodehydrocholic acid dioxime (cf. Schenck, A., 1910, i, 10) has m. p. 255° (decomp.). Ethyl dehydrocholate is converted by aluminium amalgam in the presence of ether and benzene into *ethyl reductodehydrocholate*, coarse, colourless prisms, m. p. 153 — 154° (*dioxime*, colourless leaflets, m. p. 239 — 240°). *Methyl reductodehydrocholate*, prepared by esterification of the acid, crystallises in coarse needles, m. p. 155 — 156° , whereas its *dioxime* forms colourless leaflets, m. p. 258° (slight decomp.). Ethyl reductodehydrocholate is converted by distillation under diminished pressure into *ethyl diketocholenate*, long, colourless needles, m. p. 143° (*dioxime*, unctuous leaflets, m. p. 228° ; *diketocholenic acid*, colourless prisms, m. p. 174°), which



is smoothly hydrogenated in alcoholic solution in the presence of spongy palladium to ethyl β -diketocholenate, m. p. 152 — 153° , identical with the compound described by Borsche and Wieckhorst (A., 1921, i, 729). Dehydrocholic acid

(I) and reductodehydrocholic acid (II) are therefore related to one another as indicated by the annexed formulæ.

Reduction of the ketonic group in ethyl α - or β -diketocholanates cannot be effected by means of aluminium amalgam. This is more surprising in the case of the α -compound, since α -diketocholanic acid is readily reduced by sodium amalgam and water to a hydroxyketocholanic acid, $C_{24}H_{38}O_3$ (monohydrate and anhydrous), colourless needles, m. p. about 160° after much softening at about 107° , which is probably identical with the acid described by Wieland and Boersch (A., 1919, i, 572). The corresponding ethyl ester has m. p. 131 — 132° (Wieland and Boersch, m. p. 133°).

Bilianic acid is not affected by treatment with sodium amalgam in aqueous alkaline solution; its trimethyl ester is only slowly and incompletely attacked by aluminium amalgam in the presence of moist ether. H. W.

The Constitution of the Bile Acids. V. Transformations from the Cholic to the Lithocholic Acid Series. W. BORSCHÉ and F. HALLWASS (*Ber.*, 1922, 55, [B], 3324—3331).—Lithocholic acid, $C_{24}H_{40}O_3$, has been proved by Wieland and Weyland (A., 1921, i, 178) to be a normal constituent of bile. It is a monohydroxycholenic acid which is oxidised by nitric acid to lithobilianic acid, corresponding with bilianic acid; it is therefore probable that the hydroxy-group is attached to the same carbon atom as in cholic acid. This supposition has now been confirmed by the transformation of cholic acid through reductodehydrocholic acid into lithocholic acid.

Reductodehydrocholic acid (Borsche and Hallwass, preceding abstract) is reduced by amalgamated zinc and hydrochloric acid to resinous products and cholanic acid. The formation of the latter substance is somewhat surprising, since it appears impossible to reduce cholic directly to cholanic acid by this method. More satisfactory results are obtained by Wolff's method, according to which *reductodehydrocholic acid disemicarbazone*, $C_{26}H_{72}O_5N_6$, a white, chalky powder which becomes brown but does not melt at about 300° , is heated with an alcoholic solution of sodium ethoxide at 180° (the exact maintenance of the temperature is important), whereby it becomes transformed into lithocholic acid, colourless leaflets, m. p. 185 — 186° , $[\alpha]_D^{20} +32.72^\circ$, in absolute alcohol. Direct comparison shows that the acid is identical with the product obtained by Wieland and Weyland, the only point of difference being that its optical activity is greater. The acid is converted by an ethereal solution of diazomethane into *methyl lithocholate*, long needles, m. p. 130° , and by oxidation with nitric acid into lithobilianic acid (cf. Wieland and Weyland, *loc. cit.*). It has also been transformed into dehydrolithocholic acid, $C_{24}H_{38}O_3$, leaflets, m. p. 141° (cf. Wieland and Weyland, *loc. cit.*), the *methyl ester* of which, colourless leaflets, m. p. 117° , and *methyl ester oxime*, long needles, m. p. 148° , are described.

Dehydrocholic acid trisemicarbazone, an amorphous powder which becomes brown at about 290° and decomposes completely at a slightly higher temperature, is converted by a solution of sodium ethoxide in alcohol at 200° into cholanic acid. *Bilianic acid di-*

semicarbazone, broad, colourless needles which become brown above 280° , is transformed in a similar manner into lithobilianic acid, m. p. 279° (cf. Wieland and Weyland, *loc. cit.*); the latter acid is obtained rather more readily under precisely similar conditions from *deoxybilianic acid semicarbazone*, $C_{25}H_{39}O_7N_3$, a colourless, amorphous solid, decomp. $215-220^{\circ}$. *Methyl lithobilianate*, $C_{27}H_{44}O_6$, crystallises in long, colourless needles, m. p. 112° .

isoLithobilianic acid, small, colourless needles, m. p. 261° (decomp.), is obtained by the reduction of *isobilianic acid* dissolved in glacial acetic acid with amalgamated zinc and fuming hydrochloric acid (*methyl isolithobilianate* crystallises in colourless, lustrous leaflets, m. p. $103-104^{\circ}$). For some unexplained reason, and in spite of the apparent identity of the conditions, the action does not always take place smoothly, and the product frequently contains much *isodeoxybilianic acid* and other intermediate compounds. A more certain method for the preparation of *isolithobilianic acid* consists in the treatment of *isobilianic acid disemicarbazone* (an amorphous substance which darkens at about 280° and decomposes gradually at a higher temperature) with sodium ethoxide.

H. W.

Preparation of an Unsaturated Bile Acid. J. D. RIEDEL, AKT.-GES. (D.R.-P. 352129; from *Chem. Zentr.*, 1922, iv, 161).—Bromine is added to the acid prepared by an earlier patent (A., 1921, i, 540) and the product treated with alkalis. The *dibromide* obtained by the action of bromine on the acetic acid compound of *apocholic acid*, $C_{24}H_{38}O_4 \cdot C_2H_4O_2$, is a light yellow, heavy oil. By saponification with dilute alkali and addition of excess of dilute hydrochloric acid, an *unsaturated bile acid*, needles, m. p. $245-247^{\circ}$, is obtained. It is strongly antiseptic and has therapeutic uses.

G. W. R.

Derivatives of Diphenylthiolbenzene. SAMUEL SMILES and HUGH GRAHAM (T., 1922, 121, 2506—2510).

The Solubility and Volatility of the Nitrobenzaldehydes. NEVIL VINCENT SIDGWICK and WILFRED MARSDEN DASH (T., 1922, 121, 2586—2592).

***ar*-Aldehydes of Tetrahydronaphthalene.** KARL FLEISCHER and GREGOR FELDMEIER (*Ber.*, 1922, 55, [B], 3290—3293).—A solution of 1-methyl-5:6:7:8-tetrahydronaphthalene in carbon disulphide is converted by chromyl chloride dissolved in the same solvent at 0° into a chocolate-brown additive compound which is decomposed by ice-cold water with the production of small quantities of 5:6:7:8-tetrahydronaphthalene-1-aldehyde, a colourless liquid, b. p. $130-140^{\circ}$ (mainly 135°)/18 mm., which gives a colourless, crystalline product with sodium hydrogen sulphite. Similarly, 2-methyl-5:6:7:8-tetrahydronaphthalene gives 5:6:7:8-tetrahydronaphthalene-2-aldehyde, a colourless, mobile liquid, b. p. $150-155^{\circ}$ /14 mm. The compound with sodium hydrogen sulphite and the *semicarbazone*, colourless needles, m. p. $221-223^{\circ}$, are described. Attempts to isolate an oxime or thiosemicarbazone or

to condense the aldehyde with aniline, *p*-nitroaniline, or phenylacetonitrile were unsuccessful. H. W.

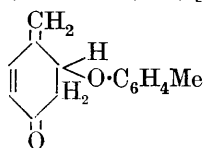
Preparation of *cyclo*Butanone by the Pyro-chemical Decomposition of 1-Hydroxycyclobutane-1-carboxylic Acid. N. J. DEMJANOV and MARIE DOJARENKO (*Ber.*, 1922, 55, [B], 2737—2742).—*cyclo*Butanone has previously been a very difficultly accessible substance, and only the semicarbazone among its derivatives has been examined. Its preparation by the pyrogenic decomposition of 1-hydroxycyclobutane-1-carboxylic acid is now recorded, the yield, according to preliminary experiments, being about 15% of that theoretically possible.

1-Bromocyclobutane-1-carboxylic acid is converted into a mixture of 1-hydroxycyclobutane-1-carboxylic acid and its anhydrides by treatment with the calculated quantity of potassium carbonate in boiling, concentrated aqueous solution (cf. Perkin, T., 1892, 61, 42); the yield is 94%. Decomposition of the mixture occurs mainly at 280—300°, with the production of a mixture of carbon monoxide and carbon dioxide, and an acidic distillate containing *cyclo*butanone. The latter is purified through its semicarbazone, m. p. 212° (decomp.), or *bisulphite* compound. It condenses with benzaldehyde in aqueous-alcoholic solution in the presence of potassium hydroxide to form *dibenzylidenecyclobutanone*, $C_{18}H_{14}O$, leaflets, m. p. 170—171°.

The *anhydrides* formed during the preparation of 1-hydroxycyclobutane-1-carboxylic acid or remaining in the residue when it is distilled under reduced pressure have been further examined. One of these is crystalline and freely soluble in organic media; it has m. p. 65°. Its molecular weight in boiling ether is in agreement with the formula $C_{10}H_{12}O_4$, whereas in freezing benzene it appears to have the composition $(C_{10}H_{12}O_4)_2$. Other anhydrides do not crystallise and are insoluble in all the usual media. They decompose when heated into carbon monoxide and *cyclo*butanone. They are remarkably stable towards water, by which, however, they are decomposed at 150—160°. Analyses are in agreement with the formula $C_{20}H_{26}O_9$ ($= 4C_5H_8O_3 - 3H_2O$); the molecular complexity is probably much greater, but it could not be determined on account of the insolubility of the substances. H. W.

Action of the Chlorides of Phosphorus on Chlorodimethyldihydroresorcinol. LEONARD ERIC HINKEL and WILLIAM DUDLEY WILLIAMS (T., 1922, 121, 2498—2502).

Oxidation of Phenols. VII. Dehydrogenation of *p*-Cresol. RUDOLF PUMMERER, DONA MELAMED, and HANS PUTTFARCKEN (*Ber.*, 1922, 55, [B], 3116—3132; cf. A., 1914, i, 714; 1915, i, 417; 1919, i, 439, 440, 442).—The oxidation of *p*-cresol

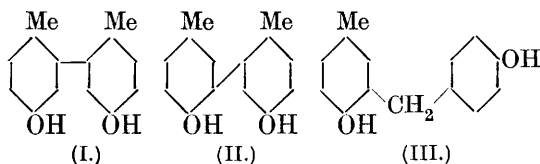


(annexed formula).

does not appear to take place in the same manner as that of α -methyl- β -naphthol. The main product is an unsaturated monoketone, the properties of which are in accord with the conception that it is 2-*p*-tolyl-oxy-2:3-dihydro-*p*-benzoquinomethane

A solution of *p*-cresol in aqueous sodium carbonate is gradually treated with a saturated solution of potassium ferrieyanide at 0° ; the product which separates is filtered and purified by fractional distillation under diminished pressure, whereby there are obtained unchanged *p*-cresol, 2-*p*-tolylloxy-2 : 3-dihydro-*p*-benzoquinomethane, 3 : 3'-di-*p*-cresol, colourless needles, m. p. 154° , and a dihydroxyphenol, $C_{14}H_{14}O_2$, m. p. 194° , which is identical with the product isolated by Fichter and Ackermann (A., 1919, i, 586) by the anodic oxidation of *p*-cresol (the latter authors erroneously attributed to it the formula $C_{14}H_{14}O_3$); the substance crystallises with one molecular proportion of ethyl or methyl alcohol, which is removed with considerable difficulty. The corresponding diacetate has m. p. 108° (Fichter gives 111°). 2-*p*-Tolylloxy-2 : 3-dihydro-*p*-benzoquinomethane (see above) crystallises in colourless leaflets, m. p. 124.5° . Its molecular weight in freezing benzene is in harmony with the formula $C_{14}H_{14}O_2$. It is insoluble in cold sodium hydroxide solution, but is somewhat dissolved by the warm solution. Concentrated alcoholic potassium hydroxide solution dissolves it completely, but it separates unchanged after addition of water. It is slowly converted by sodium wire in the presence of anhydrous ether into a yellow sodium salt which is transformed by benzoyl chloride into the *monobenzoyl* derivative, $C_{21}H_{18}O_3$, colourless crystals, m. p. $153-154^{\circ}$. Its reluctance to pass into an enolic form is evidenced by its inability to react with boiling benzoyl chloride, acetyl chloride and pyridine, or phenylcarbimide. The presence of enol in its alcoholic solution cannot be detected by titration with bromine. It couples with *p*-nitrobenzenediazonium hydroxide in alcoholic solution, and slowly dissolves in boiling sodium hydrogen sulphite solution, with the production of a sulphonic acid in place of a normal bisulphite compound. It is coloured bright red by perchloric acid. It yields an *oxime*, $C_{14}H_{15}O_2N$, colourless plates, m. p. $203-204^{\circ}$, a *phenylhydrazone*, $C_{20}H_{20}ON_2$, long, colourless needles, m. p. $181-182^{\circ}$ after becoming brown at 170° (in an atmosphere of carbon dioxide) and a *semicarbazone*, $C_{15}H_{17}O_2N_3$, colourless leaflets, m. p. $249-250^{\circ}$ (decomp.).

The ketone is transformed by the protracted action of cold, strong mineral acids into a *dihydroxyphenol*, $C_{14}H_{14}O_2$, needles, m. p. 158° , which is characterised by conversion into the corresponding *dimethyl ether*, $C_{14}H_{12}(OMe)_2$, coarse, glassy prisms, m. p. 86° . Three of the six possible dihydroxyphenols, $C_{14}H_{14}O_2$, are known; the substance under investigation is not identical with any of these,



so that the choice of its constitution lies between the three remaining (annexed) formulæ.

If the ketone has the constitution assigned to it, it might be expected to be readily transformable into 2-*p*'-tolylloxy-*p*-cresol

(annexed formula). This change has not yet been accomplished. 2-*p*'-Tolyloxy-*p*-cresol, m. p. 33—34°, has, however, been prepared synthetically by heating sodium *p*-tolyloxide with copper powder and 2-bromo-*p*-cresol (m. p. 54—55°, prepared from 2-amino-*p*-cresol). It gives a *phenylurethane*, $C_{21}H_{19}O_3N$, slender needles, m. p. 137—137·5°. The isomeric, 3-*p*'-tolyloxy-*p*-cresol, coarse, colourless needles resembling asbestos, m. p. 35—37°, is prepared from sodium *p*-tolyloxide, 3-chloro-*p*-cresol, and copper powder at 170—190°; it is converted by *m*-nitrobenzoyl chloride in the presence of pyridine at 70° into the corresponding *m*-nitrobenzoate, rhombic, bipyramidal, pseudotetragonal crystals, $a : b : c = 0·97 : 1 : 0·46$, m. p. 80°. Potassium *p*-tolyloxide is transformed by *p*-nitrobenzyl chloride in the presence of boiling alcohol into *p*-tolyl *p*'-nitrobenzyl ether, $C_6H_4Me·O·CH_2·C_6H_4·NO_2$, long, pale yellow needles, m. p. 86—87°, which is reduced by a solution of stannous chloride and hydrogen chloride in glacial acetic acid at 0° to *p*-tolyl *p*'-aminobenzyl ether, m. p. 110° (the pale yellow *hydrochloride* is described). Attempts to convert the free base through its diazonium compound into *p*-tolyl *p*'-hydroxybenzyl ether were unsuccessful, but it is placed beyond doubt that the substance, m. p. 124° (see above), is not formed in this manner. H. W.

Synthesis of Fisetole. ADOLF SONN and SUSANNE FALKENHEIM (*Ber.*, 1922, **55**, [B], 2975—2985).—A number of unsuccessful attempts to synthesise fisetole [ω -hydroxyresacetophenone] are described. The substance is finally obtained by the condensation of resorcinol with carbethoxy- or methylcarbonato-acetonitrile; fission of the ketimide hydrochloride thus produced and elimination of the carbalkoxy-group.

2-Acetoxy 5-methoxycoumaranone, $OMe·C_6H_3<\overset{O}{\underset{C(OAc)}{\parallel}}>CH$, pearly leaflets, m. p. 62°, is prepared by the action of acetic anhydride and anhydrous sodium acetate on methoxycoumaranone.

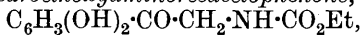
2 : 4-Dimethoxyphenyl bromomethyl ketone, $C_6H_3(OMe)_2·CO·CH_2Br$, colourless crystals, m. p. 101—102°, after previous softening, is obtained by the action of hydrogen bromide on a solution of bromoacetonitrile and resorcinyldimethyl ether in anhydrous ether in the presence of zinc chloride and decomposition of the primary product with boiling water.

2 : 4-Dihydroxyphenyl bromomethyl ketone, slender, colourless needles, m. p. 127° after previous softening, is prepared in a similar manner; it is converted by acetic anhydride in the presence of a little concentrated sulphuric acid into the corresponding diacetate, quadratic prisms, m. p. 76°, whereas acetic anhydride and sodium acetate transform it mainly into the diacetate of 5-hydroxycoumaranone, m. p. 157°, and a substance, m. p. 118° (m. p. of corresponding de-acetylated product, 257°) which has not been investigated closely, but appears to be derived by the condensation of two molecules of ω -bromoresacetophenone.

2 : 4-Dihydroxyphenyl iodomethyl ketone, $C_6H_3(OH)_2·CO·CH_2I$, long

flattened prisms, m. p. 141° , after previous softening to a red liquid, is prepared by the action of sodium iodide on the corresponding ω -chloro-compound dissolved in anhydrous acetone; the *diacetate* crystallises in coarse, flattened prisms, m. p. 97° . 4-Hydroxy-2-methoxyphenyl iodomethyl ketone, obtained in a similar manner to the preceding compound, forms needles, m. p. 128° , after previous softening.

Phthalimidoacetonitrile, $C_6H_4:(CO)_2 \cdot N \cdot CH_2 \cdot CN$, almost colourless, thin leaflets, m. p. $124-125^{\circ}$ after previous softening (prepared from chloroacetonitrile and potassium phthalimide at 140°), could not be caused to condense with resorcinol in the desired manner. ω -Benzoylaminoresacetophenone, $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot NHBz$, oblique prisms, m. p. 255° (decomp.) after darkening and softening at 252° (prepared smoothly by the Hoesch reaction from resorcinol and hippuryl cyanide), did not prove a convenient source of ω -aminoresacetophenone, since elimination of the benzoyl group could not be effected readily). The latter substance [as hydrochloride, decomp. 257° (cf. Tutin, T., 1910, **97**, 2512)] is, however, smoothly prepared by condensing resorcinol with carbethoxyaminoacetonitrile to form ω -carbethoxyaminoresacetophenone,



needles, m. p. $156-157^{\circ}$ after previous darkening and heating the carbethoxy-compound with hydrochloric acid (1 : 1).

Ethylcarbonatoacetonitrile, $CN \cdot CH_2 \cdot O \cdot CO_2Et$, a colourless, mobile liquid, b. p. $127^{\circ}/50$ mm., is obtained by the interaction of glycolonitrile and ethyl chloroformate in the presence of benzene and dimethylaniline; *methylcarbonatoacetonitrile* has b. p. $116-118^{\circ}/46$ mm. The ethyl ester condenses with resorcinol in ethereal solution in the presence of hydrogen chloride and zinc chloride to yield a *ketimide hydrochloride* which is decomposed by boiling water into ω -ethylcarbonatoresacetophenone, $C_6H_3(OH)_2 \cdot CO \cdot CH_2 \cdot O \cdot CO_2Et$, colourless, rectangular plates, m. p. $104-105^{\circ}$, to a turbid liquid which becomes clear at 107° ; the corresponding *methyl* compound crystallises in long, colourless needles, m. p. $157-158^{\circ}$. The esters are hydrolysed by 2*N*-sodium hydroxide solution at the atmospheric temperature to fisetole, m. p. 189° after previous softening and discoloration [*phenylhydrazone*, slender, pale yellow needles, m. p. 109° (decomp.)].

Ethylcarbonatoacetonitrile and resorcinyldimethyl ether give the compound, $C_6H_3(OMe)_2 \cdot CO \cdot CH_2 \cdot O \cdot CO_2Et$, colourless, rectangular plates, m. p. $74-75^{\circ}$, from which 2 : 4-dimethoxyphenyl hydroxymethyl ketone is obtained.

H. W.

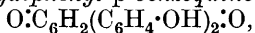
2 : 4-Dinitrobenzil. GERALD BISHOP and OSCAR LISLE BRADY (T., 1922, **121**, 2364-2370).

The Addition of Benzene to *p*-Benzoquinone. RUDOLF PUMMERER and ERNST PRELL (*Ber.*, 1922, **55**, [B], 3105-3116).—The addition of benzene to *p*-benzoquinone takes place at the atmospheric temperature with the production of 2 : 5-diphenyl-*p*-benzoquinone, yellow leaflets, m. p. 214° . The solution at first becomes intensely blue, owing to the formation of an additive compound of diphenylquinone and aluminium chloride, and then

brownish-black as the quinone is gradually reduced by the hydrogenating action of the benzene and aluminium chloride. Reaction appears to occur in accordance with the scheme : $\text{O}:\text{C}_6\text{H}_4:\text{O} \xrightarrow{+\text{C}_6\text{H}_6} \text{C}_6\text{H}_3\text{Ph}(\text{OH})_2 \xrightarrow{-2\text{H}} \text{O}:\text{C}_6\text{H}_3\text{Ph}:\text{O} \xrightarrow{+\text{C}_6\text{H}_6} \text{C}_6\text{H}_2\text{Ph}_2(\text{OH})_2 \xrightarrow{-2\text{H}} \text{O}:\text{C}_6\text{H}_2\text{Ph}_2:\text{O}$. Under similar conditions, *p*-benzoquinone tetrachloride reacts very slowly; it is therefore considered that the primary product of the change is a mixed additive compound of aluminium chloride, *p*-benzobenzene, and quinone.

The derivatives of benzene react more readily and give better yields than the parent hydrocarbon. Thus, *p*-benzoquinone, toluene, and aluminium chloride at 0° give 2 : 5-*di-p*-tolylquinol, coarse prisms, m. p. 189° (corresponding *di*-acetate, m. p. 204°), which is oxidised by air in the presence of dilute aqueous sodium hydroxide solution to 2 : 5-*di-p'*-tolyl-*p*-benzoquinone, m. p. 220°. The latter substance exists in two modifications, red, monoclinic, prismatic crystals, $a : b : c :: 1.3035 : 1 : 1.7328$, $\beta = 129^\circ 14\frac{1}{2}'$, which are obtained by crystallisation from ethyl acetate, and pale yellow, delicate leaflets which appear to belong to the triclinic system, but which are too ill-defined to permit crystallographical measurement; they are obtained by evaporation of a solution of the substance in benzene. The red modification is obtained when the yellow form is warmed on the water-bath and is stable in the dark; on exposure to light it becomes covered with a superficial layer of the yellow form. The case appears to be one of dimorphism. The action of toluene and aluminium chloride on *p*-benzoquinone in the presence of hydrogen chloride leads to the formation of ditolylquinol, m. p. 187—188°, and the *quinhydrone* of 2 : 5-*di-p*-tolylquinone.

2 : 5-*p* : *p'*-*Dihydroxydiphenyl-p*-benzoquinone,



small, brownish-red needles, m. p. above 327° after softening and blackening at about 287°, is prepared by the gradual addition of a solution of phenol in carbon disulphide to a mixture of the latter with *p*-benzoquinone and finely divided aluminium chloride at 0°. The corresponding *di*-acetate, $\text{O}:\text{C}_6\text{H}_2(\text{C}_6\text{H}_4\cdot\text{OAc})_2:\text{O}$, crystallises in aggregates of small prisms, decomp. 260° after softening at 243°. A solution of the quinone in rectified spirit is reduced by stannous chloride and hydrogen chloride to 2 : 5-*di-pp'*-*dihydroxyphenylquinol*, $\text{C}_6\text{H}_2(\text{OH})_2(\text{C}_6\text{H}_4\cdot\text{OH})_2$, pearly leaflets or small needles, m. p. 303°, which is transformed by sodium acetate and acetic anhydride into the corresponding *tetra*-acetate, a colourless, crystalline powder, m. p. 250°.

Di-p'-anisyl-*p*-benzoquinone, long, orange-red needles, m. p. 231°, is prepared from *p*-benzoquinone, anisole, and aluminium chloride in the presence of carbon disulphide at 0°. It is reduced by stannous chloride to 2 : 5-*di-p*-anisylquinol, greyish-white leaflets, m. p. 203°.

H. W.

Hydroxynaphthaquinones. V. Derivatives of 2-Bromo-5-hydroxy-1 : 4-naphthaquinone (Monobromojuglone). ALVIN S. WHEELER and B. NAIMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 2331—2334).—Monobromojuglone (2-bromo-5-hydroxy-1 : 4-naphthaquin-

one) (cf. Wheeler and Scott, A., 1919, i, 490) is best prepared by suspending juglone in glacial acetic acid and shaking the suspension with bromine for fifteen minutes. The dibromide so formed is separated by pouring the mixture into water, and is then boiled with absolute alcohol, when 2-bromojuglone is obtained. This compound gives a *benzoate*, m. p. 222° , and in alcoholic solution with dry hydrogen chloride is converted into 2-chlorojuglone, which also gives a *benzoate*, m. p. 222° . On bromination in hot glacial acetic acid, 2-bromojuglone yields 2:3-dibromo-5-hydroxy-1:4-naphthaquinone, m. p. 169° , which gives an *acetate*, m. p. 172° , and by treatment with dry hydrogen chloride in absolute alcohol is converted into 2:3-dichloro-5-hydroxy-1:4-naphthaquinone, m. p. 153° (cf. Wheeler and Scott, *loc. cit.*). When warmed with alcoholic sodium hydroxide, dibromojuglone is converted into a *bromodihydroxynaphthaquinone*, in which the bromine atom in position 2 probably remains. This compound is obtained in a yellow form, m. p. 192° , which is anhydrous, and in a red form which contains $1\text{H}_2\text{O}$. W. G.

1-Hydroxylaminoanthraquinone and some of its Derivatives. WALTER H. BEISLER and LAUDER W. JONES (*J. Amer. Chem. Soc.*, 1922, 44, 2296—2306).—1-Nitroanthraquinone is best prepared by warming anthraquinone with fuming nitric acid (*d* 1.60) and crystallising the crude product successively from glacial acetic acid, toluene, and acetone. So prepared, it has m. p. $232.5\text{—}233.5^{\circ}$ (corr.), which is much higher than that usually given in the literature (cf. Barnett, "Anthracene and Anthraquinone," 1922). The amino-compound, prepared by reduction with potassium sulphide, has m. p. $252\text{—}253^{\circ}$ (corr.). When the nitro-compound is reduced in pyridine solution by hydrogen sulphide, it yields 1-hydroxylaminoanthraquinone, which gives an unstable *potassium* salt. The hydroxylamino-compound gives a sulphonic acid derivative which dyes wool and silk without a mordant. It gives a deep bluish-green solution in alkalis, and from such solutions can be precipitated unchanged if the solution is not exposed to air. It is a fairly strong reducing agent, and is remarkably stable to aldehydes. It reacts with diazobenzene in alkaline solution, giving a reddish-brown powder, m. p. 140° (decomp.), and gives a *carbamido*-derivative, m. p. 236° . When air is bubbled through its solution in sodium hydroxide, 1-nitrosoanthraquinone, m. p. $223\text{—}224^{\circ}$, is obtained. W. G.

The Acenaphthene Series. II. FRITZ MAYER and HEINRICH SCHÖNFELDER (*Ber.*, 1922, 55, [B], 2972—2974; cf. A., 1920, i, 301).—It has been shown previously (*loc. cit.*) that the direct bromination of acenaphthenequinone does not give a uniform product. It is now found that naphthalic anhydride is produced by the action of bromine on acenaphthenequinone dissolved in nitrobenzene at 200° . The reaction is not shown by bromine or by nitrobenzene separately, or by bromine in the presence of other solvents, such as chlorobenzene.

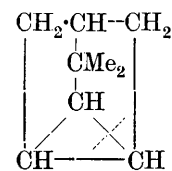
Ciba-red, obtained by the bromination of Ciba-scarlet-G-1, is

shown to contain the bromine atom in the acenaphthene nucleus, since when it is boiled with alcoholic potassium hydroxide solution it is converted into thiosalicic acid and 5(or 6)-bromo-1-keto-2-aldehydoacenaphthene, greenish-brown needles, m. p. 255°. The corresponding anil crystallises in orange-red needles, m. p. 175°, whilst the phenylhydrazone forms yellow needles, m. p. 193° (decomp.). The aldehyde is oxidised by sodium dichromate in the presence of glacial acetic acid to 4-bromonaphthalic anhydride, m. p. 215°.

H. W.

The Camphenilone Group. III. The Homogeneity of apoBornylene. apoCyclene, a New Tricyclic Hydrocarbon.

GUST. KOMPPA and R. H. ROSCHIER (*Annalen*, 1922, 429, 175—190).—In continuation of the experiments of Hintikka and Komppa (A., 1912, i, 278), it is found that the ozonide, $C_9H_{14}O_3$, (now described as a solid), m. p. 55°, decomp., obtained from apobornylene, is not formed in theoretical yield.



The reason is that apobornylene prepared from camphenilone dichloride contains 20—30% of an isomeric hydrocarbon apocyclene (annexed formula), m. p. 42·5—43°, b. p. 138—139°, d_4^{20} 0·8710, n_D^{20} 1·45144, which is the chief product in the hydrocarbon mixture obtained by heating methyl camphenilylxanthate, b. p. 147°/8 mm.

The constitution assigned to apocyclene receives support from the reaction with acetic acid and sulphuric acid which bring about fission at the point indicated by the dotted line in the formula, the product being β -fenchocamphoryl acetate, b. p. 81—82°/8 mm. This is readily hydrolysed to β -fenchocamphorol, which can be identified by oxidation to r - β -fenchocamphorone or to apofenchocamphoric acid.

C. K. I.

Essential Oils from Tonkin and Annam. JEAN GATTEFOSSÉ (*La Parfumerie moderne*, 1922, 15, 89—90; from *Chem. Zentr.*, 1922, iii, 502—503).—Star anise oil from the fruits and flowers of *Illicium verum* has d^{25} 0·983; α_D $-0^\circ 8'$; n_D^{20} 1·5546; ester number, 9·33; acetyl number, 42·93; solidification point, 9°; m. p. 13·5°. Pompelmus oil from *Citrus decumana*, obtained by distillation, has d^{15} 0·853; α_D $+97^\circ$; n_D^{20} 1·4742; ester number, 13·62; acetyl number, 44·23; citral content, 26% (?). Basilicum oil has d^{20} 0·936; α_D $+4^\circ 8'$; n_D^{20} 1·4942; ester number, 20·9; acetyl number, 111·06. Camphor oil from young branches has d^{15} 0·936; n_D^{20} 1·4704; ester number, 15·67; acetyl number, 64·21. Essential oil from *Litsaea citrata* (May-chang oil) has d^{20} 0·866; α_D $+20^\circ 2'$; n_D^{20} 1·4620; ester number, 7·65; acetyl number, 153·07; citral content, 8·15%. *Cathetus fasciculata* yields a yellow essential oil having d^{15} 0·885; α_D $-6^\circ 5'$; n_D^{20} 1·4790; ester number, 7·47; acetyl number, 53·20; aldehyde content, 5·2%; also a green oil having d^{20} 0·886; α_D $-0^\circ 6'$; n_D^{20} 1·4772; ester number, 10·45; acetyl number, 50·21. Beu-ring oil from the leaves of *Alpinia* or *Zingiber*, sp., has a pleasant tar-like odour; d^{15} 0·902; α_D $+8^\circ 8'$; n_D^{20} 1·4884; ester number, 10·92; acetyl

number, 123.57. Sau-mon oil from *Cunninghamia sinensis*, has a strong odour like terpineol, d_{15}^{25} 0.957; α_D $-23^{\circ} 6'$; n_D^{20} 1.4932; ester number, 21.09; acetyl number, 120.02. Pe-mon oil from *Fokienia hodginsii* has d_{15}^{25} 0.913; α_D $+13^{\circ}$; ester number, 23.14; acetyl number, 188.34. G. W. R.

Relation between Ability to form Resins and Chemical Constitution. III. A New Method for producing Synthetic Resins. W. HERZOG and J. KREIDL (*Z. angew. Chem.*, 1922, **35**, 641—643).—The preparation of a number of synthetic resins is described in which organic substances containing the group $-\text{CO}-\text{CH}=\text{CH}-$ are heated to temperatures of between 200° and 240° in a stream of carbon dioxide for from two to twelve hours. Resins can also be obtained from substances containing the above group as part of a cyclic ring. Such a substance is 1-keto-2-cinnamylidenetetrahydronaphthalene, $\text{C}_{10}\text{H}_8\text{O}:\text{CH}:\text{CH}:\text{CHPh}$, prepared by heating α -ketotetrahydronaphthalene (7.5 grams) and cinnamaldehyde (7 grams) in 15 c.c. of alcohol with a few drops of concentrated sodium hydroxide. It crystallises from methyl alcohol in large yellow leaves (m. p. $132-134^{\circ}$), and dissolves in concentrated sulphuric acid, giving a yellowish-red colour. All polymerisations of organic substances to resins are ascribed to the presence of the group $-\text{CO}-\text{CH}=\text{CH}-$. H. C. R.

Rhinanthin and Aucubin. Rhinanthin is Impure Aucubin. MARC BRIDEL and (Mlle) MARIE BRAECKE (*Compt. rend.*, 1922, **175**, 640—643).—Three analyses of rhinanthin did not yield concordant results, the carbon content varying from 44 to 48%, and as its reactions are similar to those of aucubin, a comparison of the two substances was made. The results led to the conclusion that rhinanthin is a mixture of aucubin and sucrose. The authors consider that as the name "rhinanthin" no longer represents a distinct substance, it should be abandoned. H. J. E.

Saponins. VIII. The Saponins from the Leaves of *Aralia montana*, Bl. (Galacturonoid-Saponins and their Magnesium and Calcium Salts.) A. W. VAN DER HAAR (*Ber.*, 1922, **55**, [B], 3041—3069).—The leaves of *Aralia montana*, Bl., are extracted successively with light petroleum and ether. The first extract (3.75% on the material taken) contains a trace of alkaloid, much chlorophyll, and a plant wax of which the alcoholic component is myricyl alcohol; the second extract (2%) contains chlorophyll, a trace of alkaloid, and a small amount of a tannin.

The powdered leaves and stems contain about 1.6% of saponins which are members of at least three groups. Free saponins are present in addition to their calcium and magnesium salts; these are precipitated by basic, but not by normal, lead acetate. The amount of the saponins appears to be variable. In the isolation of the saponins, it is necessary that the extraction with methyl alcohol (95%) should be followed by treatment with ethyl alcohol (45%), since otherwise the salts of the saponins remain undissolved. The saponins are poisonous towards fishes and exhibit hæmolytic

action; the magnesium salt is about three times as potent as the free saponin. The aralia saponins give the violet coloration with sulphuric acid which is characteristic of the other members of the class. The hydrolysis of the saponin can be effected only with very unusual difficulty. Proximate analysis and quantitative hydrolysis show the saponin to contain water, 4.8%; ash, 1.8%; *d*-galacturonic acid, 1.8%; pentoses [*L*-arabinose], 13.3%; methylpentoses, 2.1%; hexoses (*d*-galactose and dextrose), 16.15%; *d*-galactose, 2%, sapogenin, 50%. Analysis of the magnesium and calcium saponins gives: water, 7.2%; ash, 5.3%; *d*-galacturonic acid, 7.39%; arabinose, 8.64%; methylpentoses, 6.24%; dextrose, 5.6%; *d*-galactose, 3%; sapogenins, 31.2%. Other saccharides or acids are not present.

Araligenin, colourless needles, m. p. 275°, is readily isolated from the crude mixture of sapogenins. It can be sublimed. It separates from ethyl alcohol with alcohol of crystallisation which is variable in amount, and thus causes the m. p. 301°, 311°, and 273–274° to be observed. When dried at 150°, all these products give a substance which has the same specific rotation (+71° in a mixture of alcohol and pyridine) and identical composition. Araligenin dried at 150° is therefore to be regarded as a definite chemical individual. It has the composition $\text{OH} \cdot \text{C}_{25}\text{H}_{40} \cdot \text{CO}_2\text{H}$. It gives the Liebermann cholesterol reaction (violet \rightarrow blue \rightarrow green). It yields a *potassium* salt, $\text{C}_{26}\text{H}_{41}\text{O}_3\text{K} \cdot 2\text{H}_2\text{O}$, slender, colourless needles, which do not melt below 300°, a *methyl* ester (prepared by the action of methyl alcohol and methyl iodide or of methyl sulphate on sodium araligenin), m. p. 180° after softening at 120°, and a *monoacetyl methyl* ester, $\text{OAc} \cdot \text{C}_{25}\text{H}_{40} \cdot \text{CO}_2\text{Me}$, small, colourless needles, m. p. 217–218°. The methyl ester is not hydrolysed when heated during two hours with a 10% solution of potassium hydroxide in ethyl alcohol (50%), thus affording a very pronounced example of steric hindrance. The hydroxy-group of araligenin, in consequence of steric hindrance due to the proximity of the free carboxyl group, cannot be acetylated in the usual manner. The operation can, however, be effected smoothly after esterification of the carboxyl group.

Araligenin is converted into a mixture of terpene hydrocarbons, carbon dioxide, and water when distilled with zinc dust in an atmosphere of hydrogen. The hydrocarbons can be separated by distillation with steam into a light, volatile fraction which gives a violet coloration with a mixture of glacial acetic and sulphuric acids, and a non-volatile residue which gives a blue and subsequently a green colour with the mixture of acids. The volatile fraction has exactly the composition $(\text{C}_5\text{H}_8)_n$. The distillation of araligenin with zinc dust in an atmosphere of hydrogen is represented provisionally by the equation $\text{OH} \cdot \text{C}_{25}\text{H}_{40} \cdot \text{CO}_2\text{H} = (\text{C}_5\text{H}_8)_5 + \text{CO}_2 + \text{H}_2\text{O}$.

Tannins and Similar Substances. II. Chinese Tannin.

KARL FREUDENBERG and WILHELM SCILASI (*Ber.*, 1922, 55, [B], 2813–2816).—Doubts as to the homogeneity of Chinese tannin

have been strengthened by the observation of Iljin (A., 1914, i, 567) that it can be separated by repeated precipitation with zinc acetate into a fraction of high specific rotation in water $[\alpha]_D +137.85^\circ$ and one of low optical activity ($[\alpha]_D +5.16^\circ$). A repetition of Iljin's experiments with commercial tannin and with the product obtained by the authors themselves from Chinese galls has confirmed the accuracy of his observations and has also shown that the specific rotations of the fractions, although differing so widely in aqueous solution, are identical when they are dissolved in formamide, acetone, alcohol, glacial acetic acid, or pyridine. An explanation of the apparent anomaly is found in the fact that the tannin forms a colloidal solution only in water, in which, therefore, the magnitude of the specific rotation depends greatly on the degree of dispersivity of the particles; this is greatly influenced by the presence of minute quantities of impurity, which are gradually removed by precipitation in Iljin's experiments, and can also be coagulated and rendered insoluble in ethyl acetate by heating the tannin at 100° . Chinese tannin may be regarded as fundamentally homogeneous.

Highly active specimens of the tannin are prepared in the following manner. The galls are extracted with cold water, and the extract, after being neutralised with sodium carbonate, is treated with ethyl acetate; the product obtained after removal of the solvent has $[\alpha]_D +90^\circ$ in aqueous solution (3%), and the specific rotation is nearly independent of the concentration. Attempts to obtain a more active substance by the use of inorganic adsorbents (kaolin, etc.) or organic precipitants (starch, albumin, casein) were unsuccessful. If, however, the product is dried in a vacuum at 100° , and subsequently treated with anhydrous ethyl acetate, a small amount of highly coloured material remains undissolved, and the activity of the dissolved portion is increased to $+116^\circ$ in water (1%). Two further treatments in the same manner give a product which is completely soluble in ethyl acetate, and has the constant specific rotation $[\alpha]_D +138^\circ$ in aqueous solution (1.5%).

H. W.

The Formation of Melanin from Organic Substances.

O. ADLER and W. WIECHOWSKI (*Ber.*, 1922, 55, [B], 3030—3038; cf. this vol., i, 498).—The ability of a very large number of organic substances to form melanin acids has been examined in the following manner. The material under investigation (1—2 dg.) is dissolved or suspended in water (10—12 c.c.) and 3—4 drops of *N*-ferric chloride solution are added. The solution is divided into two parts, of which one serves as a control. Hydrogen peroxide (3%, 0.2—0.5 c.c.) is added to the other portion. If the substance is capable of producing melanin acids, a dark, sometimes almost black, coloration is developed after short heating, or sometimes even at the atmospheric temperature. Protracted heating is to be avoided, as the melanin acids are readily oxidised further to colourless substances. The dark mixture is rendered alkaline with sodium hydroxide when the melanin acid dissolves or remains

dissolved, as the case may be. The test must be performed in neutral or faintly acid solution.

Under the described conditions, melanin acids are only produced from cyclic substances. Compounds belonging to the terpene, triphenylmethane, phenanthrene, anthracene, and pyridine groups exhibit little or no tendency towards the formation of melanin acids. Very marked ability is exhibited by the aniline group, phenylhydrazine, and its substitution products, phenols, quinone, aromatic monoaldehydes and ketones, aromatic monocarboxylic and phenolmonocarboxylic acids and aromatic amino-acids. A positive reaction is given by *p*-diphenol, benzidine, and tolidine, but scarcely by dianisidine. Naphthalene does not yield melanin acids, which are yielded by the naphthols and naphthylamines. Among heterocyclic compounds, thiophenic acid, pyrrole, coumarone, indole, and tryptophan give melanin acids. Quinoline hydrochloride and the hydroxyquinolines give a faintly and strongly positive action respectively. Positive results are also given by *iso*quinoline, acridine, and the representatives of the tropine, cinchonine, and morphine groups.

The entrance of halogen into the nucleus diminishes or abolishes the tendency towards the formation of melanin acids, whereas the sulphonic group has no restrictive action. Aromatic arsenic compounds of the arsenic acid type have only a slight or no ability to produce melanin acids, even when they are derived from substances which are intensely active in this respect. The presence of an amino-group on the nucleus strengthens the ability of a substance to give melanin acids; the nitro-group does not exert a restrictive influence. The intensity of the melanin reaction is restricted, or production of melanin acids is entirely prevented, by the presence of methyl residues attached to the benzene nucleus. The effect of ester or ethereal groups depends to some extent on their more or less ready removal or decomposability under the influence of the oxidising mixture. As far as has been examined, the action of methyl and ethyl esters and methyl ethers of substances which themselves give the melanin reaction is positive. On the other hand, a negative reaction is observed when a cyclic residue is involved in the formation of the ester or ether (for example, phenyl salicylate, guaiacyl cinnamate), or when an inorganic component is present (guaiacyl carbonate, triguaiacyl phosphate).

H. W.

Pyranhydrones. III. The Constitution of Diarylmethylpyrylium Compounds. WILHELM SCHNEIDER and ALBERT ROSS (*Ber.*, 1922, **55**, [B], 2775—2782; cf. Schneider and Meyer, A., 1921, i, 680; Schneider and Seebach, A., 1921, i, 877).—The compound obtained by the action of acetic anhydride and sublimed ferric chloride on a mixture of acetophenone and benzaldehyde has been regarded by Diltthey (A., 1916, i, 829) as a 2 : 6-diphenyl-4-methylpyrylium salt. This view has been shared by Schneider and Seebach (*loc. cit.*), who obtained the corresponding sulphoacetate by the action of sulphoacetic acid and acetic anhydride

on acetophenone. It is now found, however, that the same sulphoacetate is prepared by the action of acetic anhydride and sulphoacetic acid on dyponone, and since the product in this instance must necessarily be 4 : 6-diphenyl-2-methylpyrylium sulphoacetate, it follows that the compounds described previously must also be 4 : 6-diaryl-2-methylpyrylium compounds. Apparently acetophenone is first transformed into dyponone in the presence of either ferric chloride or sulphoacetic acid as catalyst, and this is then condensed with the acetic anhydride to give a pyrylium salt. Further confirmation of this view is found in the observation that ω -ethylideneacetophenone and acetophenone react in the presence of acetic anhydride and sublimed ferric chloride to give undoubted 2 : 6-diphenyl-4-methylpyrylium compounds which differ from those described previously.

The formula for the bluish-violet pyranhydrones must therefore be so amended that in their molecular complex a molecule of a benzenoid 4 : 6-diaryl-2-methyloxonium base is loosely united with an ortho-quinonoid 2-methylenpyran.

Dyponone is transformed by acetic anhydride and sulphoacetic acid into 4 : 6-diphenyl-2-methylpyrylium sulphoacetate, pale yellow needles, m. p. 204°; the corresponding iodide forms red crystals, m. p. 222°.

The additive compound of 2 : 6-diphenyl-4-methylpyrylium chloride and ferric chloride, a brownish-yellow salt, m. p. 205·5°, is prepared by the action of sublimed ferric chloride on phenyl propenyl ketone and acetophenone in the presence of acetic anhydride. 2 : 6-Diphenyl-4-methylpyrylium bromide crystallises in yellow, prismatic needles; it becomes carbonised but does not melt when heated; the corresponding iodide forms orange-red needles, decomp. above 240°, whereas the perchlorate crystallises in slender, lemon-yellow needles, m. p. 273° (decomp.). Addition of sodium acetate solution to 2 : 6-diphenyl-4-methylpyrylium bromide in faintly acid solution results in the formation of a dull red, amorphous precipitate, m. p. (indefinite) 155—160° after shrinking at 70° and darkening above 95°; the substance appears to be a pyranhydrone.

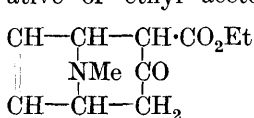
H. W.

Preparation of Thionaphthensulphonic Acid. GESELLSCHAFT FÜR TEERVERWERTUNG M. B. H. and RUDOLF WEISSGERBER (D.R.-P. 353932; from *Chem. Zentr.*, 1922, iv, 499).—In the sulphonation of thionaphthen, the reaction is conducted in the presence of sufficient acetic anhydride to combine with all the water present in the sulphuric acid used, and formed in the reaction. The free acid is a viscid mass, crystallisable with difficulty. The potassium salt forms colourless platelets. The acid decomposes when heated at 140° with dilute sulphuric acid, forming thionaphthen and sulphuric acid.

G. W. R.

Preparation of Nortropinone and its Derivatives. E. MERCK, OTTO WOLFES, and HORST MAEDER (Brit. Pat. 177807; from *Chem. Zentr.*, 1922, iv, 439).— $\alpha\delta$ -Dialdehydes or $\alpha\delta$ -diketones are condensed with ammonia or primary amines and an acetone

derivative. For example, succinaldehyde is allowed to react with the dipotassium derivative of ethyl acetonedicarboxylate, ammonia, and ammonium chloride in aqueous solution. *Ethyl nortropinonecarboxylate* is obtained. It forms a *picrate* and a *methiodide*. The *condensation product* from succinaldehyde, benzylamine, and the dipotassium derivative of ethyl acetonedicarboxylate gives the enol reaction with ferric chloride. By heating with dilute sulphuric acid, *N-benzylnortropinone* is obtained, which yields a *dibenzylidene* compound. Condensation of succinaldehyde with glycine hydrochloride and calcium acetonedicarboxylate yields a product which does not give the enol reaction and gives a *dibenzylidene* derivative with benzaldehyde. Malealdehyde diacetate is shaken with 0.1*N*-sulphuric acid, neutralised with calcium carbonate, and condensed with methylamine and the dipotassium derivative of ethyl acetonedicarboxylate. The *monocarboxylic* ester formed (annexed formula) gives, on reduction, *ethyl tropinonecarboxylate*. An *homologous* ester of tropinonecarboxylic acid is obtained by condensation of acetylacetone with the dipotassium salt of ethyl acetonedicarboxylate, methylamine, and methylamine hydrochloride in aqueous solution.



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G. W. R.

Preparation of Tropinecarboxylic Acid. E. MERCK, OTTO WOLFES, and HORST MAEDER (D.R.-P. 354696; from *Chem. Zentr.*, 1922, iv, 438).—A mixture of acetonedicarboxylic acid, methylamine, and succinaldehyde is reduced in the cold in neutral, slightly acid, or slightly alkaline solution. For example, a mixture of calcium acetonedicarboxylate, succinaldehyde, and methylamine is acidified with acetic acid and reduced with 3% sodium amalgam, the reaction of the mixture being maintained acid by addition of acetic acid. After addition of dilute sulphuric acid and removal of calcium sulphate by filtration, the filtrate is concentrated and treated with potassium hydroxide. The tropine bases are then extracted with ether. The neutralised alkaline solution is concentrated, and shaken with methyl alcohol. The methyl-alcoholic solution, after being freed from salts, contains *tropinecarboxylic acid* in the form of several optically inactive isomerides which are separable with difficulty. One of them is ecgonine (Willstätter and Bode, A., 1903, i, 36), from which the *methyl* ester, m. p. 122–126°, can be obtained. The benzoyl derivative, $\text{C}_{17}\text{H}_{21}\text{O}_4\text{N}$, m. p. 79–80°, is identical with optically inactive cocaine. G. W. R.

Preparation of Tropinonedicarboxylic Esters. E. MERCK, OTTO WOLFES, and HORST MAEDER (D.R.-P. 354950; from *Chem. Zentr.*, 1922, iv, 438–439).—Succinaldehyde is condensed in alkaline solution with acetonedicarboxylic acid and methylamine and the products of reaction are separated without saponification. For example, solutions of succinaldehyde in water, ethyl acetonedicarboxylate in ethyl alcohol, and methylamine and potassium hydroxide in water are mixed with careful cooling. After several hours, the products of reactions are neutralised with acid. After

evaporating off the alcohol, the residue is treated with ammonia and extracted several times with chloroform. After removal of the chloroform by distillation from the extract, *ethyl tropinone-dicarboxylate* remains as a viscid, uncrystallisable oil. It differs from the monocarboxylic ester in not forming a solid hydrate with water. Heating the ester with acids yields *tropinone*. The *monocarboxylic* ester is obtained by careful hydrolysis.

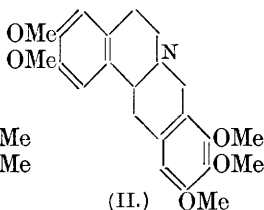
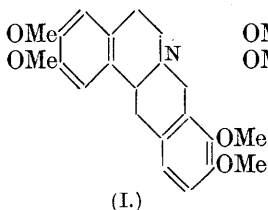
G. W. R.

The Resolution of Tropic Acid and the Stereochemical Configuration of the Cinchona Alkaloids. HAROLD KING and ALBERT DONALD PALMER (T., 1922, 121, 2577—2586).

Preparation and Racemisation of Hyoscyamine and its Sulphate. A. GORIS and P. COSTY (*Bull. Sci. Pharmacol.*, 1922, 29, 113—121; from *Chem. Zentr.*, 1922, iii, 268—269).—Hyoscyamine and atropine may be separated by making use of their differing solubilities in cold light petroleum. Hyoscyamine in absolute ethyl alcohol has $[\alpha]_D -20.72^\circ$, in 50% ethyl alcohol, $[\alpha]_D -21.89^\circ$, in 20% ethyl alcohol, $[\alpha]_D -23.43^\circ$. The sulphates of hyoscyamine and atropine may be separated by their differing solubilities in ethyl alcohol. The transformation of hyoscyamine into atropine only proceeds to a small extent at 100° . It proceeds more rapidly when the hyoscyamine is dissolved in a little chloroform. At 118° , hyoscyamine is completely changed into atropine in two hours.

G. W. R.

Constitution of the Alkaloids of the Calumba Root. ERNST SPÄTH and KARL BÖHM (*Ber.*, 1922, 55, [B], 2985—2995).—In a previous communication (Späth and Lang, this vol., i, 166), the

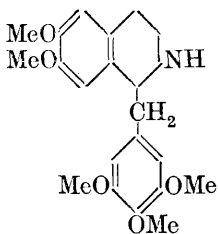


annexed formula (I) has been assigned to palmatine. The other alkaloids of the calumba root, columbamine (Günzel, A., 1906, i, 976) and jatrorrhizine (Feist, A., 1908, i, 100) have been examined in detail by Feist, who has drawn the conclusion that they contain hydroxy- and methoxy-groups and, after complete methylation and hydrogenation, give the same final product (annexed formula II). Attempts are now described to prepare this compound synthetically, but as they are not completely successful, the alkaloids themselves have been subjected to re-examination. The isolation of columbamine and jatrorrhizine from calumba root is effected as described by the previous investigations, but doubts are expressed with regard to the homogeneity of the fractions which are soluble in potassium carbonate and potassium hydroxide, respectively. They have therefore been separately completely methylated and subsequently reduced. The observed melting points of the products are in agreement with those recorded by

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Feist for columbamine methyl ether, jatrorrhizine dimethyl ether, and their hydro-compounds. The identity of the methylated products is also confirmed. On the other hand, it is shown both chemically and crystallographically that the substances are identical with palmatine and tetrahydropalmatine. The relationships of the various alkaloids of the calumba root appear therefore to be simpler than was expected. There are present, in addition to completely methylated palmatine, phenolic bases in which probably one or more of the methoxy-groups of palmatine are replaced by hydroxy-groups or by phenolic oxygen united to a readily eliminable complex.

The trimethyl ether of homogallic acid reacts with homoveratrylamine at 175° to yield *trimethylhomogalloylhomoveratrylamine*, $C_{21}H_{27}O_6N$, colourless needles, m. p. 98° , which is readily converted by phosphoryl chloride in the presence of boiling toluene into the corresponding *dihydroisoquinoline* derivative, an amorphous, glassy substance which is characterised in the form of its *picrate*, $C_{27}H_{28}O_{12}N_4$, yellow crystals, m. p. $154-155^{\circ}$. The substance is



reduced by tin and hydrochloric acid to 6:7-dimethoxy-1-3':4':5'-trimethoxybenzyl-1:2:3:4-tetrahydroisoquinoline (annexed formula), an amorphous solid which is characterised as its N-m-nitrobenzoyl compound (also amorphous) and *hydrochloride*, colourless needles. The subsequent condensation of this compound with methylal and hydrochloric acid does not proceed smoothly, yielding a crystalline compound, $C_{45}H_{54}O_{10}N_2$, m. p. 292° (decomp.), in an evacuated capillary and an amorphous substance, $C_{22}H_{27}O_5N$, which appears to be allied to tetrahydroberberine. By greatly diminishing the relative quantity of methylal and purifying the product of the reaction through the berberinium base, it was found possible to isolate a substance, $C_{22}H_{25}O_5N$, which might be identical with the pentamethoxy-compound (see above); it was, however, amorphous and certainly not identical with Feist's tetrahydrocolumbamine methyl ether.

H. W.

Strychnos Alkaloids. XXXIV. The Preparation of iso-Strychnine. HERMANN LEUCHS and RUDOLF NITSCHKE (*Ber.*, 1922, 55, [B], 3171—3174).—*iso*Strychnine has been obtained by Pictet and Bacovescu (*A.*, 1905, i, 815) by the action of water on strychnine at $160-180^{\circ}$. Attempts to repeat their work gave the substance in only 20—25% yield instead of 70—75% as recorded. More successful results were obtained by using a solution of ammonia in methyl alcohol. *iso*Strychnine, $C_{21}H_{22}O_2N_2 \cdot 3H_2O$, prismatic needles, has m. p. $223-224^{\circ}$ (particularly in an evacuated capillary) instead of $214-215^{\circ}$ as recorded. It dissolves in water at 100° to the extent of 1 part in 130—140 parts, and not 1 in 65. Contrary to Pictet and Bacovescu's observations, it is optically active, having $[\alpha]_D +24.1^{\circ}$ to $+25.1^{\circ}$ in alcohol and -39.47° to -41.9° in glacial acetic acid. It yields a well-crystallised *meth-*

iodide, $C_{22}H_{25}O_2N_2I \cdot H_2O$, colourless leaflets, m. p. about 223° (decomp.) after softening at 215° . The sulphonic acids obtained from it by means of manganese dioxide and sulphurous acid could not be caused to crystallise. It is readily oxidised by potassium permanganate in the presence of acetone, but characteristic acids, notably strychninonic acid or its dihydro-compound, could not be isolated; it is therefore improbable that strychnine and *iso*-strychnine are related in the same manner as fumaric and maleic acids.

H. W.

The Synthesis of Pyrrolidine. Reduction of Pyrrole by Catalytic Hydrogenation. N. J. PUTOCHIN (*Ber.*, 1922, 55, [B], 2742—2748).—The catalytic hydrogenation of pyrrole in the presence of nickel at 200° (cf. Padoa, A., 1906, i, 530) has been examined. The product is subjected to fractional distillation and the separate fractions are characterised by conversion into the hydrochlorides, platinichlorides, or picrates. The presence of diethylamine, methyl-*n*-propylamine, *n*-butylamine, *n*-amylamine, ethyl-*n*-propylamine, pyrrolidine, possibly 4-methylpiperidine, and (?) hexahydroindoline or α -*n*-butylpyrrolidine is established. It is remarkable that fission of the pyrrole ring must have occurred simultaneously at several different points in order to give the simpler compounds here described. The formation of amylamine and piperidine derivatives is explained by the primary condensation of two molecules of pyrrole followed by an extension of the hetero-five-membered to the hetero-six-membered ring.

The most advantageous method for the preparation of pyrrolidine is that due to Gabriel. Improved methods are described for the conversion of γ -chlorobutyronitrile by sodium phenoxide into γ -phenoxybutyronitrile and for the isolation of δ -phenoxy-*n*-butylamine by the reduction of the latter; during the change, *bis*- γ -phenoxy-*n*-butyrylamine, $(OPh \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CO)_2NH$, lustrous plates, m. p. 162 — 163° , and γ -phenoxy-*n*-butyric acid, m. p. 59.5° , are also formed.

H. W.

The Action of Formaldehyde on Pyrrolidine and Piperidine. N. J. PUTOCHIN (*Ber.*, 1922, 55, [B], 2749—2753).—Pyrrolidine is converted when heated with an equivalent amount of formaldehyde (as trioxymethylene) during six hours at 145 — 150° into 1-*hydroxymethylpyrrolidine*, $\begin{matrix} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \end{matrix} > N \cdot CH_2 \cdot OH$, 1:1'-*methylenedipyrrolidine*, $CH_2 \left(N < \begin{matrix} CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \end{matrix} \right)_2$, and resinous substances. The substance first named is a yellow, viscous liquid, b. p. 55 — $56^\circ/30$ mm., which is hydrolysed by dilute hydrochloric acid to pyrrolidine hydrochloride and formaldehyde; the change takes place with such readiness at the atmospheric temperature that it is impossible to prepare the platinichloride, etc., the corresponding compound of pyrrolidine being obtained in its place. 1:1'-Methylenedipyrrolidine is a pale yellow liquid of low density, b. p. 94 — $95^\circ/30$ mm.; it has a marked tendency towards resinification, so that definite

salts can only be prepared with great difficulty. The brown, resinous residue left after the distillation is decomposed when heated into formaldehyde, pyrrolidine, and apparently an isomeric 1-hydroxymethylpyrrolidine, b. p. about 140°/atmospheric pressure. Under precisely similar conditions, piperidine is converted by trioxymethylene into a mixture of methylpiperidines, b. p. 33—35°/35 mm. (apparently 1- and 2-methylpiperidines), and 1:1'-methylenedipiperidine, b. p. 120—122°/25 mm., d_4^{20} 0.9371, d_{11}^{20} 0.9344, d_{15}^{20} 0.9335, n_D^{15} 1.4883 (the platinichloride was also prepared).
H. W.

Condensation of Collidine with Acetaldehyde. HEIZABURŌ KONDŌ and TORIZŌ TAKAHASHI (*J. Pharm. Soc. Japan*, 1922, No. 487, 775—780).—When collidine (10 grams) is heated with paracetaldehyde (3.63 grams) in a sealed tube at 210° during fourteen hours, and the product fractionated under reduced pressure, 2:4-dimethyl-6-propenylpyridine (2 grams), a colourless oil, b. p. 110—111°/12 mm., is obtained. The constitution was proved by oxidation with 25% nitric acid, when 2:4-dimethylpyridine-6-carboxylic acid (Altar, A., 1887, 378) is formed. The *aurichloride*, yellow, rhombic plates, m. p. 135°; the *platinichloride*, yellowish-brown, thin, rhombic plates, m. p. 205—206°; and the *mercurichloride*, colourless needles, m. p. 192—193°, were prepared. When reduced by Ladenburg's method, the base gives 2:4-dimethyl-6-propylpiperidine, a colourless liquid of slightly nicotine-like odour, b. p. 184°. The *hydrochloride* forms needles, m. p. 204—206°, the *platinichloride*, orange-yellow crystals, decomposing at 210°.

K. K.

Supposed Cases of Isomerism in the Isatin Series. A. HANTZSCH (*Ber.*, 1922, 55, [B], 3180—3194).—A further chapter in the controversy between Hantzsch and Heller concerning the existence of isomerides in the isatin series (cf. Heller, A., 1920, i, 766; 1921, i, 891; Heller and Benade, this vol., i, 582; Hantzsch, A., 1921, i, 597).

The existence of the bimolecular alkylisatoids is acknowledged and demonstrated by determinations of molecular weight, but the various derivatives are not so sharply distinguished from one another as Heller and Benade (*loc. cit.*) have supposed. The isomerism of the so-called "isatole" with isatin is disproved by Heller's determinations of the molecular weight. Its re-preparation has, however, been effected, and it is shown to be derived from a complex condensation product of isatin the constitution of which will be fully elucidated in a subsequent communication.

Heller's "dimethylisatin II" has been further investigated since it is pointed out that its mode of production is exceptional in the series and the constitution ascribed to it is not consonant with its properties. Dimethylisatin silver is converted smoothly by methyl iodide at the laboratory temperature in the complete absence of moisture into dimethylisatinlactim ether,



m. p. 137°. The latter readily suffers hydrolysis in that one molecule of it becomes converted into the free lactim which condenses spontaneously with a second molecule of the ether to the so-called methylisatoid of the dimethylisatin series (annexed formula). The

direct production of this substance in Heller's experiments appears to be due to the use of an impure silver salt which only reacts at a higher temperature and to incomplete exclusion of moisture. Consequent on the non-existence of "dimethylisatin II," dimethylisatins III and IV also do not exist.

The author draws the general conclusion that isomerides of ordinary isatin and its substitution products do not exist. The substances which have been regarded as such are complex condensation products.

According to Heller, the reddish-violet silver salts of isatin and its derivatives which react readily with methyl iodide are to be regarded as *O*-salts, whereas the grey, indifferent compounds are *N*-salts. According to the author, all pure silver salts of the isatins are never grey except when they are contaminated by co-precipitated silver oxide. The grey salts are very readily formed from the more feebly acidic methylated isatins or solutions of their alkali salts by reason of their extensive hydrolysis.

[With WALTHER MEYER.]—An improved method for the production of 5 : 7-dimethylisatin is described in detail.

Pure silver salts of isatin and its derivatives are prepared by dissolving these substances in boiling alcohol and gradually adding a filtered aqueous solution of silver acetate (prepared from silver nitrate and sodium acetate). The precipitates are filtered, washed with alcohol (50%), and dried to constant weight at 100° or in a desiccator. The average yield is 60–70% of that theoretically possible. For their conversion into alkyl derivatives, the dry silver salt is moistened with anhydrous ether and treated with rather less than two molecular proportions of alkyl iodide. The mixture is placed in a desiccator shielded from light. The alkyl compounds are extracted with dry benzene in the absence of moisture and precipitated from the solutions by addition of light petroleum. The following compounds are thus prepared: isatin *O*-methyl ether, m. p. 101°; ethyl ether, m. p. 52°; *n*-propyl ether, m. p. 72°; isoamyl ether, m. p. about 40°; methyl ethers of 5-bromoisatin, m. p. 147°; 5-chloroisatin, m. p. 144°; 5-methylisatin, m. p. 134°; 5 : 7-dibromoisatin, m. p. 158°; 5 : 7-dimethylisatin, m. p. 137°. All the ethers are readily hydrolysed by aqueous alcohol to the original isatins. With the exception of the dibromo- (and probably also dichloro-) compounds they are hydrolysed by acetic acid or by atmospheric moisture to the isatoid monoalkyl ethers. The latter substances when rapidly heated darken at about 6–8° below their melting points, which are never definite, and at which total decomposition occurs. The following constants are recorded: isatoid monomethyl ether, C₁₇H₁₂O₄N₂, m. p. about

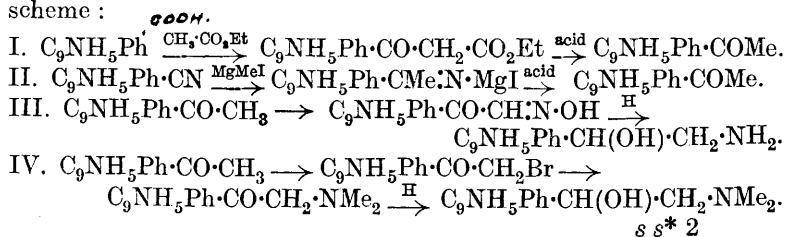
226°; ethyl ether, m. p. about 228°; propyl ether, m. p. about 189°; dimethylisatoid monomethyl ether, m. p. about 235°; tetramethylisatoid monomethyl ether, m. p. about 245°; dichloroisatoid monomethyl ether, m. p. about 239°; dibromoisatoid monomethyl ether, m. p. about 246°.

Isatindianil, $C_6H_4 \begin{smallmatrix} \text{C}(\text{NPh}) \\ \text{NH} \end{smallmatrix} > \text{C}:\text{NPh}$, m. p. 210°, is readily obtained when a solution of the lactim ether (1 mol.) and aniline (2 mols.) in benzene is heated on the water-bath for about half an hour and the benzene as it evaporates is replaced by alcohol. It dissolves in alcoholic potassium hydroxide to a reddish-violet solution. The blue coloration attributed to the solution by Heller is due to the presence of monoanil.

Isatin- α -benzyloxime, $C_6H_4 \begin{smallmatrix} \text{CO} \\ \text{NH} \end{smallmatrix} > \text{C}:\text{N} \cdot \text{O} \cdot \text{CH}_2\text{Ph}$, yellow crystals, m. p. 128° (prepared from isatin lactim ether and α -benzylhydroxylamine), yields blue alkali *salts*, differing in this respect from the dianil.
H. W.

Preparation of β -Thionaphthisatin. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 186859).— β -*Thionaphthisatin* is obtained by the interaction of oxalyl chloride and β -thionaphthol in presence or absence of a diluent or a condensing agent. It forms a red, crystalline powder, m. p. 153°, and is a valuable dye-intermediate. As an example of the preparation, 160 parts of β -thionaphthol may be mixed with 635 parts of oxalyl chloride, and after stirring some hours at the ordinary temperature the mixture is heated to the boiling point. The excess of oxalyl chloride is distilled off, and the β -thionaphthisatin extracted from the residue with aqueous sodium carbonate and reprecipitated from the extract with hydrochloric acid. Some of the oxalyl chloride may, if desired, be replaced by carbon disulphide, and aluminium chloride or sulphuric acid may be added as the condensing agent. G. F. M.

Manufacture of Amino-alcohols of the Quinoline Series. SOCIETY OF CHEMICAL INDUSTRY IN BASLE (Brit. Pat. 185913).—Amino-alcohols derived from 2-phenylquinoline-4-carboxylic acid are obtained by converting the acid, its ester, or nitrile into a 2-phenyl-4-quinolyl alkyl ketone and either reducing the latter through its oximino-compound to the 2-phenylquinolyl-4-amino-alcohol, or causing the ketone, halogenised in the alkyl group, to react with an amine or substituted amine and reducing the 2-phenyl-4-quinolyl aminoalkyl ketone thus produced to the corresponding amino-alcohol. The reactions are represented by the following scheme :



Ethyl 2-phenylquinoline-4-formylacetate, $C_9NH_5Ph \cdot CO \cdot CH_2 \cdot CO_2Et$, prepared by condensing ethyl acetate with ethyl 2-phenylquinoline-4-carboxylate, forms yellow prisms, m. p. 52—54°. By ketonic hydrolysis it is converted into *2-phenyl-4-quinolyl methyl ketone*, $C_9NH_5Ph \cdot COMe$, yellow crystals, m. p. 75°. Its *hydrobromide* forms yellow crystals, m. p. 240°. Its oximino-compound is obtained as sodium salt by the action of amyl nitrite and sodium ethoxide in benzene solution. Liberated by the addition of acetic acid, it forms yellow crystals, m. p. 182° (decomp.). 2-Phenyl-4-quinolyl methyl ketone can be prepared alternatively from 4-cyano-2-phenylquinoline by means of the Grignard reagent as indicated in scheme II above. 2-Phenyl-4-quinolyl bromomethyl ketone is obtained by brominating the ketone in concentrated hydrobromic acid or in organic solvents. The free base forms bright yellow crystals, m. p. 91°. Its *hydrobromide* also forms intensely yellow crystals, m. p. about 225°. On treatment of the bromoalkyl ketones (1 mol.) with 3 mols. of an amine the corresponding aminoalkyl ketones are formed. As these substances are not very stable, they are best isolated as their hydrochlorides. The preparation of the following is described: 2-phenyl-4-quinolyl dimethylaminomethyl ketone, of which the *monohydrochloride* is a bright yellow, crystalline powder, m. p. 208° (decomp.); 2-phenyl-4-quinolyl diethylaminomethyl ketone, forming a *monohydrobromide* in bright yellow, felted needles, m. p. 164° (decomp.); and 2-phenyl-4-quinolyl piperidinomethyl ketone, giving a *monohydrochloride*, m. p. 235°; and a *monohydrobromide*, m. p. 241° (decomp. in each case). From the above ketones by hydrogenation in presence of platinum black, or from the oximino-ketone by reduction with zinc dust and formic acid, the corresponding amino-alcohols are obtained (schemes III and IV). The free bases are precipitated from aqueous solutions of their salts in amorphous form. They soon become brown on exposure to air, but form stable mono-acid salts sparingly soluble in water, and diacid salts freely soluble in water. 2-Phenyl-4-quinolylaminoethanol dihydrochloride, $C_9NH_5Ph \cdot CH(OH) \cdot CH_2 \cdot NH_2 \cdot 2HCl$, forms yellow crystals, m. p. 145°. 2-Phenyl-4-quinolyl dimethylaminoethanol dihydrochloride is a pale yellow powder, m. p. 175° (decomp.). The corresponding diethyl compound gives a dihydrochloride, m. p. 180°, and the piperidino-compound a similar salt, m. p. 199°. G. F. M.

Aldehyde Compounds of Hydroxy-amines and the Partial Acylation of these Amines. MAX BERGMANN, REINHOLD ULPTS, and FRANCISCO CAMACHO (*Ber.*, 1922, **55**, [B], 2796—2812).—Many examples are given of the use of the aldehydic compounds of hydroxy-bases, particularly with respect to the purification of hydroxy-amines and their partial acylation.

p-Aminophenyl benzoate, m. p. 148°, is prepared by a slight modification of the method of Reddelien and Danilof (this vol.,

i, 148). 2:4:5-Triphenyloxazolidine, $\begin{array}{c} CHPh-O \\ | \\ CHPh-NH \end{array} > CHPh$, is converted by benzoyl chloride in the presence of pyridine and subse-

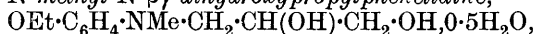
quent treatment of the product with hydrochloric acid into the *N*-benzoate of *isodiphenylhydroxyethylamine*, m. p. 223° (cf. Auwers and Sonnenstuhl, A., 1904, i, 1054).

Almost exclusive acylation of the amino-group of hydroxy-bases can be effected by means of acyl polysulphides of the type $R \cdot CO \cdot S_n \cdot COR$. These compounds react rapidly with basic amino-groups, with the formation of acid amides and hydrogen sulphide (sulphur is also liberated from the polysulphides), whereas the alcoholic and phenolic hydroxy-groups are not normally affected. Thus *l*-tyrosine ethyl ester is transformed by benzoyl disulphide in boiling alcoholic solution into the *N*-benzoyl ester, m. p. 120—121° (corr.), from which the corresponding *N*-*l*-benzoyl acid, m. p. 164°, identical with that prepared by Fischer by resolution of synthetic *r*-benzoyl-tyrosine, is obtained. Similarly, *o*-aminophenol and *p*-aminophenol are transformed into *o*-benzoylaminophenol, m. p. 169—171°, and *p*-benzoylaminophenol in excellent yield.

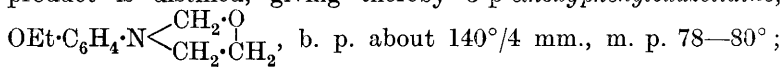
The removal of an acyl group from the nitrogen atom of fully acylated hydroxy-amino-compounds can frequently be effected by the use of phosphorus pentachloride and alcohol (cf. Bergmann, Brand, and Dreyer, A., 1921, i, 444). As an example of the applicability of the method, *o*-aminophenol is transformed into its dibenzoyl derivative, m. p. 179°, which is treated with phosphorus pentachloride at 100°; after distillation of phosphoryl chloride, the residue is treated with ethyl alcohol at 0°, whereby *o*-aminophenyl benzoate hydrochloride, slender needles, m. p. 149° (decomp.), is obtained in 89% yield. The salt is not so unstable as has been assumed previously. When heated above its melting point, warmed with water, or treated with cold sodium acetate solution, it is, however, transformed into *o*-hydroxybenzanilide, which undergoes partial conversion into 2-phenylbenzoxazole, $C_6H_4 \begin{smallmatrix} \diagup O \\ \diagdown N \end{smallmatrix} \geq CPh$, m. p. 103°. The presence of the unsubstituted amino-group in the salt is demonstrated by its diazotisation and subsequent coupling with dimethylaniline to the *dye*, $NMe_2 \cdot C_6H_4 \cdot N : N \cdot C_6H_4 \cdot CO_2Ph$, red plates, m. p. 116°.

The preparative applicability of aldehydic compounds of hydroxy-bases is illustrated in the case of certain derivatives of phenetidine. The base is converted by glycide at 0° into a mixture of the secondary and tertiary amines containing one or two dihydroxypropyl residues which can only be separated with difficulty by fractional crystallisation. The mixture is treated with freshly distilled formaldehyde solution at the atmospheric temperature, whereby the secondary base is transformed into 3-*p*-ethoxyphenyl-5-hydroxymethyl-oxazolidine, $OEt \cdot C_6H_4 \cdot N \begin{smallmatrix} \diagup CH_2 \cdot CH \cdot CH_2 \cdot OH \\ \diagdown CH_2 \cdot O \end{smallmatrix}$, b. p. 135—145°/0.3—0.4 mm., m. p. 57—59°, which is readily separated from the tertiary base by fractional distillation. The oxazolidine derivative is readily decomposed by oxalic acid in alcoholic solution into β -*di*hydroxypropylphenetidine oxalate, m. p. 161—163°, from which the free base, $OEt \cdot C_6H_4 \cdot NH \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot OH$, m. p. 90—92°, is isolated. The further action of formaldehyde on the oxazolidine

derivative in the presence of hydrochloric acid leads to the production of *N-methyl-N-βγ-dihydroxypropylphenetidine*,

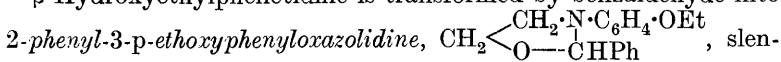


m. p. 51—53°, the identity of which is established by its formation from *N*-methylphenetidine and glycide. In a similar manner, the mixture of bases obtained from *p*-phenetidine, ethylene chlorohydrin, and sodium iodide is treated with formaldehyde and the product is distilled, giving thereby 3-*p*-ethoxyphenyloxazolidine,



the latter is transformed by dilute acids into *β-hydroxyethylphenetidine*, colourless leaflets, m. p. 50—51° (*hydrogen oxalate*, m. p. 139—140°). The base is transformed by the further action of formaldehyde in the presence of hydrochloric acid into *N-methyl-β-hydroxyethylphenetidine*, $\text{OEt} \cdot \text{C}_6\text{H}_4 \cdot \text{NMe} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{OH}$, b. p. 130°/0.5 mm., m. p. 38—39°. The *benzoic* ester of the latter, microscopic prisms or hexagonal plates, m. p. 78°, is obtained by means of benzoyl chloride in the presence of pyridine.

β-Hydroxyethylphenetidine is transformed by benzaldehyde into



In place of formaldehyde, which gives products of exceptionally low boiling point, other aldehydes or ketones may be employed, thus allowing a modification of the physical properties of the derivatives and also of their mode of production and decomposition.

H. W.

Diethylrhodanine. CLIFFORD SHATTUCK LEONARD (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, 4, No. 14, 1—13).—With the object of studying the effect of ring sulphur in a substance which might be expected to have narcotic properties, *diethylrhodanine*, $\begin{array}{c} \text{CO} \cdot \text{CEt}_2 \\ \diagup \quad \diagdown \\ \text{NH} \quad \text{CS} \end{array} > \text{S}$, was prepared, by condensing *α*-bromo-*α*-ethylbutyric acid with ammonium dithiocarbamate. It crystallises in needles, m. p. 107.5°. When injected into a rabbit, intramuscularly when dissolved in oil or intravenously when dissolved in sodium hydrogen carbonate solution, it had a narcotic effect slightly greater than that of veronal but with a quicker recovery. Given by the mouth, it was inactive. On account of its low solubility in water (1 in 3000 at 18°), it can have no practical therapeutic value. The bearing of the substance on the theory of narcosis is indecisive. E. H. R.

Selenium Organic Compounds. I. Synthesis of 4-Seleno-2-methylquinazolone, 2-Phenylbenzoselenazole, and some Derivatives of the Latter. MARSTON TAYLOR BOGERT and YÜ-GWAN CHEN (*J. Amer. Chem. Soc.*, 1922, 44, 2352—2357).—*o*-Aminobenzoselenamide, m. p. 116° (corr.), was obtained in very poor yield by saturating a solution of anthranilonitrile in absolute alcohol at 0° with dry hydrogen selenide and dry ammonia and heating the product in a sealed tube at 105—110° for ten hours.

4-*Seleno-2-methylquinazalone*, m. p. 213·5° (corr.), was synthesised from anthranilonitrile by several methods, and found to be rather unstable. On exposure to light and air, it slowly decomposed with separation of finely divided metallic selenium and formation of 2-methyl-4-quinazalone.

2-Phenylbenzoselenazole (cf. Fromm and Martin, A., 1913, i, 1323) was best prepared by gently boiling benzylideneaniline for three days on a sand-bath with selenium dust. On nitration in sulphuric acid solution at below 0°, it gave 6-nitro-2-phenylbenzoselenazole, m. p. 202·4° (corr.). On reduction with tin and hydrochloric acid, this yielded 6-amino-2-phenylbenzoselenazole, m. p. 201·2—202·3° (corr.), giving an *acetyl* derivative, m. p. 188·1—188·7° (corr.), and a *benzylidene* derivative, m. p. 156·7—157·6° (corr.). The amine, when diazotised and the product coupled with β -naphthol, gave 2-phenylbenzoselenazole-azo- β -naphthol, m. p. 284·2° (corr.), which dyed silk a fine pink. The diazotised amine was similarly coupled with a number of phenols and amines, and most of the azo-compounds dyed silk. If the nitration of the phenylbenzoselenazole was pushed further (?) 4 : 6-dinitro-2-phenylbenzoselenazole, m. p. 246·8° (corr.), was obtained and on reduction gave (?) 4 : 6-diamino-2-phenylbenzoselenazole, m. p. 269—270·5°, which yielded a *diacetyl* derivative, m. p. 239·5—240·5°, and a *dibenzylidene* derivative, m. p. 186—187°. The diamine was diazotised and coupled with a number of phenols and amines, giving new selenium azo-dyes.

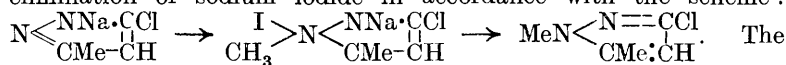
W. G.

3-Chloro-1-alkylpyrazoles and 1-Alkylpyrazol-3-one.

C. A. ROJAHN (*Ber.*, 1922, **55**, [B], 2959—2971).—1-Alkyl derivatives of 3-chloropyrazole are formed by the alkylation of chloromethylpyrazole under certain conditions. In each case, two isomerides are obtained by the alkylation of 3-methyl- or 3-phenyl-pyrazolones, among which 1 : 5-dimethylpyrazol-3-one has been almost certainly identified.

5-Chloro-3-methylpyrazole dissolved in anhydrous ether is converted by sodium into its soluble *sodium* salt, which is transformed by a slight excess of methyl iodide at 100° into 3-chloro-1 : 5-dimethylpyrazole, $\text{NMe} \begin{smallmatrix} \diagup \\ \text{CMe} \cdot \text{CH} \end{smallmatrix} \begin{smallmatrix} \diagdown \\ \text{N} = \text{CCl} \end{smallmatrix}$, plate-like crystals, m. p. 45—

47°, b. p. 208—210° (slight decomp.)/atmospheric pressure, 138°/72 mm. The substance may also be prepared by the action of methyl toluene-*p*-sulphonate on the sodium compound; in this case, 5-chloro-1 : 3-dimethylpyrazole, b. p. 155—160°, is also produced. The course of the reaction is somewhat unusual, and is most readily explained by an initial addition of methyl iodide and subsequent elimination of sodium iodide in accordance with the scheme:



The validity of the constitution assigned to the product depends on a comparison of its properties with those of previously described chlorodimethylpyrazoles and the demonstration that it contains an unsubstituted CH group in position 4 and a methyl group

attached to the nitrogen atom in position 1 as evidenced by its insolubility in alkali hydroxide and its conversion into 3-*chloro-4-nitroso-1:5-dimethylpyrazole*, green needles, m. p. 87°, and 3-*chloro-4-bromo-1:5-dimethylpyrazole*, long needles, m. p. 56°. 3-*Chloro-1:5-dimethylpyrazole 2-methiodide*, colourless, crystalline leaflets, decomp. 184°, is prepared by the successive action of methyl sulphate and potassium iodide on the parent pyrazole. 3-*Chloro-5-methyl-1-ethylpyrazole*, an almost colourless liquid, b. p. 216—218°/atmospheric pressure, is obtained by the action of ethyl iodide on the sodium derivative of 5-*chloro-3-methylpyrazole*; it is converted by bromine in the presence of glacial acetic acid into 3-*chloro-4-bromo-5-methyl-1-ethylpyrazole*, m. p. 39°. 3-*Chloro-5-methyl-1-benzylpyrazole*, b. p. 295—300°, is obtained in a similar manner.

5-*Chloro-3-phenylpyrazole* is converted by successive treatment with sodium and methyl alcohol and methyl toluene-*p*-sulphonate into chlorophenylmethylpyrazole, m. p. 43°, b. p. 295—297°/atmospheric pressure, which with bromine in glacial acetic acid solution gives ?-*chloro-4-bromo-?-phenyl-1-methylpyrazole*, needles, m. p. 67°.

5-*Chloro-3:4-dimethylpyrazole* is prepared by the action of phosphoryl chloride on 3:4-dimethylpyrazol-5-one, m. p. 269°; it crystallises in long needles, m. p. 124—125°, b. p. 251—252°/atmospheric pressure. It does not give a bromo-derivative, 5-*chloro-1-benzoyl-3:4-dimethylpyrazole* forms long, silky needles, m. p. 90—91°.

3-*Chloro-1:5-dimethylpyrazole* is transformed by ethyl bromide at 180—200° owing to interchange of alkyl groups into 3-*chloro-5-methyl-1-ethylpyrazole ethobromide*, coarse crystals, m. p. 225° (decomp.), which is converted by heat into 3-*chloro-5-methyl-1-ethylpyrazole*, b. p. 215—220°.

3-*Methylpyrazol-5-one* is converted by methyl iodide and methyl alcoholic sodium methoxide solution at 100° into a mixture of 1-methylantipyrine, b. p. 310°/760 mm., and 1:5-dimethylpyrazol-3-one, $\text{NMe} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{N} = \text{C} \cdot \text{OH} \end{smallmatrix}$ or $\text{NMe} \begin{smallmatrix} \text{CMe} \cdot \text{CH} \\ \text{NH} \cdot \text{CO} \end{smallmatrix}$, m. p. 172—173°.

Under similar conditions, the latter compound is generally obtained when methyl toluene-*p*-sulphonate is used as methylating agent, but on one occasion a previously undescribed *dimethylpyrazolone*, m. p. 181—182° (*bromide*, m. p. 218°), was formed; the preparation of this compound could not be repeated. 4-*Bromo-1:5-dimethylpyrazol-3-one* crystallises in small, colourless needles, m. p. 209°.

5-*Methyl-1-ethylpyrazol-3-one*, colourless needles, m. p. 135—136° (*bromo-derivative*, m. p. 39°), is prepared from 3-methylpyrazol-5-one, ethyl iodide and ethyl alcoholic sodium ethoxide solution.

The alkylation of 3-phenylpyrazol-5-one with methyl toluene-*p*-sulphonate leads to the formation of two *phenyl-1-methylpyrazolones*, m. p. 165° and 96°, respectively; the former is converted by phosphoryl chloride at 210° into 5-*chloro-3-phenyl-1-methylpyrazole*, m. p. 62—63°, whereas under similar conditions the latter is resinified.

1:5-Dimethylpyrazole, m. p. 173°, is transformed by phosphoryl

chloride at 200—210° into 3-chloro-1:5-dimethylpyrazole, m. p. 46—47°. H. W.

Molecular Compounds of Diketopiperazine and Phenols. G. POVARNIN and P. TICHOMIROV (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 40—46).—When 10—15% aqueous solutions of diketopiperazine (1 mol.) and a phenol (1 mol.), either with or without a few drops of 10% sulphuric acid solution, are boiled together for some minutes, crystalline molecular compounds of the two components are formed. These are decomposed by solvents of the phenols with the exception of water, and when heated lose phenol and do not melt, but sometimes carbonise.

Dicatechol-diketopiperazine and *dirosorcinol-diketopiperazine*, $2C_6H_6O_2 \cdot C_4H_6O_2N_2$, form colourless crystals. *Monoguinol-diketopiperazine*, $C_6H_6O_2 \cdot C_4H_6O_2N_2$, forms a stable lilac form and a labile white form. *Dipyrogallol-diketopiperazine*, $2C_6H_6O_3 \cdot C_4H_6O_2N_2$, and *protocatechuic acid-di-diketopiperazine*, $C_7H_6O_4 \cdot 2C_4H_6O_2N_2$, form white crystals. Diketopiperazine yields condensation products with protocatechualdehyde and furfuraldehyde, and an unstable compound with phenol.

The theory of oscillating affinity is applied in arriving at an explanation of the structure of these compounds. T. H. P.

Bromo-derivatives of 2-Methylglyoxaline. LOUIS LIGHT and FRANK LEE PYMAN (*T.*, 1922, **121**, 2626—2630).

Orientation of the 1:4- and 1:5-Dimethylglyoxalines.
Mode of Fission of 5-Aminoglyoxalines. FRANK LEE PYMAN (*T.*, 1922, **121**, 2616—2626).

The Reactions of the Formamidines. X. The Thioimidazolones [Thiolglyoxalones]. F. B. DAINS, RUTH THOMPSON, and W. F. ASENDORF (*J. Amer. Chem. Soc.*, 1922, **44**, 2310—2315).—2-Thio-4-glyoxalone and its mono- and di-substituted derivatives react readily with formamidines, giving 5-R-amino-methylene derivatives. The following compounds are described: 2-thiol-1:3-diphenyl-5-anilinomethylene-4-glyoxalone, m. p. 175°; 2-thiol-1-phenyl-3-p-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 197—198°; 2-thiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 252°; 2-thiol-3-p-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 250°; 2-thiol-3-o-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 215°; 2-thiol-3-m-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 207—208°; 2-thiol-3-p-chlorophenyl-5-anilinomethylene-4-glyoxalone, m. p. 274—276°; 2-thiol-3-p-ethoxyphenyl-5-anilinomethylene-4-glyoxalone, m. p. 227°; 2-thiol-3-phenyl-5-p-bromophenylaminomethylene-4-glyoxalone, m. p. 190°; 2-thiol-3-phenyl-5-naphthylaminomethylene-4-glyoxalone, m. p. 160°.

Two new thioimidazolones were prepared, namely, 2-thiol-3-m-tolyl-4-glyoxalone, m. p. 167°, and 2-thiol-3-p-chlorophenyl-4-glyoxalone, m. p. 234.5°.

The above anilinomethyleneglyoxalones react with alkyl haloids to give alkyl thio-ethers, of which there were prepared. 2-Methylthiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 173°;

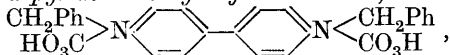
2-ethylthiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 164.5°;
 2-n-butylthiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 124°;
 2-allylthiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 218°;
 2-benzylthiol-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 145°;
 2-benzylthiol-3-o-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 148°;
 2-benzylthiol-3-m-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 154°;
 2-benzylthiol-3-p-ethoxyphenyl-5-anilinomethylene-4-glyoxalone, m. p. 170°.

When hippuric acid and phenylthiocarbimide were heated together at 150° for one and a half hours 2-thiol-1-benzoyl-3-phenyl-4-glyoxalone, m. p. 177—179°, was obtained, and yielded 2-thiol-1-benzoyl-3-phenyl-5-anilinomethylene-4-glyoxalone, m. p. 184—186°. Similar compounds are 2-thiol-1-benzoyl-3-m-tolyl-4-glyoxalone, m. p. 197°; 2-thiol-1-benzoyl-3-m-tolyl-5-anilinomethylene-4-glyoxalone, m. p. 187°; 2-thiol-1-benzoyl-3-p-ethoxyphenyl-4-glyoxalone, m. p. 168°; 2-thiol-1-benzoyl-5-anilinomethylene-4-glyoxalone, m. p. 164—165°, and its 2-benzylthio-ether, m. p. 165°; and 2-thiol-5-anilinomethylene-4-glyoxalone, m. p. 264°.

When boiled for six hours with a mixture of alcohol and hydrochloric acid, 2-thiol-1-benzoyl-3-phenyl-4-glyoxalone was hydrolysed, giving aniline, a little benzoic acid, and hippuric acid. The 5-anilinomethylene derivative behaved similarly. W. G.

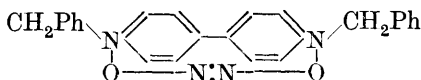
The Synthesis of *m*- α -Benzbispyrrole Derivatives. WILLIAM DAVIES and EDGAR HERBERT CUTHBERT HICKOX (T., 1922, 121, 2640—2655).

Free Ammonium Radicles. IV. Further Investigations on 1:1'-Dibenzyl-4:4'-dipyridinium and its Homologues and on the so-called 1:1'-Disubstituted Tetrahydro-4:4'-dipyridyls. ERNST WEITZ and THEODOR KÖNIG (Ber., 1922, 55, [B], 2864—2889).—It has been observed recently by Weitz and Ludwig (this vol., i, 365) that the dark blue solution of 1:1'-dibenzyl-4:4'-dipyridinium, $\text{CH}_2\text{Ph} \cdot \text{N}^+\text{C}_5\text{H}_4 \cdot \text{C}_5\text{H}_4 \cdot \text{N}^+ \cdot \text{CH}_2\text{Ph}$, in methyl alcohol reacts with nitric oxide, but a definite product of the change could not be isolated. A repetition of the action in chloroform solution has led to the surprising isolation of 1:1'-dibenzyl-4:4'-dipyridinium hydrogen carbonate,



a colourless substance which decomposes rapidly on exposure to air, but is more stable in an atmosphere of carbon dioxide. It decomposes with evolution of gas at about 80° after blackening at about 65°. It dissolves readily in water to an alkaline solution and is converted by potassium iodide and perchloric acid into dibenzylidipyridinium iodide, m. p. 248—249°, and dibenzylidipyridinium perchlorate, m. p. 257°, respectively. Carbon dioxide is by itself without action on the radicle; the nitric oxide acts as an oxidising agent, being reduced to nitrous oxide the formation of which is established experimentally. In all probability an unstable nitroso-derivative, $\begin{array}{c} \text{CH}_2\text{Ph} \\ \text{ON} \end{array} > \text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} \text{C}_6\text{H}_4 \text{---} \text{C}_6\text{H}_4 \text{N} \begin{array}{c} \diagup \diagdown \\ \diagdown \diagup \end{array} < \begin{array}{c} \text{CH}_2\text{Ph} \\ \text{NO} \end{array}$,

is primarily formed which passes into the isomeric salt, 1:1'-dibenzyl-4:4'-dipyridinium-1:1'-hyponitrite (annexed formula); the latter is then decomposed by carbon dioxide into nitrous oxide and the carbonate. As is to be expected, the carbonate



is also produced by the combined action of oxygen and carbon dioxide on 1:1'-dibenzyl-4:4'-dipyridinium, whereby approximately one atom of oxygen is absorbed by each molecule of the radicle. The action of oxygen or air alone leads to the formation of only very small amounts of soluble and alkaline products, as is to be expected when the instability of the anhydride is taken into consideration.

In a similar manner, the so-called 1:1'-dibenzyltetrahydro-4:4'-dipyridyl of Hofmann and Emmert (bis-*N*-benzylpyridinium according to the author) is converted by carbon dioxide and oxygen in chloroform solution into unimolecular 1-benzylpyridinium hydrogen carbonate, $C_5H_5N(C_7H_7) \cdot CO_3H$; dibenzylidipyridinium hydrogen carbonate is formed simultaneously in subordinate amount. A similar result is obtained when nitric oxide is substituted for oxygen.

The reduction of 1:1'-dibenzyl-4:4'-dipyridinium salts (chloride and iodide) to the radicle by metals in different media in the absence of acids has been investigated. The blue solutions in acetone are characterised by relative stability towards air (although they react instantaneously with iodine). Similar solutions prepared electrolytically or from the crystalline radicle behave in an analogous manner. On the other hand, the solutions of the dihaloids in acetone are reduced when heated with copper gauze, whereas the similar solutions in water or methyl alcohol are only affected by less noble metals such as zinc. In explanation of these observations, the hypothesis is put forward that the radicle exists in a readily oxidisable form, the corresponding salts of which resemble ammonium salts, and a difficultly oxidisable condition which gives rise to quinone-like haloids. The two extremes may be represented by the scheme $R \cdot N \langle \text{pyridine ring} \rangle = \langle \text{pyridine ring} \rangle N \cdot R \rightleftharpoons R \cdot N \langle \text{pyridine ring} \rangle - \langle \text{pyridine ring} \rangle N \cdot R$, but the authors regard the two forms, on account of the subsidiary valencies, as rather less distinct from one another than is thus suggested.

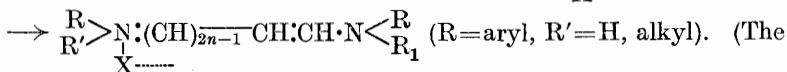
If the correctness of the formula $RN \langle \text{pyridine ring} \rangle - \langle \text{pyridine ring} \rangle NR$ is regarded as established, 2- or 3-alkylpyridines would be expected to yield radicles; in the case of 4-alkylpyridines, this is impossible unless the alkyl group suffers replacement. It is found that the almost colourless, oily *product* of the reduction of 2-methylpyridinium benzyl chloride by sodium amalgam gives a blue coloration, due to the corresponding radicle, when its alcoholic solution is heated; it is readily oxidised. Similarly, 2:6-dimethylpyridine is converted by benzyl iodide into the corresponding benzyl iodide, which is reduced to two products, one of which has m. p. 121° , whereas the

other remains semi-solid; either substance gives a blue radicle coloration when its alcoholic solution is warmed in contact with air. On the other hand, *bis*-1-benzyl-2:4-dimethylpyridinium, obtained as a pale yellow, viscous liquid by reduction of 2:4-dimethylpyridinium benzyl chloride, does not develop a blue coloration when its alcoholic solution is heated. A similar behaviour is observed with *bis*-1-benzyl-2:4:6-trimethylpyridinium, colourless needles, m. p. 102—103°, which is prepared by the reduction of 2:4:6-trimethylpyridinium benzyl iodide, pale yellow crystals, m. p. 102° (corresponding perchlorate, m. p. 135°). The action of iodine on the new "leuco-compounds" dissolved in cold chloroform leads invariably to the formation of the corresponding mono-iodides; if the titration is performed rapidly, the derivatives substituted in position 4 absorb almost exactly one molecular proportion of iodine, thus giving two molecular proportions of the mono-iodide thus: $C_5NH_2Me_3(C_7H_7)_2 + I_2 \rightarrow 2C_5NH_2Me_3(C_7H_7)I$; the reaction with the 2-methyl derivative is less quantitative. *Bis*-1-benzyl-2:4:6-trimethylpyridinium is rapidly decomposed by carbon dioxide and nitric oxide when dissolved in chloroform, but an alkaline hydrogen carbonate or a derivative soluble in water could not be isolated. *Bis*-1-benzyl-2:4:6-trimethylpyridinium is decomposed rapidly in boiling benzene into 2:4:6-trimethylpyridine and dibenzyl: $2C_5NH_2Me_3 \cdot CH_2Ph \rightarrow 2C_5NH_2Me_3 + (CH_2Ph)_2$. The rapid decomposition of the molecule is obvious during determinations of the molecular weight in boiling benzene, whereas the bimolecular compound is completely stable in the freezing solvent. New determinations of the molecular weight of bisbenzylpyridinium in freezing benzene have given accurately bimolecular values, whereas in the boiling solvent the molecular weight diminishes gradually but much more slowly than that of the collidyl compound. *Bis*-1-methyl-2:4:6-trimethylpyridinium appears to be practically stable in boiling benzene.

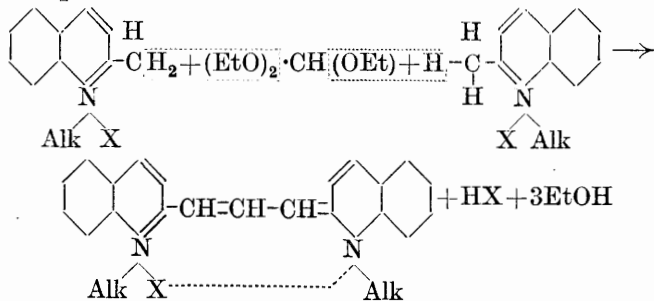
If an alcoholic solution of 1:1-dibenzyl-4:4'-dipyridinium dichloride or di-iodide is treated with solid or dissolved bisbenzylpyridinium, the intensely oxidisable blue coloration of the radicle is immediately developed. The same effect is produced by other leuco-compounds. Similarly, the action of bisbenzylpyridinium on 1:1-diphenyl-4:4'-dipyridinium di-iodide causes the production of the intensely emerald green diphenyl radicle. The action appears to be most readily explained by the hypothesis that the leuco-compounds—as in their action towards iodine, etc.—behave as unimolecular radicles, passing into the corresponding iodides and liberating the nobler dipyridinium radicle: $I(R)N:C_5H_4 \cdot C_5H_4:N(R) \cdot I + 2C_5H_5:N(R) \rightarrow R \cdot N:C_5H_4 \cdot C_5H_4:N \cdot R + 2C_5H_5:N(R) \cdot I$.
H. W.

The Constitution of the Pinacyanols, a Contribution to the Chemistry of the Quinocyanines. W. KÖNIG (*Ber.*, 1922, 55, [B], 3293—3313).—Constitutional formulæ for pinacyanol have been proposed by O. Fischer (*A.*, 1921, i, 56), Wise, Adams, and Lund (*A.*, 1919, i, 416), and Mills and Hamer (*T.*, 1920, 117, 1150;

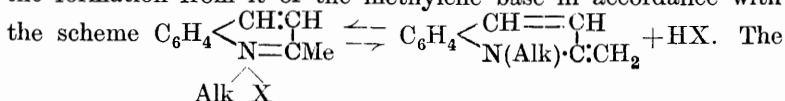
cf. Braunholtz, T., 1922, **121**, 169). Objection is raised to the first of these, since its carbon atom with twin double bonds places it in a category by itself and quite apart from the other quino-cyanines, and to the second since it represents pinacyanol as a peculiar member of the class of lepidinecyanines and does not take into account its oxidation to *N*-alkyl-2-quinolones and the differences between the sensitising effect of the cyanines (in the narrower sense) and the pinacyanols and in their behaviour towards acids. The conception of Mills and Hamer is thus considerably strengthened. It is deduced, however, mainly from the results of oxidative degradation of the pinacyanols. Confirmatory evidence in its favour is brought by two different methods. A comparison of the absorption spectra of pinacyanol and ψ -isocyanine and estimation of their persistence and maxima shows that the same differences exist between them as between polymethine dyes and the compounds obtained from them by the streptostatic introduction of a vinylene group into the chromophore system, thus : $\text{R}'\text{--}\text{N}^+(\text{CH})_{2n-1}\text{N}^-\text{R}$



description of this work will be published elsewhere.) The second confirmation of Mills and Hamer's formula is obtained by a direct synthesis of pinacyanol. For this purpose, quinaldinium salts are condensed with ethyl orthoformate in the presence of suitable agents such as acetic anhydride or zinc chloride, whereby pinacyanols are readily prepared in about 50% yield. The synthesis may be represented thus :



It is thus similar to the author's syntheses of pentamethine dyes of the indole series. Since it is also found that 4-methylquinolinium salts can condense, although with greater difficulty, with orthoformic ester, it is expected that the dicyanines will also prove capable of synthesis along these lines. The ability of the quinoline derivative to enter into the reaction is considered to be due to the formation from it of the methylene base in accordance with



possible mechanism of the synthesis is discussed at length, but the original communication should be consulted for details.

Since the constitution of the cyanines has been largely elucidated, the author considers it desirable that the common names (cyanines, *isocyanines*, ψ -*isocyanines*, dicyanines, ψ -dicyanines, carbocyanines, and cryptocyanines) should be deleted from the scientific literature and replaced by the general term quinocyanines, by which is understood the salts of quinolyldihydroquinolylenemethanes which are not methylated at the nitrogen atom. The three classes, 2:2', 2:4', and 4:4'-quinocyanine salts are thus suitably distinguished. The further derivatives are termed benzothiazolocyanines (thiocyanines) and indoleninocyanines (indocyanines). Further types are produced by the streptostatic introduction of *n*-vinylene-groups between the quinoline residues and are designated mono-(di-, tri-, etc.) vinylene-2:2'- or 2:4'- or 4:4'-quinocyanine salts. As examples may be quoted: dimethyl- ψ -*isocyanine* iodide = 1:1'-dimethyl-2:2'-quinocyanine iodide; pinaverdol = 1:6:1'-trimethyl-2:4'-quinocyanine iodide; ψ -dicyanine bromide = 1:1'-diethyl-4:6:4':6'-tetramethylstreptomono-vinylene-2:2'-quinocyanine bromide; dicyanine = 1:1'-diethyl-4:6:2':6'-tetramethylstreptomono-vinylene-2:4'-quinocyanine iodide.

[With H. ZORN.]— ψ -*isoCyanine* iodide [1:1'-dimethyl-2:2'-quinocyanine iodide] is synthesised by heating 2-chloroquinoline with quinaldine methiodide at 211° and treating the product successively with methyl sulphate and potassium iodide.

Pinacyanol iodide [1:1'-diethylstreptomono-vinylene-2:2'-quinocyanine iodide] is prepared by the gradual addition of ethyl orthoformate to a solution of quinaldine ethiodide in gently boiling acetic anhydride. 1:1'-*Dimethylstreptomono-vinylene-2:2'-quinocyanine iodide* is obtained in a similar manner. The synthesis is capable of wide variation. The ester may be added to a solution of the quinaldinium salts in boiling nitrobenzene or the quaternary salts may be dissolved in quinaldine or pyridine and heated for some time under a reflux condenser with zinc chloride and the ortho-ester. Trihalogenomethanes, in particular iodoform, may be used in these syntheses. H. W.

Di- and Tri-quinolylmethanes united by the Pyridine Nuclei. III. Symmetrical Di-2-quinolyl Ketone. GÜNTHER SCHEIBE and GUSTAV SCHMIDT (*Ber.*, 1922, **55**, [B], 3157—3160; cf. A., 1921, i, 62, 451).—*Di-2-quinolyl ketone*, colourless prisms, m. p. 164°, is obtained by the atmospheric oxidation of di-2-quinolylmethane dissolved in alcohol or acetic anhydride or by the action of dilute nitric acid on di-2-quinolylmethane. It is most conveniently prepared by condensing the latter with *p*-nitrosodimethylaniline to the compound $(C_9H_6N)_2C:N \cdot C_6H_4 \cdot NMe_2$, yellow crystals, m. p. 252°, which is hydrolysed subsequently by dilute acid to the desired ketone and *p*-aminodimethylaniline. The ketone yields a *picrate*, m. p. 179°, a *phenylhydrazone* (also prepared by coupling di-2-quinolylmethane with benzenediazonium chloride), m. p. 199°, an *oxime* (also derived from di-2-quinolylmethane and

nitrous acid), colourless prisms, m. p. 201° , and an *anil*, m. p. 161° . When warmed with aniline at 120 – 130° the ketone yields a colourless compound, m. p. 120° , which appears to contain two molecular proportions of aniline.

H. W.

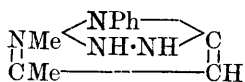
Extension of the Kishner-Wolff Method of Reduction. II.

ERNST THIELEPAPE and OTTO SPRECKELSEN (*Ber.*, 1922, 55, [B], 2929–2939).—The applicability of the method to derivatives of quinoline has been examined previously (this vol., i, 271). It has now been applied successfully to pyridine compounds. In the pyrazole series, on the other hand, difficulties are experienced in the preparation of the hydrazino-compounds on account of displacement reactions and the compound which has been isolated is decomposed in a different direction.

2-Hydrazinopyridine, b. p. $130^{\circ}/12$ mm. (cf. Fargher and Furness, *T.*, 1915, 107, 688) is decomposed when heated with potassium hydroxide at 140 – 160° with formation of pyridine, but the change proceeds slowly, and is not complete after fourteen hours; it is much more readily effected by copper sulphate or ferric chloride in boiling aqueous solution. 2:6-Dichloropyridine-4-carboxylic acid is converted by the successive action of hydrazine hydrate at the temperature of boiling water and copper sulphate into 2-chloropyridine-4-carboxylic acid, m. p. 245° (decomp.), and by boiling hydrazine hydrate and copper sulphate into isonicotinic acid, m. p. 304° (in sealed tube).

1-Phenyl-3-methylpyrazol-5-one is converted by boiling hydrazine hydrate into phenylhydrazine and 3-methylpyrazol-5-one. The latter reacts with hydrazine hydrate at 150 – 160° to give ammonia and 4:4'-bis-3-methylpyrazol-5-one.

Antipyrine does not appear to react with boiling hydrazine hydrate, by which, however, it is converted at 180° into *s*-phenylmethylhydrazine and 4:4'-bis-3-methylpyrazol-5-one. The reaction appears to be remarkably dependent on the temperature employed. 5-Chloro-1-phenyl-3-methylpyrazole does not appear to react with hydrazine hydrate at 220° , whereas its methochloride [antipyrine chloride] is readily transformed into hydrazinopyrine, a yellow liquid which solidifies to a glassy solid when cooled in liquid air, but re-melts at the atmospheric temperature. It decomposes slowly on exposure to air, very rapidly when distilled. After prolonged exposure to air, it is only incompletely soluble in ether, leaving a residue, m. p. 155 – 156° . *Hydrazinopyrine picrate* forms star-shaped crystals, m. p. 126° . Hydrazinopyrine does not decompose in the normal manner when treated with potassium hydroxide, sodium ethoxide, or copper sulphate; it appears doubtful if it contains a free hydrazone group, and the constitution shown



in the annexed formula is suggested for it.

The product obtained by means of potassium hydroxide, sodium ethoxide, or boiling water crystallises in colourless or pale yellow prisms, m. p. 130° , is soluble in dilute acids, and neutral towards litmus. It reduces Fehling's solution readily in the cold. It is scarcely affected

by boiling concentrated hydrochloric acid. Analyses and determinations of molecular weight agree with the formula $C_{14}H_{16}N_4$. It gives a *monopicrate*, m. p. 195° (decomp.), and a *di-methiodide*, $C_{16}H_{22}N_4I_2$, colourless crystals, m. p. 188° after previous softening. It is converted quantitatively by boiling dilute nitric acid into a *dinitro-derivative*, $C_7H_6N_2(NO_2)_2$, microscopic, yellow crystals which do not melt below 280° . The substance appears most probably to be 1:4-diphenylhexahydro-1:2:4:5-tetrazine, $NPh<\begin{smallmatrix} CH_2 \cdot NH \\ NH \cdot CH_2 \end{smallmatrix}>NPh$; if this is the case, its stability towards hydrochloric acid is somewhat remarkable, as is also the production of a *monobenzoyl* derivative, colourless crystals, m. p. 90° .

H. W.

Physical Chemistry of Colloidal and Supersaturated Solutions of Uric Acid. H. SCHADE (*Z. Klin. Med.*, 1922, **93**, 1—65; from *Chem. Zentr.*, 1922, iii, 622—623; cf. A., 1913, i, 404, 910).—Further observations on colloidal and supersaturated uric acid (urate) solutions. The colloidal solution is a labile system from which uric acid gel and, finally, crystalline uric acid are formed. Optimum stability is found at p_H 6.0 which is the isoelectric point. Stability is also greater at low temperatures. Supersaturated solutions of uric acid develop a colloidal character owing to aggregation in the disperse phase. The presence of a uric acid-urate complex with amphoteric properties is postulated. Increasingly favourable effect of kations on colloidal stability is shown by the series $NH_4 < Na < K < Li$.

G. W. R.

Decomposition of Dithiocarbazines. SIMA M. LOSANITCH (*T.*, 1922, **121**, 2542—2545).

The Capacity for Migration of Acyl Residues in Acyl Derivatives of the Phenylhydrazones of Hydroxy-ketones. K. VON AUWERS, E. HILLIGER, and E. WULF (*Annalen*, 1922, **429**, 190—246).—In continuation of previous work on the migration of acyl groups from oxygen to nitrogen in these substances, two groups of experiments are now described, one relating to derivatives of 3-propionyl-*p*-cresol, and the other to derivatives of 7-hydroxy-1-hydrindone.

The main difficulty in the case of 3-propionyl-*p*-cresol is the lability of the *O*-acyl derivatives which usually undergo hydrolysis in the attempt to prepare their phenylhydrazones. Thus the *acetate*, which is prepared with the help of acetyl chloride, and forms short needles, m. p. 58° , gives the *phenylhydrazone* of the free hydroxy-ketone, needles or leaflets, m. p. 146° , when treated with phenylhydrazine. The *benzoate*, prisms, m. p. 97° , prepared by the Schotten-Baumann method, gives an *oxime*, prisms, m. p. 138 — 138.5° ; the *acetate*, on the other hand, gives the oxime of the free hydroxy-ketone when treated with hydroxylamine under similar conditions. The *anil* of the hydroxy-ketone is easily obtained, but the aniline residue is eliminated when the attempt is made to acetylate or benzoyle. The *p*-nitrophenylhydrazone

of the hydroxy-ketone, orange-red needles, m. p. 187—188°, is obtained by the action of *p*-nitrophenylhydrazine on either the hydroxy-ketone itself or its acetyl derivative; the benzoyl derivative, however, yields a *p*-nitrophenylhydrazone, m. p. 159—160°, without elimination of the acyl group. The benzoyl derivative also yields a phenylhydrazone, prisms, m. p. 92°, which on energetic reduction gives aniline and 3- α -benzoylamino-*propyl-p*-cresol, small needles, m. p. 145—146°, a migration of a benzyl group having occurred at some stage of the reaction. On heating the same benzoyl compound with acetic acid, α -benzoyl- β -acetyl- α -phenylhydrazine and 2-*p*-hydroxy-*m*-tolyl-3-methylindole, m. p. 176°, are produced. Attempts to convert the phenylhydrazones of the hydroxy-ketone itself, and of acetophenone, and 3-acetyl-*p*-cresol, into indoles met with no success. The benzoylphenylhydrazone of acetophenone forms needles, m. p. 125.5°.

7-Hydroxy-4-methyl-1-hydrindone is converted successively into its *O*-acetate, needles, m. p. 107°, and the phenylhydrazone of the *O*-acetate, m. p. 226°, which on boiling with acetic acid is isomerised into the *N*-acetyl derivative, prisms, m. p. 130—131°. This, on further acetylation, gives the *ON*-diacetyl derivative, needles, m. p. 132.5°. The *O*-benzoate, m. p. 124°, yields a phenylhydrazone, m. p. 247°, which may also be obtained by benzoylating the phenylhydrazone of the hydroxy-ketone. An attempt to convert this into the benzoylphenylhydrazone, m. p. 115—116°, was not successful, but this hydrazone was actually obtained from benzoylphenylhydrazine and the hydroxy-ketone. The *O*-benzoyl-*N*-acetyl derivative of the phenylhydrazone, prepared either by acetylation of the phenylhydrazone of the benzoate or by the action of acetylphenylhydrazine on the benzoate itself, has m. p. 192—192.5°, and on reduction gives acetanilide and the *N*-benzoyl derivative, m. p. 166—168°, of 7-hydroxy-4-methyl-1-hydrindamine. The *N*-benzoyl-*O*-acetyl derivative, m. p. 152.5—153.5°, prepared from benzoylphenylhydrazine and the acetate of the hydroxy-ketone, on reduction gave benzanilide and the *N*-acetyl derivative, m. p. 158°, of the same hydroxymethylhydrindamine.

The *p*-nitrophenylhydrazone of the hydroxy-ketone has m. p. 298°, its *O*-acetate, m. p. 264—265°, and its *O*-benzoate, m. p. 299° (decomp.). The *anil* of the hydroxy-ketone has m. p. 88—89°, its *oxime*, m. p. 140°, and the *dibenzoyl* derivative of the *oxime*, m. p. 186.5—187.5°. The *oxime* on reduction gives 7-hydroxy-4-methyl-1-hydrindamine, which is isolated as its *dibenzoyl* derivative, m. p. 150°. 7-Methoxy-4-methyl-1-hydrindone gives a phenylhydrazone, m. p. 150—152°, a *p*-nitrophenylhydrazone, m. p. 215°, and a phenylmethylhydrazone, m. p. 83—85°.

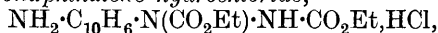
7-Hydroxy-2:4-dimethyl-1-hydrindone gives a phenylhydrazone, m. p. 136.5°, an *O*-acetate, m. p. 91.5—92°, and an *O*-benzoate, m. p. 113°. The phenylhydrazone yields an *O*-acetate, m. p. 184.5—185.5°, and an *O*-benzoate, m. p. 232°, which does not undergo isomeric change similarly to its lower homologue. The *N*-benzoyl derivative of the hydrazone has m. p. 133—135°, and the *N*-acetyl derivative of the *O*-benzoate of the phenylhydrazone has m. p. 171°.

7-Hydroxy-3 : 4-dimethyl-1-hydrindone gives a *phenylhydrazone*, m. p. 166·5—167·5°, an *O-acetate*, m. p. 135°, and an *O-benzoate*, m. p. 106°; the hydrazone gives an *O-acetate*, m. p. 210—211°, and an *O-benzoate*, m. p. 221—222°, which on heating with acetic acid is converted into the *N-benzoyl* derivative, m. p. 147—148·5°, also prepared from the hydroxy-ketone and benzoylphenylhydrazine. The *O-acetyl-N-benzoyl* derivative of the hydrazone is obtained by acetylation of the *N-benzoyl* derivative, and has m. p. 176·5—177°.

5-Hydroxy-1-hydrindone gives a *benzoyl* derivative, a *phenylhydrazone*, m. p. 165—166°, an *O-benzoyl* derivative of the phenylhydrazone, m. p. 180—181°, and an *N-benzoyl* derivative, m. p. 227°, prepared by using benzoylphenylhydrazine. C. K. I.

The Azo-ester Reaction with Amines and Enols. OTTO DIELS (*Annalen*, 1922, 428, 1—55).—An introductory account of this research has already been published (cf. this vol., i, 774).

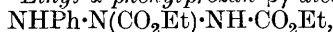
[With SÖRENSEN.]—The additive product of α -naphthylamine with ethyl azodicarboxylate (cf. A., 1921, i, 280) is readily converted by alcoholic hydrochloric acid into 1-amino-4- $\alpha\beta$ -dicarbethoxyhydrazinonaphthalene hydrochloride,



which undergoes hydrolytic fission in solution in water with the formation of the original additive product, and is reduced by hydriodic acid to 1 : 4-naphthylenediamine. Sodium 1-amino-2- $\alpha\beta$ -dicarbethoxyhydrazinonaphthalene-4-sulphonate, m. p. 204—210°, the product obtained using sodium naphthionate in place of α -naphthylamine, loses alcohol on treatment with piperidine, giving ethyl 2-keto-6-sulpho-1 : 3 : 4-naphthisotriazine-4-carboxylate, m. p. 135°, whilst with concentrated alkali the carbethoxyl group is eliminated, giving 2-keto-1 : 3 : 4-naphthisotriazine-6-sulphonic acid, m. p. about 330°. On reduction by sodium amalgam, the hydrazino-compound loses its sulphonic acid group, giving 1-amino-2- $\alpha\beta$ -dicarbethoxyhydrazinonaphthalene, m. p. 147°, which on treatment with hydriodic acid and acetic acid gives 2-methyl- α -naphthiminazole, and on treatment with piperidine or concentrated alkali give, similarly to the sulphonic acids above mentioned, ethyl-2-keto-1 : 3 : 4-naphthisotriazine-4-carboxylate, m. p. 272—273°, and 2-keto-1 : 3 : 4-naphthisotriazine, m. p. 299°. $\beta\beta$ -Dinaphthylamine and ethyl azodicarboxylate give a small yield of an additive product, $\text{C}_{32}\text{H}_{35}\text{O}_8\text{N}_5$, m. p. 250—252°.

[With MÖHL.]—9-Aminoanthracene combines with ethyl azodicarboxylate, forming 9-amino-10- $\alpha\beta$ -dicarbethoxyhydrazinoanthracene, m. p. 199°, which gives a *monoacetyl* derivative, m. p. 277° (decomp.), and a *diacetyl* derivative, m. p. 219—220° (decomp.), and is convertible into anthraquinone by way of 9 : 10-anthrylenediamine. It also forms an additive product, m. p. 220°, with carbethoxycarbimide.

[With AUBART.]—Ethyl α -phenylprozan- $\beta\gamma$ -dicarboxylate,



m. p. 138°, and ethyl α -p-tolylprozan- $\beta\gamma$ -dicarboxylate, m. p. 113°, are formed by the action of ethyl azodicarboxylate on aniline

and *p*-toluidine, respectively. The latter ester decomposes on heating into ethyl hydrazodicarboxylate and an oil from which *p*-toluidine, ethyl *p*-tolylcarbamate, and *p*-azotoluene can be isolated.

[With ECKELMANN.]—Ethyl azodicarboxylate and *p*-xylylidine form 3-amino-6- $\alpha\beta$ -dicarbomethoxyhydrazino-*p*-xylene, m. p. 117°, which crystallises from acetonitrile with 1 mol. of solvent, and gives a crystalline *hydrochloride* and *oxalate*, m. p. 176°. On treatment with acetic anhydride, it yields an *acetyl* derivative, m. p. 193°, and with acetic and hydriodic acid it is hydrolysed with the formation of 3:6-diamino-*p*-xylene; sulphuric acid converts the hydrazino-compound into *p*-xyloquinone. *p*-Xylylidine unites with two molecules of the azo-ester, giving a compound, $C_{20}H_{31}O_8N_5$, m. p. 168° (decomp.), from which one molecule of the azo-ester is easily removed with the formation of the preceding hydrazino-compound.

[With KLEINFELLER.]—The azo-ester combines with dimethyl- β -naphthylamine, giving 2-dimethylamino-1- $\alpha\beta$ -dicarbomethoxyhydrazinonaphthalene, m. p. 163.5° (*perchlorate*, m. p. 124°), the constitution of which follows from its formation from 2-amino-1- $\alpha\beta$ -dicarbomethoxyhydrazinonaphthalene by methylation. Methyl azodicarboxylate and dimethyl- α -naphthylamine yield 1-dimethylamino-4- $\alpha\beta$ -dicarbomethoxyhydrazinonaphthalene, m. p. 154° (*hydrochloride* decomposes at 100°), and methyl azodicarboxylate and monomethyl- α -naphthylamine yield 1-methylamino-4- $\alpha\beta$ -dicarbomethoxyhydrazinonaphthalene, m. p. 193°; both the mono- and di-methyl compounds are produced on methylation of 1-amino-4- $\alpha\beta$ -dicarbomethoxyhydrazinonaphthalene, m. p. 203–204°, by means of methyl iodide.

[With WACKERMANN.]—2-Amino-1- $\alpha\beta$ -dicarbomethoxyhydrazinonaphthalene, m. p. 210°, gives a *hydrochloride*, m. p. 218°, and an *acetyl* derivative, m. p. 244°, and when treated with piperidine yields a substance, $C_{11}H_9ON_3$, m. p. 315°. On oxidation with hydrogen peroxide, it gives methyl 3-hydroxy- α -naphthatriazole-2:3-dicarboxylate, m. p. 117°.

[With SÖRENSEN.]—1-Amino-4- $\alpha\beta$ -dicarboxymethylamidohydrazinonaphthalene, m. p. 214°, and 1-amino-4- $\alpha\beta$ -dicarboxyethylamidohydrazinonaphthalene, m. p. 213°, are obtained from α -naphthylamine and the appropriate azodicarboxylamide, and can be oxidised to α -naphthaquinone. 2-Amino-1- $\alpha\beta$ -dicarboxymethylamidohydrazinonaphthalene, m. p. 230°, is prepared from β -naphthylamine and azodicarboxymethylamide; on treatment with alkali it yields methyl-1- α -naphthiminiazolonecarbamide, m. p. 220–221°, and, on treatment with hydriodic acid and acetic acid, gives α -naphthiminiazolone (1:2-naphthylenecarbamide), m. p. 377°, which was prepared also from 1:2-naphthylenediamine and carbonyl chloride for comparison.

[With KLEINFELLER.]—Azodibenzoyl unites with dimethyl- β -naphthylamine to give an *additive* product, $C_{26}H_{23}O_2N_3$, m. p. 214–215°, which forms both a *hydrochloride* and a *potassium* compound.

[With FULDNER.]—An additive reaction takes place between

ethyl azodicarboxylate and ethyl β -aminocrotonate, but the product is not crystalline. On acid hydrolysis, however, it gives *ethyl α -NN'-dicarbethoxyhydrazinoacetoacetate*, m. p. 75° . *Ethyl β -amino- α -NN'-dicarbomethoxyhydrazinocrotonate* has m. p. 140° , and its hydrolysis product, *ethyl α -NN'-dicarbomethoxyhydrazinoacetoacetate*, has m. p. 113° .

Ethyl acetoacetate reacts directly with ethyl azodicarboxylate, giving ethyl α -NN'-dicarbethoxyhydrazinoacetoacetate, and acetylacetone gives β -dicarbethoxyhydrazinoacetylacetone, m. p. 123° , and β -dicarbomethoxyhydrazinoacetylacetone, m. p. 120° , on treatment with the appropriate azo-ester. C. K. I.

Catalytic Preparation of Azobenzene and Aniline. II. C. O. HENKE and O. W. BROWN (*J. Physical Chem.*, 1922, **26**, 631—638; cf. this vol., i, 586).—A continuation of work previously published on the reduction of nitrobenzene in the presence of metallic catalysts. The method of procedure is the same as that previously adopted, and in the present work the effect of using thallium and gold as catalysts has been investigated. Thallium prepared from thallic oxide at 260° is shown to be an excellent catalyst for the reduction of nitrobenzene to azobenzene. With a rate of flow of 4.1 grams of nitrobenzene per hour with a 13% excess of hydrogen a material yield of 90.2% of azobenzene and 4.3% of aniline is obtained. The activity of the thallium catalyst decreases very rapidly with use, and this is probably caused by it melting and running together. Gold has a high catalytic activity for producing aniline which decreases with use. With this metal as catalyst, the yield of aniline at 355° is almost quantitative.

J. F. S.

The Reaction between Azobenzene Hydrochloride and Aromatic Hydrocarbons. II. RUDOLF PUMMERER, JOSEF BINAPFL, KARL BITTNER, and KARL SCHUEGRAF (*Ber.*, 1922, **55**, [B], 3095—3104).—It has been shown previously (this vol., i, 24) that azobenzene reacts with benzene in the presence of aluminium chloride and hydrogen chloride to give *p*-aminodiphenyl as main product. The examination of the change has been extended, whereby it is found that the *p*-aminophenyl residue can be conveniently introduced into many aromatic compounds by the help of azobenzene.

In the previous communication (*loc. cit.*), the carbonium formula has been suggested tentatively for azobenzene hydrochloride, $\left[\text{C}_6\text{H}_4\cdot\text{NH}\cdot\text{N}\cdot\text{C}_6\text{H}_4\leq^{\text{H}} \right] \text{Cl}$. An analogy between the compound and triphenylcarbonium chloride is found in the observation that they yield dark brown solutions in phenol or *p*-cresol, whereas only a slight deepening of colour is observed in other solvents. Benzylideneaniline and benzophenoneanil, which are constitutionally closely related to azobenzene, do not show this colour change with phenol and hydrogen chloride; they do not act as phenylating agents in the Friedel-Crafts' reaction.

The reaction between azobenzene hydrochloride and toluene in

the presence of aluminium chloride is more vigorous than that observed with benzene, so that in order to avoid the hydrogenating action of toluene and aluminium chloride the temperature should not be allowed to rise above 10–15°. The product consists of a mixture of the hydrochlorides of 4'-amino-4-methyldiphenyl, benzidine, aniline, and possibly semidine bases from which the former is most conveniently separated by fractional sublimation at 190–200°/20 mm. (the temperature being that of the bath). 4'-Amino-4-methyldiphenyl, $C_6H_4Me \cdot C_6H_4 \cdot NH_2$, has m. p. 98·5–99°, in agreement with the observations of Kliegl and Huber (A., 1920, i, 835).

o-Azotoluene hydrochloride is transformed by benzene in the presence of aluminium chloride into the *hydrochloride* of 4-amino-3-methyldiphenyl which is isolated from the crude product of the reaction by fractional sublimation in a vacuum. 4-Amino-3-methyldiphenyl, $C_6H_5 \cdot C_6H_3Me \cdot NH_2$, is a pale yellow, viscous liquid, b. p. 190–191°/15 mm., which does not solidify when placed in a freezing mixture. Its *acetyl* derivative forms colourless crystals, m. p. 165·5°, whereas the *benzylidene* compound crystallises in yellow leaflets, m. p. 108·5°.

The action of naphthalene on azobenzene hydrochloride in the presence of aluminium chloride has been examined in carbon disulphide solution; the yields of the products and the success of the experiments depend greatly on the purity of the reagents. The crude product is a mixture of the hydrochlorides of benzidine and *p*- α -naphthylaniline with *naphthylazobenzene* and *dinaphthylazobenzene* (the azo-compounds have only been examined qualitatively up to the present). *p*- α -Naphthylaniline, $C_{10}H_7 \cdot C_6H_4 \cdot NH_2$, crystallises in colourless leaflets, m. p. 94–95°; it yields a *benzylidene* compound, pale yellow crystals, m. p. 164·5°.

Azobenzene hydrochloride and diphenyl yield 1-phenyl-4-*p*-aminophenylbenzene, $C_6H_4Ph \cdot C_6H_4 \cdot NH_2$, silvery leaflets, m. p. 198° (in an atmosphere of carbon dioxide). The base yields solid yellow diazonium salts which are relatively very stable and couple with R-salt with the formation of a bluish-red dye. The *diazonium sulphate* is deaminated by an alkaline solution of sodium stannite with the formation of 1 : 4-diphenylbenzene, m. p. 209°. H. W.

Attempts to Prepare Red Sulphide Dyes. II. Mercaptan Derivatives of Azo-dyes. EDWIN ROY WATSON and SIKHIBHUSHAN DUTT (T., 1922, 121, 2414–2419).

Some Arylazoglyoxalines. FRANK LEE PYMAN and LAURENCE BARNETT TIMMIS (*J. Soc. Dyers and Col.*, 1922, 38, 269–272).—The arylazoglyoxalines of the type
$$\begin{array}{c} CH \cdot NH \\ | \\ CH \cdots N \end{array} > C \cdot N : NR,$$

where R is an aryl group, formed by coupling glyoxaline with diazonium salts in alkaline solution, are produced in widely varying yield according to whether the diazonium compound contains an ortho-substituent or not. Thus the yield of 2-benzeneazoglyoxaline is 74% of the theory, 2-*p*-bromobenzeneazoglyoxaline

85%, 2-*p*-tolueneazoglyoxaline 84%, 2-*p*-ethoxybenzeneazoglyoxaline 64%, and 2-*p*-sulphobenzeneazoglyoxaline 52%, as against 2-*o*-tolueneazoglyoxaline 26%, and 2-*o*-methoxybenzeneazoglyoxaline 10%. The yields of 2-aminoglyoxaline, formed by reduction with stannous chloride of such arylazoglyoxalines as have a para-substituent in the benzene ring also vary widely, ranging from only 15% from 2-*p*-tolueneazoglyoxaline to 26% from the *p*-ethoxy-compound, 43% from the *p*-sulpho-compound, and 56% from the *p*-bromo-compound. Those not containing a para-substituent give under similar treatment 65–75% yields of diaminophenylglyoxalines. These diamines cannot be tetrazotised, as the glyoxaline amino-group does not react normally with nitrous acid. The arylazoglyoxalines dye wool brownish-yellow shades, but the colours are not fast. 2-*o*-Methoxybenzeneazoglyoxaline forms orange prisms, m. p. 161° (corr.), which on reduction with stannous chloride yield 2:4'-diamino-4-m-methoxyphenylglyoxaline, isolated as its dihydrochloride, white needles, m. p. 268° (corr., decomp.). It also forms a picrate, m. p. 202° (corr.), and a sparingly soluble sulphate. 2-*p*-Ethoxybenzeneazoglyoxaline forms brownish-red plates, m. p. 216° (corr.).
G. F. M.

The Triazo-group. XXII. Cinnamic Acid Chlorohydrin and its Conversion into α -Triazo- β -hydroxy- β -phenylpropionic Acid. MARTIN ONSLOW FORSTER and WILLIAM BRISTOW SAVILLE (T., 1922, 121, 2595–2601).

The Coagulation of Proteins by Heat. W. W. LEPESCHKIN (*Biochem. J.*, 1922, 16, 678–701).—The coefficient of denaturation is equal to 1.5–2.5 per one degree. From the study of the influence of alkalis and acids on denaturation, it is concluded that denaturation is a weak hydrolysis of protein. The denaturation of protein is increased by the presence of salts—potassium thiocyanate has a greater effect than potassium sulphate and potassium chlorate takes the middle position, that is, the effect depends on the lyotropic properties of the salts. The coagulation of denaturated protein proceeds at a certain temperature considerably more rapidly than the denaturation at the same temperature if the protein solution contains a sufficiently large amount of salt. The temperature coefficient of coagulation of denaturated albumin is greater than that of arsenic trisulphide or lecithin, but is nearer to that of lecithin, which occupies an intermediate position between a suspensoid and an emulsoid. Acid strongly increases and alkali strongly diminishes the coagulation rate of denaturated albumin. The increase, however, is not proportionate to the concentration of the hydrogen or hydroxyl ions, and is evidently due to the formation of acid and alkali compounds of the denaturated protein. The colloidal state of the acid compounds is nearer to that of a typical suspensoid, whilst that of alkali compounds is nearer to that of an emulsoid. The colloidal state of the acid compounds of denaturated albumin is not identical with that of the denaturated acid compounds of native albumin formed in the presence of the same concentration of acid. The coagulation velocity of denaturated albumin formed

in the presence of potassium chloride is greater than the coagulation velocity of denaturated albumin formed when the salt is not present. Serum-albumin and egg-albumin are altered after prolonged dialysis in such a manner that after denaturation they show a greater susceptibility to salts than before. This is not in agreement with the observations of Pauli and Handovsky. The action of the kations on the velocity of coagulation of denaturated albumin is not proportional to their valency; tervalent kations produce an acceleration which is almost the same as that produced by univalent ions, and consequently the coagulation of denaturated albumin cannot be regarded simply as a process of electrical discharge of protein particles by the ions, but must be held also to be a chemical phenomenon. S. S. Z.

Adsorption of Proteins, Ferments, Toxins, and Sera by Aluminium Hydroxide. M. A. RAKUSIN (*Z. Immunit.*, 1922, **34**, 155—193; from *Chem. Zentr.*, 1922, iii, 644).—Albumin in egg-white solution is separated into two components by anhydrous aluminium hydroxide. The two components differ in optical rotatory power. Casein is adsorbed without separation. Chondrin is separated from chondroitin-sulphuric acid which remains in solution whilst the colloidal chondrin residue is irreversibly adsorbed. Pepsin, trypsin, and pancreatin are partly adsorbed. Papain in aqueous solution is not adsorbed. Diastase is decomposed. Koch tuberculin and Denys tuberculin may be distinguished through their adsorption by aluminium hydroxide. Pöhl spermin, diphtheria antitoxin, and pepsin-fibrin peptone all undergo separation into simpler components on treatment with aluminium hydroxide.

G. W. R.

The Nitrogen Distribution in Bence Jones's Protein. A New Colorimetric Method for the Estimation of Tryptophan in Protein. ERY LÜSCHER (*Biochem. J.*, 1922, **16**, 556—563).—Bence Jones's protein differs from all the proteins analysed up to the present time, not only in its physical behaviour, but also in its nitrogen distribution as determined by Van Slyke's method. There is, however, some evidence that the same protein appears in the urine in all cases of Bence Jones's proteinuria.

The author proposes to use benzaldehyde instead of formaldehyde in Fürth's and Sieben's colorimetric method for the estimation of tryptophan (*A.*, 1921, ii, 71).

S. S. Z.

The Content of the Proteins of the Lens in Histidine, Arginine, and Lysine. A. JESS (*Z. physiol. Chem.*, 1922, **122**, 160—165).—The three proteins in the lens, α -crystallin, β -crystallin, and albumoid contain, respectively, 3.8%, 2.6%, and 2.7% of histidine, 8.0%, 7.5%, and 10.3% of arginine, and 3.7%, 4.6%, and 3.8% of lysine.

W. O. K.

The Physical Chemistry of Hæmoglobin in Blood. W. E. L. BROWN and A. V. HILL (*Arch. Néerland. physiol.*, 1922, **7**, 174—178).—It has been suggested that hæmoglobin is polymerised by salts, and that it combines with oxygen according to the equation

$\text{Hb}_n + n\text{O}_2 \rightleftharpoons (\text{HbO}_2)_n$. This view is supported by measurements of the heat of reaction of hæmoglobin with oxygen. W. O. K.

Nucleic Acid-Protein Compounds. H. STEUDEL and E. PEISER (*Z. physiol. Chem.*, 1922, **122**, 298—306).—In order to elucidate the structure of nucleoproteins, presumably salts of nucleic acid and protein, salts of this type have been prepared from clupein and guanylic acid, from clupein and yeast-nucleic acid, and from clupein and eosin, and their content in phosphorus and in nitrogen has been determined. W. O. K.

The Diastatic Action of Albumoses and Amino-acids. W. BIEDERMANN (*Arch. Néerland. physiol.*, 1922, **7**, 151—156).—If blood-fibrin is heated with water in a sealed tube at $160\text{--}170^\circ$, the resulting solution after filtration shows a definite diastatic action on starch. This does not take place in the absence of oxygen or of sodium chloride. Certain amino-acids, for example, glycine and leucine, have a similar action, and with these, too, the presence of oxygen and of salt ions is necessary. W. O. K.

Invertase. III. RICHARD WILLSTÄTTER, JOHANNA GRASER, and RICHARD KUHN (*Z. physiol. Chem.*, 1922, **123**, 1—78; cf. A., 1921, i, 823; this vol., i, 598).—Preparations of autolysed yeast change with age in such a way that the invertase becomes practically completely precipitable by lead acetate. This, in combination with the methods previously used (*loc. cit.*)—particularly adsorption with aluminium hydroxide and dialysis—gives a means of obtaining extremely active invertase preparations. The precipitation by lead acetate is affected also by other factors such as incidental substances present in the invertase solution, particularly phosphates. The phosphorous content of these very highly active invertase preparations is very low.

The activity of invertase appears to be independent of the other compounds which accompany it, and also independent of the state of aggregation. Incidental impurities are, however, important in this respect, that the very pure preparations are much less stable. They can be protected by the addition of, for example, calcium chloride or yeast-gum.

Purified invertase has an optimum activity at P_H 4.6. Experiments carried out on the kinetics of the reaction indicate that it is unimolecular. W. O. K.

The Phosphorus Content of Purified Saccharase Preparations. H. VON EULER and O. SVANBERG (*Arkiv Kem. min. Geol.*, 1922, **8**, No. 12, 1—13).—By estimating the concentration of silver ions electrometrically, the dissociation constants of the silver salts of the following acids have been determined: cysteine, 0.89×10^{-6} ; combined nucleic acid, 0.28×10^{-7} ; guanylic acid, 4.2×10^{-6} ; inosic acid, 9.3×10^{-5} ; adenylic acid, 1.85×10^{-3} ; guanosine, 1×10^{-4} ; adenosine, 5.0×10^{-3} ; caffeine, 4.9×10^{-2} ; guanine, about 10^{-4} ; uric acid, about 10^{-4} . These may be compared with the value of 0.87×10^{-6} obtained for a highly purified saccharase. It is probable that the presence in the saccharase molecule of

components of the nature of nucleic acids may explain the poisoning of the enzyme by silver salts, as these acids have a strong affinity for silver ions.

Purified saccharase solutions after exhaustive dialysis leave an ash which can be completely accounted for by the phosphoric acid present, indicating the absence of any corresponding metal as base.

W. O. K.

Enzyme Chemistry. HANS VON EULER and KARL MYRBÄCK (*Arkiv Kem. Min. Geol.*, 1922, 8, No. 17, 1—15).—By acting on a purified saccharase solution with *Bacillus macerans*, or with the digestive enzyme from *Helix pomatia*, and then dialysing, the authors have obtained a preparation of only slightly diminished activity, but with a much smaller dry residue. The activity of the material left behind was therefore much increased. The enzyme from *Aspergillus oryzae* and also Taka diastase gave similar results.

In presence of phenol, dextrose is more easily esterified by phosphate under the influence of yeast than is maltose. In the presence of toluene, the initial fermentation of dextrose and maltose is inhibited much more than that of saccharose.

W. O. K.

Reductases. I. Some Conditions of the Activity of Starch Reductase. I. A. SMORODINCEV (*Z. physiol. Chem.*, 1922, 123, 130—144).—Estimations made of the amount of nitrite produced from nitrate by an extract of potatoes in presence of acetaldehyde indicate an increase in the reaction with increase of the amount of ferment used, but not nearly so marked an increase with increasing amount of aldehyde. Neither formaldehyde nor vanillin is so efficient as acetaldehyde. With acetaldehyde, the reaction ceases after thirty to sixty minutes. Atmospheric oxygen does not appear to be harmful, and very dilute acid is favourable, although greater concentrations markedly retard the reaction.

W. O. K.

Synthesis of Aromatic Arsinic Acids. HEINRICH BART (*Annalen*, 1922, 429, 55—103).—The method of preparing arylarsinic acids by the interaction of aromatic diazonium solutions with acid or alkaline arsenite solutions, which has been widely used of recent years, was nevertheless originated by the author (D.R.-P. 250264).

Details are given for the preparation of a number of arylarsinic acids certain of which are new: phenylarsinic acid, *o*-tolylarsinic acid, *m*-tolylarsinic acid, *p*-tolylarsinic acid, *p*-ethoxyphenylarsinic acid, *p*-acetylaminophenylarsinic acid, *o*-chlorophenylarsinic acid, needles, m. p. 181°, *m*-chlorophenylarsinic acid, m. p. 175°, *p*-chlorophenylarsinic acid, *o*-carboxyphenylarsinic acid, *m*-carboxyphenylarsinic acid, needles which lose water at 250°, *p*-carboxyphenylarsinic acid, *p*-phenylenediarsinic acid, *o*-hydroxyphenylarsinic acid, m. p. 191°, *p*-hydroxyphenylarsinic acid, *o*-nitrophenylarsinic acid, needles, m. p. 233°, *m*-nitrophenylarsinic acid, needles, m. p. about 200°, *p*-nitrophenylarsinic acid, m. p. above 300° (decomp.), *op*-dinrophenylarsinic acid, 5-nitro-2-hydroxyphenylarsinic acid, decomp.

250°, *o*-nitro-*p*-hydroxyphenylarsinic acid, m. p. 228°, and *m*-nitro-*p*-hydroxyphenylarsinic acid.

Diphenylarsinic acid, m. p. 178°, is obtained from benzene-diazonium chloride and phenylarsine oxide. *p*-Nitrophenylarsenious acid is obtained by reduction of *p*-nitrophenylarsinic acid; on treatment with a diazo-solution prepared from *p*-nitroaniline it yields *di-p*-nitrophenylarsinic acid, m. p. 278°. C. K. I.

Synthesis of Aromatic Arsinic Acids by the Interaction of isoDiazo-compounds with the Arsenite-ion. HEINRICH BART (*Annalen*, 1922, 429, 103—113).—The same end-product is obtained if in the general reaction referred to in the preceding abstract the diazonium solution is replaced by alkaline isodiazotates. Details are given for the preparation by this method of the following substances: *o*-nitrophenylarsinic acid, *m*-nitrophenylarsinic acid, *p*-nitrophenylarsinic acid, phenylarsinic acid, *o*-carboxyphenylarsinic acid, and *p*-carboxyphenylarsinic acid. C. K. I.

Two New Syntheses of *mm'*-Diamino-*pp'*-dihydroxyarsenobenzene (Salvarsan Base). HEINRICH BART (*Annalen*, 1922, 429, 113—122).—The first synthesis consists in converting 3-amino-6-hydroxyazobenzene into 4-hydroxy-3-benzenediazophenylarsinic acid (cf. preceding abstracts) which on reduction yields the required substance and two molecules of aniline.

The starting point of the second synthesis is *p*-nitro-*o*-aminophenol, which is condensed with ethyl chloroformate and the urethane, m. p. 208°, reduced to give *p*-amino-*o*-carbethoxyaminophenol. The latter is readily converted into *m*-carbethoxyamino-*p*-hydroxyphenylarsinic acid, m. p. 200°, which on reduction gives the urethane of the required base. C. K. I.

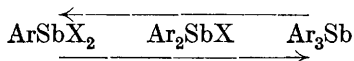
The Colloidal Properties of Arsphenamine [Salvarsan] and Allied Products. GEORGE W. RAIZISS and JOSEPH L. GAVRON (*J. Pharm. Expt. Ther.*, 1922, 20, 163—179).—Experiments on the dialysis of 3:3'-diamino-4:4'-dihydroxyarsenobenzene hydrochloride (salvarsan) through a parchment membrane indicate that the solution in water is of a colloidal nature as it diffuses through the membrane but slightly, whilst in methyl-alcoholic solution it diffuses more readily. The disodium salt diffuses about four times as quickly as the hydrochloride. By dialysing silver sodium salvarsan, it is found that the arsenic diffuses to the extent of about 26% in thirty-six hours, whilst the silver remains completely behind. Similar results have been found with gold sodium salvarsan. This is taken to indicate that in these compounds the silver or gold is probably in a colloidal form and not chemically combined with the arsenic organic compound. W. O. K.

The Sulphur Content of Arsphenamine [Salvarsan] and its Relation to the Mode of Synthesis and Toxicity. III. WALTER G. CHRISTIANSEN (*J. Amer. Chem. Soc.*, 1922, 44, 2334—2342; cf. A., 1921, i, 370; this vol., i, 186, 601; Fargher and Pyman, T., 1920, 117, 370).—It is shown that in reducing 3-nitro-4-hydroxyphenylarsinic acid to salvarsan the formation of relatively

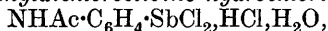
toxic products with a high sulphur content is not due to impurities in the commercial sodium hyposulphite. The salvarsan base is fairly uniform in regard to toxicity and sulphur content irrespective of the period of formation during the reduction. Amino-hydroxyarseno-compounds in general contain the fewest sulphur atoms when prepared from the amino-acids. Fixation of the hydroxyl hydrogen atom in the nitrohydroxyarsinic acids tends to make the hyposulphite reduction abnormal, and the products, when they can be isolated, contain more sulphur than analogous substances prepared without fixation of this hydrogen atom. The hydroxyl hydrogen ortho to the nitro-group seems to play an important rôle in the formation of arseno-compounds of the type under consideration. The sulphonic acid group found in certain samples of arspenamine probably enters the ring by way of the nitrogen atom with the intermediate formation of a sulphamic acid.

Compounds described are: 3-nitro-4-methoxyphenylarsinic acid; 3-nitro-4-hydroxy-5-methylphenylarsinic acid; 4-methoxy-5-methylphenylarsinic acid and its 3-nitro-derivative; 3-nitro-4-carbomethoxyphenylarsinic acid; 3-nitro-4:6-dimethoxyphenylarsinic acid; 3-acetyl-amino-4-methoxyphenylarsinic acid; 3:3'-diamino-4:4'-dimethoxyarsenobenzene dihydrochloride; 3:3'-diamino-4:4'-dihydroxy-5:5'-dimethylarsenobenzene dihydrochloride; and 3:3'-diamino-4:4':6:6'-tetramethoxyarsenobenzene dihydrochloride. W. G.

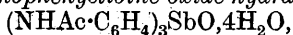
Aromatic Antimony Compounds. HANS SCHMIDT (*Annalen*, 1922, 429, 123—152).—VI. *New Reciprocal Interconversions of Mono-, Di-, and Tri-arylantimony Compounds.*—The examples given in this paper show that it is possible to realise the reciprocal interconversion, in the sense of the formulæ following, of mono-, di-, and tri-aryl derivatives of tervalent antimony.



p-Acetylaminophenyldichlorostibine hydrochloride,



is obtained as colourless crystals, sintering at 125°, by reducing *p*-acetylaminophenylantimonious acid with stannous chloride. It decomposes on keeping, but free *p*-acetylaminophenyldichlorostibine, which is obtained from it by rubbing with methyl alcohol, is quite stable, forming colourless crystals, m. p. 200°. This substance on treatment with ammonia yields *p*-acetylaminophenylstibinous oxide, $\text{NHAc} \cdot \text{C}_6\text{H}_4 \cdot \text{SbO}, \text{H}_2\text{O}$, sinters at 180°, which on boiling with methyl alcohol is converted into *tri-p*-acetylaminophenylstibine. This crystallises from methyl alcohol as needles, with $0.5\text{H}_2\text{O}$, sintering at 205°, m. p. 270°, from acetone in an anhydrous form, m. p. 268°, and from aqueous acetone in a form containing $(2/3)\text{H}_2\text{O}$, which sinters at 225°. On oxidation with hydrogen peroxide it yields *tri-p*-acetylaminophenylstibine oxide hydrate,



m. p. 200°.

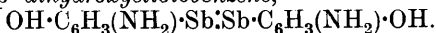
Tri-*p*-acetylaminotriphenylstibine, on treatment with methyl alcoholic hydrogen chloride, passes into *di-p*-acetylaminophenylchlorostibine hydrochloride, m. p. 135°, which yields *di-p*-acetylaminophenylhydroxystibine, $(\text{NHAc}\cdot\text{C}_6\text{H}_4)_2\text{Sb}\cdot\text{OH}\cdot 1\cdot5\text{H}_2\text{O}$, m. p. about 130°, on treatment with methyl-alcoholic sodium hydroxide. Any of these compounds on oxidation with hydrogen peroxide under appropriate conditions gives *di-p*-acetylaminophenylstibinic acid, $(\text{NHAc}\cdot\text{C}_6\text{H}_4)_2\text{SbO}\cdot\text{OH}\cdot 3\text{H}_2\text{O}$, which sinters and turns brown at 235°.

Diphenylacetoxystibine, needles, m. p. 132°, is produced from triphenylstibine when the latter is heated with methyl alcoholic hydrochloric acid and the product obtained after making alkaline is crystallised from acetic acid. Triphenylstibine diacetate, $\text{Ph}_3\text{Sb}(\text{OAc})_2$, m. p. 215°, is formed when triphenylstibine is oxidised in acetone solution with hydrogen peroxide and the product treated with acetic acid.

Derivatives of diphenylhydroxystibine readily pass on treatment with such reagents as formic, acetic, and hydrochloric acids into derivatives of phenyldihydroxystibine.

VII. *p*-Amino-, *p*-Hydroxy-, and *p*-Ethoxy-phenylantimonious Acids. — *p*-Aminophenylstibinic acid, $3\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{SbO}(\text{OH})_2\cdot 4\text{H}_2\text{O}$, is obtained by hydrolysis of *p*-acetylaminostibinic acid, and on treatment with hydrochloric acid gives *p*-aminophenyltetrachlorostibine hydrochloride, $\text{NH}_2\text{Cl}\cdot\text{C}_6\text{H}_4\cdot\text{SbCl}_4\cdot 1\cdot5\text{H}_2\text{O}$, m. p. 155° (decomp.). *p*-Hydroxyphenylstibinic acid, $3\text{OH}\cdot\text{C}_6\text{H}_4\cdot\text{SbO}(\text{OH})_2\cdot 6\text{H}_2\text{O}$, is prepared from the amino-compound by the diazo-reaction, and gives a characteristic pyridine double salt, m. p. 176°. *p*-Ethoxyphenylstibinic acid, $3\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{SbO}(\text{OH})_2\cdot 2\text{H}_2\text{O}$, is obtained by the diazo-reaction from *p*-phenetidine; it forms a colourless powder which turns dark but does not melt at 270°.

VIII. *mm'*-Diamino-*pp'*-dihydroxystibiobenzene. — *m*-Nitro-*p*-hydroxyphenylstibinic acid on reduction by stannous chloride gives *m*-amino-*p*-hydroxyphenyldichlorostibine hydrochloride, m. p. 165—170°, which on further reduction with hypophosphite yields *mm'*-diamino-*pp'*-dihydroxystibiobenzene,



C. K. I.

Organo-metallic Compounds. III. The Mechanism of the Wurtz-Fittig Synthesis. HANS HEINRICH SCHLUBACH and EDUARD C. GOES (*Ber.*, 1922, **55**, [B], 2889—2902; cf. A., 1920, i, 19).—The extension of the observations of the action of carbon monoxide on sodium alkyls (Schlubach, *loc. cit.*) to the Wurtz-Fittig synthesis leads the authors to the following general conception of the course of the latter change. The primary phase consists in the transformation of alkyl haloid into the corresponding radicle: $\text{R}\cdot\text{Hal} + \text{Na} \longrightarrow \text{R}\cdot + \text{NaHal}$. In the second phase, the radicle may combine with sodium to yield the sodium alkyl, RNa , may become polymerised to the saturated hydrocarbon, $\text{R}\cdot\text{R}$, or, if a hydrogen atom is readily displaced, may become transformed into $\text{R}_{-\text{H}}$ and $\text{R}_{+\text{H}}$. In the third phase, the sodium alkyl

may react with alkyl haloid to give a saturated hydrocarbon, $RNa + RHal \rightarrow R \cdot R + NaHal$, or the transformation to R_{-H} and R_{+H} , may again occur. In the aliphatic series from ethyl upwards, the last is the main change. With methyl, on the other hand, this change is not observed, the main result being the union of the alkyl radicles with production of ethane. With increasing length of the aliphatic hydrocarbon chain, the transformation becomes less marked and the union of the radicles more pronounced, so that (with cetyl bromide, for example) good yields of saturated hydrocarbons are ultimately obtained. In the aromatic series, the formation of sodium aryls takes place smoothly; the slight reactivity of aromatically combined halogen makes the further production of compounds, $R \cdot R$, difficult, whereas it is easy with aliphatic haloids. Complications of the reaction which are due to the solvent can also arise. Thus sodium ethyl reacts with diethyl ether to yield ethylene and ethane in accordance with the equation $Et \cdot O \cdot Et + NaEt = NaOEt + C_2H_4 + C_2H_6$. With benzene and its homologues, a reaction can also occur: $R \cdot Na + R'H = R \cdot H + R'Na$ (cf. Schorigin, A., 1910, i, 547).

The characteristic phenomena on which the hypothesis of the pre-existence of free radicles is based are found, not only with sodium alkyls, but also with many organometallic compounds. The reducing properties of the organometallic derivatives of zinc and magnesium are well known, and Späth (A., 1914, i, 1) has observed that the same anomalous products are obtained when alkyl haloids react with Grignard's reagents and with sodium alkyls. It therefore appears probable that free radicles are also formed in this case; Hess's recent assumption of the existence of magnesium hydrogen haloids (A., 1921, i, 777) appears to be unnecessary.

Blue products are invariably produced during the course of a Wurtz-Fittig synthesis. These have been considered by Schorigin (A., 1908, i, 866) to be entirely inorganic. With this view the authors concur, since examination of the product from benzyl chloride and sodium shows it to be discoloured sodium chloride.

When bromobenzene is added gradually to sodium beneath dry benzene in an atmosphere of carbon monoxide, absorption of the gas begins after about two hours and is complete within about eight days. The products are benzoic acid, diphenyl, benzophenone, and triphenylcarbinol. Ethyl bromide, sodium, and carbon monoxide in the presence of ethyl ether give ethylene, diethyl ketone, and triethylcarbinol.

The hope of isolating the cetyl radicle has led the authors to study the action of sodium on cetyl bromide in the presence of a little ether; carbon monoxide is not absorbed during the change, and the crystals of metallic lustre which separate do not yield any organic substance when treated with water. At a somewhat higher temperature, dicetyl, m. p. 70.5° , is obtained in 88% yield.

Definite evidence of the transitory existence of sodium alkyls in the Wurtz-Fittig synthesis is found in the observation that benzyl chloride and sodium give an immediate wine-red coloration

(benzyl sodium in contrast to the other alkyl sodium compounds is red in colour) which gradually passes to the customary dark blue.

A mixture of equivalent quantities of ethyl bromide and bromobenzene is converted by sodium in an atmosphere of carbon monoxide into benzoic acid, benzophenone, and triphenylcarbinol; it thus appears that under similar conditions sodium phenyl is produced more readily than sodium ethyl, and that unchanged ethyl bromide reacts more readily than bromobenzene with sodium phenyl. In the main, the change occurs through the phases: $\text{PhBr} + 2\text{Na} \rightarrow \text{PhNa} + \text{NaBr}$ and $\text{PhNa} + \text{EtBr} \rightarrow \text{Ph}\cdot\text{Et} + \text{NaBr}$.

The tendency of the radicles to saturate their free valency is evidenced not only by polymerisation, but also by loss of hydrogen; as a general rule, a second radicle plays the part of acceptor (for example, $2\text{C}_2\text{H}_5 \rightarrow \text{C}_2\text{H}_4 + \text{C}_2\text{H}_6$), but this rôle may also be played by a readily oxidisable material. Thus sodium ethyl and benzaldehyde, when heated in the presence of toluene, give ethylene, benzyl alcohol, and phenylethylcarbinol (cf. also Schorigin, A., 1908, i, 881). H. W.

The Preparation and Properties of Organic Stanno- and Stanni-chlorides. V. The Salts of certain Special Bases. J. G. F. DRUCE (*Chem. News*, 1922, 125, 265—267; cf. this vol., i, 639).—*Hydroxylamine stannichloride*, $(\text{NH}_2\cdot\text{OH})_2\text{H}_2\text{SnCl}_6$, forms a microcrystalline deposit from dilute hydrochloric acid, soluble in cold water, but hydrolysed in the hot. *5-Aminoquinoline stannochloride*, $\text{C}_9\text{H}_8\text{N}_2\text{H}_2\text{SnCl}_4$, forms pale yellow prisms, m. p. 160° ; *5-aminoquinoline stannichloride*, $\text{C}_9\text{H}_8\text{N}_2\text{H}_2\text{SnCl}_6$, forms orange crystals, m. p. 242° ; these give cloudy solutions in water. *6-Amino-2-methylquinoline stannochloride*, $\text{C}_{10}\text{H}_{10}\text{N}_2\text{H}_2\text{SnCl}_4$, forms felted masses of deliquescent, white crystals giving a clear solution in cold water; it decomposes at 180° . *6-Amino-2-methylquinoline stannichloride*, $\text{C}_{10}\text{H}_{10}\text{N}_2\text{H}_2\text{SnCl}_6$, forms nacreous plates, m. p. $224\text{—}228^\circ$ (decomp.), soluble in cold water to a clear solution which slowly deposits hydrated stannic oxide. *isoQuinoline stannichloride*, $(\text{C}_9\text{H}_7\text{N})_2\text{H}_2\text{SnCl}_6$, forms almost colourless, prismatic crystals, m. p. 265° , soluble in cold but hydrolysed by hot water.

E. H. R.

Physiological Chemistry.

Influence of Hydrogen Sulphide on Respiration. H. W. HAGGARD and Y. HENDERSON (*Amer. J. Physiol.*, 1922, **61**, 289—297).—An atmosphere containing 0.05% of hydrogen sulphide causes the death, from lung œdema, of dogs only after many hours' continued breathing, whereas a concentration of 0.1% causes death in fifteen to twenty minutes. Estimations of the carbon dioxide and oxygen content of the blood and its carbon dioxide combining power indicate that hydrogen sulphide in sufficient

amount stimulates the respiration through an action on the vagi. As a result, carbon dioxide is removed from the blood and the hydrogen-ion concentration of the blood lowered until alkalosis of sufficient degree is produced, when the stimulating action of the hydrogen sulphide is counteracted and an apnoea follows, before and during which the hydrogen sulphide of the blood is oxidised. Small amounts of hydrogen sulphide are generally without perceptible effect on the respiratory centre, whereas larger amounts paralyse respiration.

CHEMICAL ABSTRACTS.

Relation between Changes of Temperature and Consumption of Oxygen by Cold-blooded Animals. M. N. J. DIRKEN (*Arch. Néerland. physiol.*, 1922, 7, 126—131).—Measurements of the oxygen consumption of cockroaches (*Periplaneta americana*) show an increase with rise of temperature, the temperature coefficient being 4.3 between 10° and 20° and 1.7 between 20° and 30°.

W. O. K.

Gas and Electrolyte Equilibria in Blood. I. Technique for Collection and Analysis of Blood, and for its Saturation with Gas Mixtures of Known Composition. J. H. AUSTIN, G. E. CULLEN, A. B. HASTINGS, F. C. MCLEAN, J. P. PETERS, and D. D. VAN SLYKE (*J. Biol. Chem.*, 1922, 54, 121—147).—The authors describe a technique for the preliminary treatment of blood by means of which it is hoped, in conjunction with analytical methods previously described (Van Slyke and Stadie, this vol., ii, 78), to obtain accurate quantitative data concerning the various reactions involved (cf. Henderson, A., 1921, i, 473) in the respiratory changes in blood. The main features of the technique are two methods for saturating the blood with gas mixtures whereby changes in the gaseous equilibrium, due to the changes in pressure and temperature which result when the tonometer is removed from the bath, may be avoided. In the first method, the tonometer consists of two chambers connected by means of a rubber tube. When saturation is complete, the blood is run into the smaller chamber, the rubber connexion is closed at two points by means of clamps, and the chambers are then separated by cutting the rubber at a point between the two clamps. Before removing the smaller chamber from the bath, the gases are displaced from it by mercury from a levelling bulb. In the second method, analysis of the gas phase is avoided by calculating the amount of carbon dioxide and oxygen taken from it by the blood during saturation. The whole technique, from the drawing of the blood to the analysis of the blood gases, is described in detail in the original, and a diagram is provided illustrating the apparatus employed. Equations necessary for the calculations involved are also developed. E. S.

Gas and Electrolyte Equilibria in Blood. II. The Reversibility of the Effects of Changes in Carbon Dioxide and Oxygen Tensions on the Carbon Dioxide Content of Defibrinated Horse Blood. JOHN P. PETERS, GLENN E. CULLEN, and J. HAROLD AUSTIN (*J. Biol. Chem.*, 1922, 54, 149—152).—No irreversible changes in the carbon dioxide capacity of defibrinated

horse blood are produced by reducing the carbon dioxide or oxygen tension to 15 mm. The reduction of the carbon dioxide capacity of dog's blood by similar treatment is probably due, as Evans (this vol., i, 890) suggests, to the formation of acid, which occurs rapidly in dog's blood. E. S.

Calcium in the Blood. P. VAN PAASSEN (*Nederland. Tijdschr. Geneeskunde*, 1921, **65**, ii, 1162—1171).—The concentration of the calcium-ions, on which the effect of the calcium content of the blood depends, in serum is given by the expression $K[H^+]/[HCO_3^-]$ where $K=350$. Thus, when the concentration of the hydrogen-ions is constant in the blood, a change in the concentration of calcium ions can be brought about only by increasing or decreasing the concentration of the hydrogen carbonate-ions.

CHEMICAL ABSTRACTS.

The Blood-sugar Content of Capillary Blood as Compared with that of Venous Blood. ISAAC NEUWIRTH and I. S. KLEINER (*J. Lab. Clin. Med.*, 1922, **7**, 495—497).—In twenty individuals the capillary blood sugar was found to parallel the venous blood sugar. The average of all twenty capillary figures for blood-sugar is 0.136% as against 0.130% for the venous. The slight difference in this sense would be expected. The blood-sugar estimations were made by the Kleiner micro-method.

CHEMICAL ABSTRACTS.

Blood-sugar. A. STASIAK (*Z. physiol. Chem.*, 1922, **123**, 104—115).—Dog's blood shows an increase of its sugar content if it be boiled with 2% hydrochloric acid before precipitating the proteins with colloidal ferric hydroxide. Blood does not contain maltose. The bound sugar probably exists as a polysaccharide. If mercuric chloride is used to precipitate the proteins, no marked increase of reducing power is caused by hydrolysis. W. O. K.

Exchange of Chlorine between the Red Blood Corpuscle and the surrounding Solution. I. The Influence of Narcotics on the Exchange of Chlorine. R. SIEBECK [in part with D. HACKMACK] (*Arch. expt. Path. Pharm.*, 1922, **95**, 93—103).—Urethane increases the permeability of the red blood-cells to chlorine-ions, and its action is parallel to its effect in inhibiting the oxidation processes in the cell. For example, both effects are reversible on removal of the urethane. Similar results are obtained by the use of other narcotics such as methyl, ethyl, propyl, *n*-butyl, and amyl alcohols, diethylurea, and phenylurea. W. O. K.

Coagulation of the Blood. II. Thrombin and Antithrombins. JOHN WILLIAM PICKERING and JAMES ARTHUR HEWITT (*Biochem. J.*, 1922, **16**, 587—598; cf. this vol., i, 393).—The failure of the blood to coagulate after the injection of thrombin is not due to the secretion by the liver of an excess of antithrombin. The antithrombin obtained from liver is a post-mortem product. Yeast and hydrolysed edestin are also capable of yielding a similar principle which is a product resulting from the hydrolysis of pro-

tein. The addition of thrombin to blood in the state of a reversible gel causes immediate coagulation. Thrombin seems to be the accelerator rather than the initiator of coagulation. S. S. Z.

The Carbamino-reaction of the Blood-proteins and their Alleged Importance in the Transport of Carbon Dioxide by the Blood. CAMILLO AUSENDA (*Biochem. Z.*, 1922, **132**, 188—196).—From experiments on blood, serum, ascites-fluid, and pleural exudate, the author finds no evidence that Siegfried's alleged "carbamino-acids" play any part in the transport of carbon dioxide. If these fluids be saturated with carbon dioxide in the presence of milk of lime, or sodium carbonate or hydroxide and the proteins then precipitated by ammonium sulphate or obtained free from simple constituents by dialysis, there is no greater quantity of carbon dioxide fixed by the protein than in the normal physiological state of the blood. H. K.

Colloidal Equilibrium of Blood Serum. ROGER FISCHER (*Compt. rend. Soc. Biol.*, 1922, **87**, 124—126).—Experiments were carried out on serum, and on the isolated proteins from serum and from egg, in order to determine whether or not there is a physical equilibrium between the albumin and globulin in the blood, the coagulation either by alcohol or by heat being examined in the presence of a 0.2% solution of gelatin. The globulin, like the whole serum, is found to be stabilised whilst the albumin becomes less stable. The globulin acts as a stabiliser for the serum-albumin, and this relationship is found to be general. The most stable ratio (50 parts of globulin to 100 parts of albumin) closely approaches that of the two proteins in the blood.

CHEMICAL ABSTRACTS.

The Separation of the Globulins of Horse's Serum. M. VILA (*Compt. rend.*, 1922, **175**, 728—731; cf. Piettre and Vila, this vol., i, 63).—The globulins in the serum may be fractionated into three groups by addition of *N*/100-hydrochloric acid and subsequent treatment of the precipitate with acetone. The fraction so obtained contains globulin which is insoluble in acid under the conditions specified by the author. Another fraction separates on elimination of the added acid. The third fraction remains in solution: it has the character of serum-albumin. H. J. E.

Cholesterol Content of Blood-serum. HERMANN STRAUSS and WOLFGANG SCHUBARDT (*Zentr. inn. Med.*, 1922, **43**, 425—432; from *Chem. Zentr.*, 1922, iii, 582).—Data are given for the cholesterol content of pathological blood-sera. From a consideration of fat exchange, it would appear that necrobiotic processes play a part in the changes in cholesterol content of sera. G. W. R.

Human Mixed Saliva. I. Determination of the Hydrogen-ion Concentration of Human Mixed Saliva. II. Variations in the Hydrogen-ion Concentration. HENRY E. STARR (*J. Biol. Chem.*, 1922, **54**, 43—54, 55—64).—I. The saliva is collected under oil to prevent loss of carbon dioxide. A portion (1 c.c.) is

diluted with freshly-boiled distilled water (9 c.c.) and the P_H estimated colorimetrically, using bromo-thymol blue (1 c.c. of a 0.01% solution) as indicator.

II. Using this method, the P_H values of 610 specimens of human mixed saliva were found to vary between 5.75 and 7.05, 86% of the specimens giving values between 6.35 and 6.80. The hydrogen-ion concentration of saliva varies directly with the alveolar carbon dioxide, increases after a meal and during exercise, and decreases as a result of voluntary deep breathing in the open air or of emotional excitement. Ingestion of large doses of sodium hydrogen carbonate decreases the salivary P_H and increases the urinary P_H .
E. S.

Metabolism of Inorganic Salts. I. The Inorganic-ion Balance of the Blood in Parathyroid Tetany. ERWIN G. GROSS and FRANK P. UNDERHILL (*J. Biol. Chem.*, 1922, 54, 105—120).—The blood of dogs with parathyroid tetany showed a low calcium and a high potassium content; the values for other inorganic ions were approximately normal. Tetany is thus allied to a disturbance in the ratio of potassium to calcium and consequently of total univalent to total bivalent ions.
E. S.

The Metabolism of Calcium. R. ROSEMAN (*Arch. Néerland. physiol.*, 1922, 7, 358—361).—The consumption of large quantities of flesh increases the excretion of calcium. A low body content of calcium increases the readiness to hay-fever, the administration of calcium chloride acting beneficially. With increased calcium in the diet there results a retention of potassium, presumably to be explained by the antagonistic physiological action of calcium and potassium, and also an increased output of sodium.
W. O. K.

Some Induced Reactions and their Analogues in the Animal Body. N. N. MITTRA and N. R. DHAR (*Z. anorg. Chem.*, 1922, 122, 146—150).—The authors point out that many substances—proteins, carbohydrates, fats, etc.—which undergo oxidation in the animal body are under ordinary conditions stable in the presence of oxygen. The oxidation of these substances is readily induced by ferrous hydroxide, and it is argued that the iron of the blood induces the oxidation in the body. In the case of oxidation, the authors find that only easily oxidisable substances can act as negative catalysts; this is supported by several examples.
W. T.

The Gonads of *Rhizostoma Cuvieri*. FELIX HAUROWITZ (*Z. physiol. Chem.*, 1922, 122, 145—159; cf. A., 1921, i, 206).—The gonads, after being freed from fat, were extracted with alcohol and with water, and in these extracts and in the residue the following substances were found on examination: potassium, sodium, magnesium, calcium, iron, chlorine, sulphate and phosphate, taurine, *o*- and *p*-cresolsulphonic acids, trimethylamine, betaine, choline, and various peptides and proteins containing alanine, tyrosine,

glutamic acid, arginine, phenylalanine, cystine, lysine, proline, and leucine. W. O. K.

Influence of the Dextrose Concentration and of the Alkalinity on Glycolysis in Vitro. P. MAURIAC and L. SERVANTIE (*Compt. rend. Soc. Biol.*, 1922, **87**, 200—201).—Experiments with blood and with various organs (lung, testes) show that the amount of dextrose that is destroyed under standard experimental conditions bears a close relation to the initial dextrose content of the solution. The glycolysis is not always proportional to the quantity of sugar. The curve of the percentage loss of sugar gives the optimum point at a concentration of dextrose of about 0.3%. Similarly, the glycolysis is dependent on the reaction of the medium, a P_H of 7.8 being the optimum. This reaction corresponds with that which has also been shown to be most favourable to the consumption by the heart of sugar from the artificial circulating fluid. CHEMICAL ABSTRACTS.

The Evolution of Oxidative Enzymes. G. MARINESCO (*Compt. rend. Soc. Biol.*, 1922, **87**, 31—34).—The author studied the oxydase reaction of various tissues, especially the nerve-tissue, in human embryos of different age and concludes that there is a double mechanism of respiration in the cell: (1) The iron plays the role of a catalyst and is present in the nucleus where there are no oxydases, and (2) the oxydase granules found in abundance in the cell are identified as mitochondria. CHEMICAL ABSTRACTS.

Rôle of Hydrogen and Hydroxyl-ion Diffusion in Nerve and Muscle Action. ELLIOT Q. ADAMS (*J. Physical Chem.*, 1922, **26**, 639—649).—A theoretical paper in which calculations have been made based on the assumptions that nerve and muscle action depend on an autocatalytic conversion of dextrose or galactose into lactic acid, kept in check by diffusion, and that the significant factors in the initiation of a response are the autocatalytic reaction and the diffusion of hydrogen and hydroxyl ions. In plasma, the reaction of which is that of normal blood, $[H^+]$ 0.45×10^{-7} , P_H 7.35, and X_H —0.55 where X_H is the hydrogen-ion potential relative to pure water at 37° , the reaction within the excitable nerve or muscle fibre is calculated to lie between $[H^+]$ 0.51×10^{-7} , P_H 7.29, X_H —0.49, and $[H^+]$ 1.03×10^{-7} , P_H 6.99, X_H —0.19. For effective stimulation, the reaction must be acidified locally within the fibre to a critical value which depends on the concentration of enzyme (lactacidase) present in the fibre, and must be more acid than the last-named figure $[H^+] > 1.03 \times 10^{-7}$, $P_H > 6.99$, $X_H > -0.19$. It is calculated that a plasma reaction of P_H 6.92, $[H^+]$ 1.20×10^{-7} , X_H —0.12 will abolish the response of nerve or muscle. This is in agreement with the observation of Van Slyke that the most acid reaction during life (in deep coma) is P_H 6.95, $[H^+]$ 1.12×10^{-7} , X_H —0.15. J. F. S.

Production of Acetoacetic Acid from Urocanic Acid in the Surviving Liver. M. KONISHI (*Z. physiol. Chem.*, 1922, **122**, 237—240).—On transfusing the liver of a dog with urocanic

acid or with glyoxalinelactic acid, a small amount of acetoacetic acid is formed; the amount is rather more than after transfusion with histidine.

W. O. K.

The Proteolytic Enzymes of the Kidneys. S. G. HEDIN (*Z. physiol. Chem.*, 1922, **122**, 307—317).—The kidneys of horses contain an enzyme attacking peptone with an optimum P_H of 7.8, and an enzyme attacking casein in acid solution. Preliminary treatment of the kidneys with acid increases the action of the enzymes, due apparently to the fact that the enzymes are gradually destroyed at approximate neutrality.

W. O. K.

A New Constituent of the Thyroid. UBALDO SAMMARTINO (*Biochem. Z.*, 1922, **132**, 293—294).—Freshly and finely divided thyroids (400 grams) were extracted with hot dilute acetic acid, and the solution concentrated and precipitated with basic lead acetate. The lead-free filtrate was concentrated and precipitated with alcohol. The filtrate from this gave potassium picrate, and then a red picrate unmelted at 300°, and a picrate, m. p. 255—295°. After removal of picric acid from the mother-liquors, addition of alcohol precipitated a crystalline substance, m. p. 225—228°, which contained calcium, nitrogen, carbon, and a large proportion of oxygen.

H. K.

The Influence of the Thyroid on Creatine-Creatinine Metabolism. PAUL SCHENK (*Arch. expt. Path. Pharm.*, 1922, **95**, 45—63).—In thyroidectomised rabbits, the blood creatinine is not markedly decreased, but the excretion of preformed creatinine in the urine shows a marked diminution. A marked increase then takes place on administration of thyroid extract.

W. O. K.

Mechanism of the Contraction of Striated Muscle produced by Poisons. V. The Action of Specific Muscle Poisons on Lifeless Colloids. OTTO RIESSER and S. M. NEUSCHLOSZ (*Arch. expt. Path. Pharm.*, 1922, **94**, 190—221).—Characteristic changes in the viscosity of a gelatin solution are produced by addition of muscle poisons such as veratrine, strophanthin, digitalin, quinine, caffeine, nicotine, and novocaine, but not by poisons (morphine, codeine, atropine, acetylcholine) which have no typical action on muscle. Where the physiological actions of the poisons are similar, as, for example, in the cases of strophanthin and digitalin, the influence on the viscosity is also similar; in other cases it is dissimilar. The physiological antagonism between veratrine and novocaine and veratrine and atropine is paralleled by an antagonistic influence on the viscosity of gelatin solutions; the mechanism of the antagonism is, however, different in the two cases. It is concluded that the action of muscle poisons is due to the changes which they produce in the colloids of the muscles.

E. S.

Tension and Extensibility of Muscle during Contraction by Acids or Chemical Means. F. VERZÁR, J. BÖGEL, and W. SZÁNYI (*Biochem. Z.*, 1922, **132**, 64—81).—The tension developed

in an acid solution of P_H less than 3 is less than that in normal contraction of muscle, whilst aqueous solutions of chloroform, ethyl and methyl alcohols, glycerol, aniline, and ammonia produce considerable tension. The extensibility of muscle is increased by acid over that of normal muscle and the above-named reagents diminish it. The results support von Fürth's theory of muscle contraction.
H. K.

The Replaceability of Potassium by Uranium in Cross-stripped Muscle. F. VERZÁR and W. SZÁNYI (*Biochem. Z.*, 1922, **132**, 53—63).—The sartorius muscle of the frog, immersed in sodium chloride solution, exhibits fibrillary movements which are inhibited by equimolecular quantities of potassium or uranium salts. The action is reversible in both cases, but only so in the case of uranium if long contact is avoided. Emanation is without action on the fibrillary movements. If the movements be inhibited by potassium or uranium, then addition of the other restores the movements to some extent.
H. K.

The Materials Extracted from Muscles. XXI. The Organic Bases of the Flesh of Swine. I. A. SMORODINCEV (*Z. physiol. Chem.*, 1922, **123**, 116—129).—Using more than 2 kilos. of pig's flesh, the following approximate figures are found for the content in organic bases: creatine, 0.228%; purines, 0.086%; carnosine, 0.289%; methylguanidine, 0.032%; carnitine, 0.032%. As compared with other animals investigated, it is particularly rich in creatine and carnosine.
W. O. K.

The Action of Digitalis, Calcium, and Barium on Strips of Heart Muscle (Löwe) and the Antagonistic Influence of Cocaine, Magnesium, and Potassium. MARTIN BRANN (*Arch. expt. Path. Pharm.*, 1922, **94**, 222—234).—Contrary to Löwe's statement, digitalin produces contractions in strips of ventricle free from ganglia, an action which is antagonised by cocaine and potassium chloride. Calcium chloride, which resembles digitalin in its action, is similarly antagonised by cocaine, magnesium chloride, and potassium chloride. The two last substances, but not cocaine, also antagonise the tonic action of barium chloride.
E. S.

Potassium-Calcium Equilibrium in Animal Systems. H. ZWAARDEMAKER (*Biochem. Z.*, 1922, **132**, 95—102).—A discussion of this subject with reference to replacement of potassium by uranium and thorium in Ringer's solution.
H. K.

Decarboxylation. K. SPIRO (*Arch. Néerland. physiol.*, 1922, **7**, 227—233).—A general review of the place of decarboxylation in biochemical phenomena.
W. O. K.

The Non-protein Nitrogen in Goat's Milk. WILLIAM TAYLOR (*Biochem. J.*, 1922, **16**, 611—612).—There was found a correlation in a lactating goat between the output of nitrogen in the urine and the percentage of non-protein nitrogen in the milk. Both seem to be determined by the amount of protein in the food.
S. S. Z.

The Excretion by the Gastric Mucous Membrane and the Salivary Glands of Alkaloids Administered Subcutaneously. KARL JAKOB HUBER (*Arch. expt. Path. Pharm.*, 1922, **94**, 327—351).—The literature on the excretion of alkaloids after administration to animals is reviewed. In experiments described, various alkaloids were injected subcutaneously in dogs. Atropine and eserine were excreted neither in the stomach nor in the saliva; arecoline was detected in the saliva, but not in the stomach; papaverine and veratrine, on the other hand, appeared in the stomach. E. S.

Permeability of the Intestine to Sucrose. PIERRE WORINGER (*Compt. rend. Soc. Biol.*, 1922, **86**, 1093—1095).—When either mono- or di-saccharides are ingested in quantities exceeding the assimilative capacity of the organism, the excess is eliminated through the urine. In this case the disaccharides must first undergo cleavage into two monosaccharide molecules. The disaccharide, however, also appears in the urine as such and can be demonstrated by the change in the reducing power of the urine following acid hydrolysis. In this way the author shows that, both in dogs and in babies, a fixed amount of disaccharide (on the average 1.56% and 1.58% respectively) appears in the urine and this is independent of the actual amount of sucrose fed or the body weight of the organism. This is thought to demonstrate direct permeability of the intestinal mucosa to sucrose. CHEMICAL ABSTRACTS.

Application of the Methods of Correlation to the Study of the Urine. CHARLES POWELL WHITE (*Lancet*, 1922, [I], **202**, 369—371).—An attempt to determine the manner in which the various radicles in urine are associated in solution by an examination of the correlation coefficients derived from existing series of analyses of the urine of cancerous persons. As preliminary conclusions evolved from this statistical inquiry, it is suggested that (a) sodium, potassium, and chlorine are excreted in association with the water and hence through the glomeruli; urea, uric acid, and sulphate are excreted independently of the water and therefore presumably through the tubules; phosphate, magnesium, and calcium may be excreted by both channels; (b) the association of urea with sulphuric and phosphoric acids demands further investigation; (c) uric acid may be excreted as calcium and potassium urates, but not as sodium urate; (d) potassium is excreted chiefly as chloride; (e) sodium is excreted as chloride, phosphate, and sulphate; (f) calcium and magnesium are excreted chiefly as chlorides, phosphates, and sulphates; (g) there are no indications of the excretion of alkali salts of ethereal sulphuric acids.

A. A. E.

The Relation between the True Reaction of the Urine and the Alveolar Tension of Carbon Dioxide. GUSTAV ENDRES (*Biochem. Z.*, 1922, **132**, 220—241).—Parallel observations have been made on the P_H of the urine by a colorimetric method and the alveolar tension of carbon dioxide. After a meal, both curves

show a similar tendency, the P_H curve rising to a maximum after two or three hours and the alveolar tension of carbon dioxide rising to a maximum. The form of the curves also depends on the diet, flesh diet giving steeper curves than carbohydrate diet. It is very probable that the hydrochloric acid secretion of the stomach is largely responsible for these variations. Drugs, sleep, muscular activity, and bleeding have their effects traceable in the curves.

H. K.

Some New Observations on the Relation between the True Sugar Content of Urine and the Sugar Content of Blood.

D. G. COHEN TERVAERT (*Arch. Néerland. physiol.*, 1922, 7, 352—354).—There does not seem to be any direct quantitative relation between the sugar content of the urine and that of the blood, following the consumption of quantities of dextrose. W. O. K.

Organic Acids in Urine. R. GOIFFON and F. NEPVEUX (*Compt. rend. Soc. Biol.*, 1922, 86, 1132—1133; from *Chem. Zentr.*, 1922, iv, 409).—Using the method of Van Slyke and Palmer (A., 1920, i, 459), the authors found in cases of acetonuria increase in total organic acids and in β -hydroxybutyric acid in the urine. Sufficient agreement was not obtained for these acids to be regarded as the sole factor in acetonuria. The organic acid content is independent of the acidity. Sodium hydrogen carbonate renders the urine alkaline without diminution in the organic acid content.

G. W. R.

Blood in Impaired Cell Respiration. Cause of Avian Beri-beri. ALFRED FLEISCH (*Arch. expt. Path. Pharm.*, 1922, 95, 17—35).—Pigeons suffering from avian beri-beri show a decrease in the difference of the arterial and venous tensions of carbon dioxide, and also a similar decrease with regard to oxygen. A similar effect is found in pigeons suffering from cyanide poisoning. These results are taken to support Hess's view that the essential change in avian beri-beri is a decrease in the rate of cell oxidations (cf. this vol., i, 399).

W. O. K.

Diabetes, β -Hydroxybutyric Acid, and Lævulose. A. DESGREZ, H. BIERRY, and F. RATHERY (*Compt. rend.*, 1922, 175, 536—539).—Different sugars are not interchangeable in a diabetic ration; their molecular structures affect to a considerable extent the results of assimilation. The authors consider that it is necessary to deal with the specific results to be obtained from each sugar. The ingestion of lævulose furnishes a remedy for certain irregularities of metabolism; in cases of diabetes, it provides a means of preventing or reducing the elimination of β -hydroxybutyric acid. When the carbohydrate tolerance of a diabetic patient has been determined, it is sufficient to administer lævulose associated with phosphates and with vitamin-B to the ascertained limit.

H. J. E.

Examination of the Pentose in a New Case of Pentosuria.

A. N. WRZESNEVSKI (*Biochem. Z.*, 1922, 132, 135—137).—The pentose excreted in a case of pentosuria in a female was identified

as *r*-arabinose, by means of its diphenylhydrazone and its phenyl-osazone. H. K.

The Chemical Nature of Toxins and Antitoxins. E. SALKOWSKI (*Biochem. Z.*, 1922, **132**, 84—88).—The author recalls some unpublished experiments made by himself in 1896 on the preparation of diphtheria antitoxin free from protein. The diphtheria antitoxin serum was saturated with sodium chloride, treated with two volumes of saturated sodium chloride solution, and trichloroacetic acid added so long as there was a precipitate. The protein precipitate carried the antitoxin down with it. The product is filtered off and triturated with water which dissolves the antitoxin. The solution is free or practically so from protein. The same procedure has been employed by Blumenthal (*Z. klin. Med.*, 1896, **30**) for the preparation of protein-free toxin from the spinal marrow of a case of tetanus. H. K.

Influence of the Sodium-ion in the Production of Tetany. FREDERICK F. TISDALL (*J. Biol. Chem.*, 1922, **54**, 35—41).—Disodium phosphate, injected intravenously into four dogs, produced a condition resembling active tetany in one case and an incipient tetany in the remainder; phosphoric acid, on the other hand, produced no marked effect. Analyses of the inorganic constituents of the blood indicate that the important factor in the production of tetany is a disturbance of the sodium-calcium ratio. In the case of gastric tetany, however, increase in the bicarbonate ion is apparently responsible. E. S.

The Behaviour of Phenyl-lactic Acid in the Animal Organism. I. Y. KOTAKE and Y. MORI (*Z. physiol. Chem.*, 1922, **122**, 176—185).—After *dl*-phenyl-lactic acid has been administered to dogs, rabbits, or monkeys, their urine contains the *d*-acid, along with the inactive isomeride. With man, on the other hand, the *l*-acid is present in excess in the urine after administering *dl*-phenyl-lactic acid. W. O. K.

The Behaviour of Phenyl-lactic Acid in the Animal Organism. II. Y. MORI (*Z. physiol. Chem.*, 1922, **122**, 186—190).—The resolution of phenyl-lactic acid by means of the strychnine salt is described, and the following rotations were found: *d*-phenyl-lactic acid, m. p. 124°, $[\alpha]_D +20.92^\circ$, *l*-phenyl-lactic acid, m. p. 124°, $[\alpha]_D -19.86^\circ$. After *d*-phenyl-lactic acid is administered to man, phenylpyruvic acid is found in the urine along with unchanged material. If the *l*-acid be administered, smaller amounts of phenylpyruvic acid are found. With dogs, only very small amounts of phenylpyruvic acid are formed from either acid. W. O. K.

The Behaviour of Phenylpyruvic Acid in the Animal Organism. Y. KOTAKE and Y. MORI (*Z. physiol. Chem.*, 1922, **122**, 191—194).—Both in men and in dogs, phenylpyruvic acid is reduced to *l*-phenyl-lactic acid, this being found in the urine. W. O. K.

The Behaviour of Phenylalanine in the Animal Organism. Y. KOTAKE, Y. MASAI, and Y. MORI (*Z. physiol. Chem.*, 1922, **122**, 195—200).—After the administration of *dl*-phenylalanine to rabbits, phenylpyruvic acid, hydroxyphenylpyruvic acid, and *l*-hydroxyphenyl-lactic acid, along with *d*-phenylalanine, are found in the urine. *d*-, *l*-, and *dl*-Phenylalanines can all be oxidised by the animal organism to phenylpyruvic acid. W. O. K.

The Excretion of Hydroxyphenyl-lactic Acid after Administration of Tyrosine to Rabbits. Y. KOTAKE and M. OKAGAWA (*Z. physiol. Chem.*, 1922, **122**, 201—205).—Only very small quantities of hydroxyphenyl-lactic acid are found along with much larger amounts of hydroxyphenylpyruvic acid in the urine of rabbits after administration of *l*- or *dl*-tyrosine. No evidence could be obtained that hydroxyphenyl-lactic acid can be converted into hydroxyphenylpyruvic acid. W. O. K.

The Asymmetrical Reduction of Ketonic Acids to the Corresponding Alcohols in Organs. Y. MORI and T. KANAI (*Z. physiol. Chem.*, 1922, **122**, 206—210).—Phenylpyruvic acid and hydroxyphenylpyruvic acid are reduced by the liver, kidney, and spleen to *l*-phenyl-lactic acid and *l*-hydroxyphenyl-lactic acid. W. O. K.

The Behaviour of Amino-acids in Vitrally Stained Animals. I and II. Y. KOTAKE, Y. MASAI, and Y. MORI (*Z. physiol. Chem.*, 1922, **122**, 211—219, 220—224).—If phenylalanine or tyrosine be administered to a rabbit which has been vitally stained by the injection of an alkaline carmine solution, there is less phenylpyruvic acid or hydroxyphenylpyruvic acid in the urine than in the absence of the staining. Vital staining, therefore, appears to inhibit the oxidative deamination of amino-acids. It also inhibits the oxidation of phenylalanine to tyrosine as shown by transfusion experiments on the liver after death. On the other hand, the production of acetoacetic acid from phenylalanine is not interfered with. W. O. K.

Comparative Researches on the Production of Acetoacetic Acid from *d*- and *l*-Phenyl-lactic Acids and from *d*- and *l*-Hydroxyphenyl-lactic Acid in the Surviving Liver. Y. MORI (*Z. physiol. Chem.*, 1922, **122**, 225—229).—*dl*-Hydroxyphenyl-lactic acid has been resolved through its morphine salt, and the following constants have been found: *d*-hydroxyphenyl-lactic acid, $[\alpha]_D +18.87^\circ$; *l*-hydroxyphenyl-lactic acid, $[\alpha]_D -18.92^\circ$. On transfusion through the liver of a dog, both forms of phenyl-lactic acid give rise to small amounts of acetoacetic acid, the *l*-form being the more effective. *l*-Hydroxyphenyl-lactic acid likewise yielded a small amount of acetoacetic acid, the *d*-form, none at all. W. O. K.

The Production of Urocanic Acid from Histidine in the Dog. Y. KOTAKE and M. KONISHI (*Z. physiol. Chem.*, 1922, **122**, 230—236).—Urocanic acid can be isolated from the urine of

a dog after the administration of histidine either by the mouth or by subcutaneous injection. No urocanic acid was found after the administration of glyoxaline-lactic acid. W. O. K.

The Deaminating of Tyrosine in the Animal Organism. Y. KOTAKE, Z. MATSUOKA, and M. OKAGAWA (*Z. physiol. Chem.*, 1922, **122**, 166—175).—In the urine of a rabbit to which *l*-tyrosine had been administered, *l*-hydroxyphenyl-lactic acid and hydroxyphenylpyruvic acid were found, and also a small amount of *dl*-hydroxyphenyl-lactic acid; whilst, after *dl*-tyrosine had been given, hydroxyphenylpyruvic acid, *l*-phenyl-lactic acid, and *d*-tyrosine were found. Phenol is also present. W. O. K.

The Deamination of Amino-acids and the Reversible Transformations of the Products so arising in the Animal Organism. Y. KOTAKE (*Z. physiol. Chem.*, 1922, **122**, 241—244).—A summary of the work of the author and his collaborators on this subject (cf. preceding abstracts). W. O. K.

Formaldehyde in the Urine after Administration of Hexamethylenetetramine. KURT VOIT (*Arch. exp. Path. Pharm.*, 1922, **95**, 124—128).—Formaldehyde may be detected in the urine after the administration of hexamethylenetetramine, but its presence has not been established in blood or other body fluids. W. O. K.

Physiological Researches on Vitamin-B and Water-soluble Biocatalysts. G. J:SON BLOHM, C. G. SANTESSON, and H. VON EULER (*Arkiv Kem. Min. Geol.*, 1922, **8**, No. 13, 1—27).—Various preparations from yeast and malt which accelerate the growth of yeast lower the blood-pressure if injected into rabbits, reduce the pulse-rate, and also affect the breathing. They are, however, only very slightly less active as biocatalysts after inactivation by heating, except in the case of particularly pure preparations where the difference is more marked. W. O. K.

Chloroform in the Blood after Death. C. S. GIBSON and P. P. LAIDLAW (*Guy's Hospital Reports*, 1922, July, 359—366).—Estimations of the chloroform in the heart blood of rabbits killed by an overdose of chloroform show a larger amount a few days after death than at death, an increase apparently due principally to the passage of liquid from the vascular system after death. W. O. K.

Chemistry of Vegetable Physiology and Agriculture.

The Mechanism of the Reversal in Reaction of a Medium which takes place during growth of *Bacillus diphtheriæ*. CHARLES GEORGE LEWIS WOLF (*Biochem. J.*, 1922, **16**, 541—547).—The reversal of reaction from acidity to alkalinity in carbohydrate-free media caused by the growth of *Bacillus diphtheriæ* is due

partly to the production of volatile acids. These acids are converted into carbonates when the medium becomes more alkaline. Organic acids such as malic and succinic acids are also utilised to produce carbonates. Formic acid is not formed as an intermediate product. S. S. Z.

Decomposition of Citric Acid of Cow's Milk by some Bacteria. HEINRICH KICKINGER (*Biochem. Z.*, 1922, **132**, 210—219).—The citric acid content of milk is unchanged when the milk is boiled or pasteurised, but falls off on long keeping. In fractionally sterilised milk, the citric acid content falls off during the first day but remains constant after the third sterilisation. This is not due to lactic acid forming bacteria but to peptonising bacteria (*Bacillus subtilis*, *Proteus vulgaris*). H. K.

Influence of Radioactive Substances on Acetic Fermentation. LABORDE, JALOUSTRE, and M. LEULIER (*Bull. Soc. Chim. Biol.*, 1922, **4**, 415—418).—The acetic fermentation of wine is at first accelerated and later retarded by the addition of mesothorium in amounts not greater than that equivalent to one micro-gram of radium bromide per 100 c.c. Concentrations of thorium-X greater than this completely stop the fermentation. E. S.

Action of Ultra-violet Rays on *Saccharomyces cerevisiæ*. ROMOLO DE FAZI and REMO DE FAZI (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 463—464).—The results previously obtained (A., 1916, i, 236) have been confirmed in a large scale experiment on a brewery wort. T. H. P.

Activators of Fermentation. ERNST LINDBERG (*Biochem. Z.*, 1922, **132**, 110—134).—The accelerating influence of yeast water, yeast co-enzyme, and milk has been determined on washed and unwashed dried yeast; and also the influence of abietic acid, amylin, and cholesterol. The former group accelerate the fermentation but the latter are without action. Pyruvic acid is fermented more rapidly than dextrose but lactic acid was practically untouched. H. K.

Behaviour of some Amino-acids towards Oxygenated Yeast. FRITZ LIEBEN (*Biochem. Z.*, 1922, **132**, 180—187).—Unlike lactic acid, amino-acids are not quickly destroyed by oxygenation of their solution in presence of yeast-cells. H. K.

Further Experiments on the Destruction of Lactic Acid by Yeast. OTTO FÜRTH and FRITZ LIEBEN (*Biochem. Z.*, 1922, **132**, 165—179; cf. this vol., i, 502).—The disappearance of lactic acid observed on shaking yeast suspensions in a current of oxygen could not be attributed to the formation of simple derivatives such as acetaldehyde or β -hydroxybutyric acid, etc.; half of the carbon of the lost lactic acid does, however, appear as carbon dioxide, the other half possibly being utilised in the building up of tissue. H. K.

The Chemical Composition and the Bouquet of Wines.

PHILIPPE MALVEZIN (*Ann. Chim. Analyt.*, 1922, **4**, 298—301).—The fact of a substance being capable of exciting the sense of smell is attributable to the presence of certain chemical groups in its molecule, which by analogy to chromophores are termed osmophores. Thus the groups $-\text{CHO}$, $-\text{CN}$, and $-\text{NO}_2$ are osmophores which when attached to the benzene nucleus give rise to the odour of almonds. Similarly, the traces of ethers, esters, and other odorous substances which are slowly formed in wines on keeping exert a marked effect on the odour of the wine, and owing to the extreme sensitiveness of such organoleptic tests, it is possible to detect the presence of combinations of osmophores, as, for example, $-\text{CO}-$ and $-\text{CH}_3$ in ethyl acetate, an important constituent of matured wines, when ordinary chemical tests would fail.

G. F. M.

The Influence of the Constitution of Nutritive Media on the Composition of *Aspergillus niger*.

ÉMILE F. TERROINE, R. WURMSEER, and J. MONTANÉ (*Compt. rend.*, 1922, **175**, 541—544).—The nitrogen content of *Aspergillus niger* decreases during the course of development, does not vary with concentration of nitrogenous food, and decreases considerably in media rich in sugar with the exception of young cultures which increase in nitrogen content with increasing concentration of available carbohydrate. The substitution of urea or sodium nitrate for ammonium sulphate in the nutritive medium scarcely modifies the quantity, that of peptone or guanidine considerably lowers it, whilst changes in the sugar exert little influence except for the lower values obtained in presence of galactose. When nitrogen is absent from the culture medium, the nitrogen content is considerably lower.

H. J. E.

Fermentation of Pentoses by Moulds.

W. H. PETERSON, E. B. FRED, and E. G. SCHMIDT (*J. Biol. Chem.*, 1922, **54**, 19—34).—Out of twenty-five species of moulds investigated, sixteen were found rapidly to ferment both xylose and arabinose; the destruction of the pentoses was, however, somewhat less rapid than that of dextrose. *Aspergillus niger* and other species of *Aspergillus* were especially active in fermenting the pentoses; *Penicillium glaucum* was also active, but with other *Penicillia* the fermentation proceeded slowly. In agreement with results obtained by others, it was found that more than 90% of the carbon of the pentose consumed could be accounted for as carbon dioxide and mycelium. No volatile acid or alcohol was produced, but a small quantity of a non-volatile acid appeared to be formed.

E. S.

Urea and Urease in Fungi.

A. GORIS and P. COSTY (*Compt. rend.*, 1922, **175**, 539—541; cf. Goris and Mascré, A., 1909, ii, 175).—The results of a considerable number of experiments show that urease is present in almost all the higher fungi. In those species

in which the ferment is absent or is present only in very small quantity, urea is found in variable percentage in the mycelium.

H. J. E.

The Relation between the Colloidal State and the Physiological Functions of Protoplasm. RENÉ WURMSER and RAYMOND JACQUOT (*Compt. rend.*, 1922, 175, 782—784).—Sea-weed, when heated for two minutes in sea-water, undergoes a greater reduction in its assimilative than in its respiratory function, the excess of disengaged oxygen over absorbed oxygen decreasing and eventually being reversed with rise of temperature. The respiration effect was also determined in darkness, thus excluding assimilation, and was found to be small in comparison with the latter, although its rate of diminution with rise of temperature is considerably less.

H. J. E.

The Effect of the Reaction of a Nutritive Solution on Germination and the First Stages of Plant Growth. RALPH M. HIXON (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, 4, No. 9, 1—28).—To study the effect of hydrogen-ion concentration on the germination of seeds and the early growth of plants, experiments were made with peas, cereals, and carrots. The nutritive solution used was Tollen's solution, of which the P_H was varied as required by the addition of hydrochloric acid or sodium hydroxide; other experiments were made with tap water and with sterilised agar. Germination took place over the wide range of P_H 4 to 7.6 with only slight variation at the two extremes, but in the middle part of the range there was a point where the rate of germination was a minimum. This point was at P_H 5.0 for peas, P_H 6.0 for maize, wheat, and oats, and P_H 5.5 for carrots. On the other hand, the root growth of carrots was a maximum at this critical point at the end of the tenth day. The author is inclined to interpret the critical point as that of greatest efficiency and the point of normal growth. It is difficult, however, to define a standard for normal growth. There is always a tendency, when a plant is growing in a solution with a P_H value lying towards one extreme, for the plant to modify this value towards one lying between P_H 5.0 and 6.8. These and other observations by different authors indicate an ionic equilibrium between the roots of the plant and the salts of the solution. The greater rate of germination of seeds in solutions with P_H values lying on either side of the critical value may be due to the stimulating effect, in small concentrations, of the two toxic ions H^+ and OH^- .

E. H. R.

Some Relations of Arsenic to Plant Growth. I. JOHN STEWART (*Soil Sci.*, 1922, 14, 111—118).—The solubility of lead arsenate in solutions of salts, comparable to those existing in the soil solution was determined. In water, the solubility was three parts per million. This figure was scarcely affected by the presence of neutral sulphates and nitrates but was markedly increased by acid salts and salts hydrolysing in solution to give an alkaline reaction. The solubility of lead arsenate in soil is roughly pro-

portional to the amount of soluble salts in the soil, with the exception of alkali soils where the figure is lower than would be expected. The presence of carbonate, hydrogen carbonate, and potassium ions appears in most cases to facilitate the solution of lead arsenate.

A. G. P.

Some Relations of Arsenic to Plant Growth. II. JOHN STEWART and EDWIN S. SMITH (*Soil Sci.*, 1922, **14**, 119—126).—Crops were grown in soil to which varying amounts of disodium arsenate were added. Distinct evidence of stimulation in low concentrations was observed, although no decisive information could be obtained from the dry weights of crops obtained. Higher concentrations of arsenate proved injurious. It is suggested that the accumulation in the soil of arsenates from sprays may be beneficial, since the solubility of lead arsenate in the soil solution is sufficiently small to prevent the concentration of arsenic reaching the toxic dose.

A. G. P.

Hippuric Acid and Urea as Nutrient Materials for Plants. TH. BOKORNY (*Biochem. Z.*, 1922, **132**, 197—209).—In higher strengths than 0.09%, hippuric acid is toxic to plant-cells, urea at 1% being harmless.

H. K.

The Influence of Sucrose on the Greening of Etiolated Cotyledons at Various Stages of Germination. (FRL.) S. MANSKY (*Biochem. Z.*, 1922, **132**, 18—25).—The etiolated embryos or shoots of the pumpkin were grown in the dark and then exposed to sucrose solutions of different strengths and at different periods of growth, in sunlight. There is a minimum concentration of sucrose which favours chlorophyll formation, an optimum and a maximum concentration, and each of these depends on the age of the embryo.

H. K.

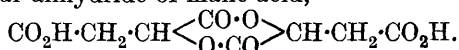
What Becomes of Carbohydrates when the Leaves of Trees Die ? RAOUL COMBES and (MLLE) DENISE KOHLER (*Compt. rend.*, 1922, **175**, 590—592).—When the leaves turn yellow and die on the trees the amount of soluble carbohydrates decreases by about one-half during the change. Leaves which have been plucked and subsequently undergo the change of colour also diminish in carbohydrate content, but only by one-third. In both cases the insoluble easily hydrolysed carbohydrates increase in quantity; this is due to a transformation of the less easily hydrolysed polysaccharides into those more easily hydrolysed. These conclusions are drawn from a study of the leaves of *Fagus sylvatica* and *Æsculus hippocastanum*, both of which species give analogous results.

H. J. E.

Changes which Occur in the Pectic Constituents of Stored Fruit. MARJORIE HARRIOTTE CARRÉ (*Biochem. J.*, 1922, **16**, 704—712).—Pectin reaches a maximum during the process of ripening and then gradually falls as the fruit (apple) becomes over-ripe. The date of picking of the fruit has no effect on the development of the pectin in either cold or ordinary store. Protopectin—the

precursor of soluble pectin—can be estimated by hydrolysing the residue with *N*/20-hydrochloric acid after the soluble pectin has been extracted and utilising the calcium pectate method. Preliminary work suggests the existence of a definite relationship between the quantities of soluble pectin and protopectin constituents and that the production of soluble pectin is due to enzyme action. There is a possibility of the existence of a third soluble pectin. S. S. Z.

Chemical Constituents of Green Plants. XXI. The Non-existence of Crassulaceæ Malic Acid. HARTWIG FRANZEN and RUDOLF OSTERTAG (*Z. physiol. Chem.*, 1922, **122**, 263—297).—It appears that the third optically active form of malic acid, said to exist in *Bryophyllum*, *Crassula arborescens*, *Echeveria secunda glauca*, and other plants, does not really exist. A review of the literature suggests that it is really an impure form of ordinary malic acid, and an investigation on the acids of *Echeveria* has shown that the impurity which has been responsible for the erroneous conclusion is a bimolecular anhydride of malic acid,



The presence of this has been shown by using the ester-hydrazide method previously employed. Besides this anhydride, and much malic acid, the presence of traces of succinic acid and possibly of citric acid has been demonstrated by the same method. W. O. K.

Carrageen (*Chondrus crispus*). III. The Constitution of the Cell-wall. BARBARA RUSSELL-WELLS (*Biochem. J.*, 1922, **16**, 578—586).—The chemistry of the hot and cold extracts of carrageen as prepared by Haas and Hill and by Haas (A., 1921, i, 839) was studied. Both extracts contain pentose radicles and calcium and ammonium ethereal sulphates. The ash also contains calcium, magnesium, sodium, potassium, and traces of iron. Pectic radicles are absent from both extracts. The cold extract contains a dialysable organic substance. On oxidation the cold and hot extracts yield mucic, oxalic, and tartaric acids—more mucic but less oxalic acid is derived from the cold than from the hot extract. The extracted residue of carrageen contains cellulose. There are indications that *Ceramium rubrum* also contains ethereal sulphates. S. S. Z.

Botanico-chemical Notes. EDMUND O. VON LIPPMANN (*Ber.*, 1922, **55**, [B], 3038—3041).—During an exceptionally warm summer drops of nectar fell from the garden foxglove which solidified readily and contained large quantities of sucrose.

Trehalose has been isolated from a sample of wild oats grown near Kissingen.

An exudation from the stems of a quince tree which had been damaged by smoke and was nearly dead consisted of a viscous, white gum which was very rapidly and almost completely hydrolysed by dilute acid with production of *r*-galactose.

Malic, citric, tartaric, and succinic acid have been isolated from the berries of the mountain ash; the nature and relative amounts of the acids appear to depend on the variety of berry and the degree of ripeness. H. W.

The Relation between Anthocyanin and Oxydases. MARCEL MIRANDE (*Compt. rend.*, 1922, **175**, 595—597).—The development of colouring matter in scales from bulbs of *Lilium candidum* and *L. martagon* on exposure to light depends on an oxidising action. The presence of an oxydase in the scale is shown, but it is confined to that portion in which the anthocyanin is formed or which is capable of formation of anthocyanin. H. J. E.

The Relation between Tissue-acidity and the Presence of Anthocyanin in the Scales of Lily Bulbs exposed to Light. MARCEL MIRANDE (*Compt. rend.*, 1922, **175**, 711—713; cf. this vol., i, 1100, and preceding abstract).—Scales from bulbs of *Lilium candidum* and *L. martagon* when detached and exposed to light undergo an increase in acid content which is due partly to the fracture and partly to the acidification which is correlated with pigmentation. The author has shown that an oxydase is present but that its distribution is limited to those cells in which the pigment is formed, whilst acidification occurs at all points. If the oxydase is a factor in the acidification which accompanies pigmentation, this is clearly differentiated from the general development of acid; if not, its only function appears to be the part played in anthocyanin development. The conclusion is drawn that this work confirms the author's statement that oxidation is a factor in anthocyanin synthesis. H. J. E.

The Transformation of a Chromogen of Yellow Flowers of *Medicago falcata* under the Action of an Oxydase. ST. JONESCO (*Compt. rend.*, 1922, **175**, 592—595).—An alcoholic extract of the yellow flowers of *M. falcata* gave a clear liquid of an intense yellow colour, and a series of tests showed that the pigment was of the flavone type. Reduction of the pigment by nascent hydrogen gave a colourless solution, but the action of the oxydase obtained from *Russula delica* resulted in the production of a substance of the same colour as the violet flowers of *M. falcata*, which responded to tests in a manner characteristic of anthocyanins. Similar results are obtained by oxidation of the yellow pigment with hydrogen peroxide and the author concludes that oxidation of the chromogen leads to its transformation into an anthocyanin pigment. H. J. E.

The Phytosterols of Ragweed Pollen. FREDERICK W. HEYL (*J. Amer. Chem. Soc.*, 1922, **44**, 2283—2286).—From the unsaponifiable fraction of the ether extract of the pollen of ragweed, *Ambrosia artemisiifolia*, L., the author has isolated a new phytosterol, *ambrosterol*, $C_{20}H_{34}O$, m. p. 147—149°, giving an *acetate*, m. p. 112—113°. In addition, this fraction contains a phytosterol, $C_{27}H_{46}O$, m. p. 147.5—148°, and considerable amounts of a more highly

oxygenated substance, probably an oxyphytosterol. Appreciable quantities of the higher homologues of the methyl alcohol series, of which cetyl and octadecyl alcohols were identified, and traces of a hydrocarbon were also found.

W. G.

The Presence of Aucubin and Sucrose in Seeds of *Rhinanthus Crista-Galli*, L. MARC BRIDEL and (MLLE) MARIE BRAECKE (*Compt. rend.*, 1922, **175**, 532—534; cf. A., 1921, i, 840).—Aucubin and sucrose were obtained in pure crystalline condition from the seed.

H. J. E.

Nitrogenous Metabolism of Higher Plants. III. The Effect of Low-temperature Drying on the Distribution of Nitrogen in the Leaves of the Runner Bean. ALBERT CHARLES CHIBNALL (*Biochem. J.*, 1922, **16**, 599—607).—On drying the leaves of the runner bean at a low temperature, some of the protein is autolysed with the production of water-soluble nitrogenous products which chiefly consist of ammonium salts, asparagine, and amino-acids. The reduced protein is, however, not appreciably changed in character. The dried leaves contain enzymes which are activated by water. The presence is indicated of an asparaginase which is activated by the addition of water and under the specified conditions manifested marked synthetic activity.

S. S. Z.

Nitrogenous Metabolism of the Higher Plants. IV. Distribution of Nitrogen in the Dead Leaves of the Runner Bean. ALBERT CHARLES CHIBNALL (*Biochem. J.*, 1922, **16**, 608—610).—For comparison with the seasonal variations previously described (this vol., i, 908), the nitrogen content of, and its distribution in, the dead leaf of the runner bean killed by a frost in the twenty-fourth week of its life is given.

S. S. Z.

Application of Bourquelot's Biochemical Method to the Investigation of Sugars and Glucosides in some of the *Scrophulariaceæ*. (MLLE) MARIE BRAECKE (*Bull. Soc. Chim. Biol.*, 1922, **4**, 407—414; cf. A., 1915, i, 631).—Nine plants were investigated and all were found to contain sugars hydrolysable by invertase and a glucoside hydrolysable by emulsin. In the cases of *Pentstemon hybridus*, *Collinsia bicolor*, Benth., *Pentstemon barbatus*, Roth., and *Freylinia cestoides*, Colla, the glucoside appears to be identical with aucubin (cf. this vol., i, 209), although in the three last plants other principles decomposable by emulsin are probably also present.

E. S.

The Presence of the Glucoside of an Essential Oil in the Leafy Stems and Roots of *Sedum telephium*, Linn. MARC BRIDEL (*J. Pharm. Chim.*, 1922, [vii], **26**, 289—298).—Bourquelot's biochemical method reveals the presence in the leafy stems and roots of *Sedum telephium*, a glabrous plant growing in the Vosges and elsewhere in France, a glucosidal principle giving on hydrolysis by emulsin an aromatic substance having an odour of roses. So far the glucoside has only been obtained in an amorphous condition. It is soluble in water, alcohol, acetone, or chloroform.

Its aqueous solution reduces Fehling's solution, 1 gram being equivalent to 0.103 gram of dextrose. It has $[\alpha]_D -28.57^\circ$. On hydrolysis with sulphuric acid, an aromatic substance having an odour reminiscent of eucalyptol or terpineol is produced. The different substances produced by the action of emulsin and sulphuric acid, respectively, might indicate that the fermentation product is a substance related to geraniol, which, as is known, gives terpene derivatives by the action of sulphuric acid. The reducing sugar was identified as dextrose.

G. F. M.

Carbon Monoxide in Tobacco Smoke. HENRY E. ARMSTRONG and E. V. EVANS (*Brit. Med. J.*, 1922, (I), 992—993).—Hydrogen sulphide and carbon monoxide are present in tobacco smoke in minute amounts. The carbon monoxide was estimated in a Bone and Wheeler apparatus, or by Gautier's method, and found to vary with the rate of smoking, being the greater the more rapidly air is artificially drawn through the glowing tobacco, the length and temperature of the glowing portion being thereby increased. Cigarettes, smoked normally, yield a smoke containing 0.6—0.88% of carbon monoxide, pipes from 0.7—1.14%, and cigars from 6—8% (when smoked quickly). As regards cigars, the results are little affected by make or quality, closeness of packing and rate of smoking being the determining factors.

A. A. E.

Differences Effected in the Protein Content of Grain by Applications of Nitrogen made at Different Growing Periods of the Plant. W. F. GERICKE (*Soil Sci.*, 1922, 14, 103—109).—Pot cultures of various cereals were fertilised with sodium nitrate periodically during the first three to four months after sowing. In general, the later the application of nitrogen was made the higher became the protein content of the matured grain. The relative variations of protein content produced, depended on the length of the normal growing period of the plant. Thus no differences were produced by fertilisation during the dormant periods of growth of winter wheat and, to a lesser extent, of rye. The hardness of the wheat grains followed the increased protein content; from a soft seed wheat the whole range from a typically soft to a typically hard grain could be produced according to the period at which nitrates were added. The size of the grains varied but little.

A. G. P.

Biochemistry of Phosphorus. F. ROGOZINSKI (*Bull. Acad. Sci. Cracovie*, 1915, [B], No. 5, 87—98).—In the milling by-products of the cereals, 16—35% of the phosphate is present in an insoluble form, whilst in the residues from oil-bearing seeds the corresponding figure is 50—82%. Most of the soluble phosphate of the maize kernel, including all the phytin phosphate, is present in the germ. In the case of sprouted malt, the inorganic phosphate is found to increase at the expense of the phosphorus in the proteins and the phytin. The phytin phosphate appears to be stored in the outer

portion of the wheat kernel. Rye bran is comparatively poor in phytin phosphate but rich in inorganic phosphate. For the preparation of phytic acid, wheat bran, rice fodder, and rape press cake are the only considerable sources. Coconut press cake has a high content of phytin, and a low content of phosphate, whilst the reverse is true for palm nut press cake. It was observed in the case of the wheat kernel that all the inorganic phosphate is soluble in water, and is present as potassium phosphate. This appears to be the case also in other seeds. CHEMICAL ABSTRACTS.

Absorption (by Soil) of Ammonium Ions from Solutions of Ammonium Salts and the Effect of Electrolytes thereon. B. AARNIO (*Z. Pflanz. Düng.*, 1922, [A], 1, 320—325).—The absorption by soil of ammonium ions from solutions varies according to the ammonium salt used for the experiment, being approximately the same for ammonium chloride and ammonium sulphate, but greater for ammonium hydrogen phosphate. The effect of the addition of electrolytes on absorption from ammonium sulphate and ammonium hydrogen phosphate solutions was also studied. In most cases, absorption is decreased; hydroxyl ions, however, cause increase in absorption. It is held that absorption is influenced according to the effect of the substances present on the degree of dispersion of the absorbent. Electrolytes which flocculate soil decrease absorption, whilst, where a dispersing effect is exerted, absorption is increased. Soil consists both of positively and negatively charged particles and anions are absorbed to some extent as well as cations. G. W. R.

Some Investigations on the Electrical Method of Soil Moisture Estimation. THOMAS DEIGHTON (*J. Agric. Sci.*, 1922, 12, 207—230).—The method examined consists of measuring the resistance between carbon electrodes pressed into the soil to a measured depth.

It is shown that the resistance measured is the mean resistance of a volume of soil rather larger than a sphere of which the two electrodes are the poles. The limitations of the method are discussed, and a mathematical investigation of the path of the current in the soil agrees well with experimental data.

From a consideration of a number of moisture-resistance curves, it is concluded that with moisture contents greater than 10%, the resistance varies inversely with the square of the moisture content. With less than 10% of moisture, one or more irregularities appear in the curves, depending, it would seem, on the physical conditions of the soil colloids. The possibility of determining, by this method, the depth of water tables in arid lands is indicated.

A. G. P.

Origin of Soil Colloids. NEIL E. GORDON (*Science*, 1922, 55, 676—677).—The author disagrees with Whitney's theory (this vol., i, 708) regarding the mode of formation of soil colloids, preferring to regard the process as being based largely on chemical

reactions. Many soil particles are hydrated silicates containing varying amounts of aluminium, iron, silicon, sodium, potassium, calcium, magnesium, and other elements in smaller quantities; they are surrounded by an aqueous film, the salts in the outer layer being subjected to constant hydrolysis. The hydrolytic products of the soluble compounds are partly dissolved by the film, and partly adsorbed by the insoluble products of the iron and aluminium salts which form a gel casing. Percolating rain-water removes part of the soluble salts, thus destroying the salt equilibrium between the water film and the gel, and releasing some of the soluble adsorbed salt to the water film, with eventual peptisation of the gel. The latter, in the course of percolation, may again be coagulated, whilst the soil particle is again exposed to hydrolytic action. There is experimental support for this view of the origin of soil colloids.

A. A. E.

Absorption of Water by Soil Colloids. W. O. ROBINSON (*J. Physical Chem.*, 1922, **26**, 647—653).—Samples of colloidal matter extracted from thirty-four soils, which differed in texture, origin, mode of formation and chemical composition, showed a relatively constant absorption of water. The soils examined included loam, clay loam, silt loam, sandy loam soils, and subsoils. The extreme absorptions were 0.240 gram and 0.348 gram of water per gram of colloid and the mean value was 0.298. It is suggested that the colloidal matter in a soil might be fairly closely estimated by determining under certain conditions the water absorption of the soil and dividing the result by the average factor 0.298.

J. F. S.

Occurrence of Sulphate Reduction in the Deeper Layers of the Earth. C. A. H. VON WOLZOGEN KÜHR (*Proc. K. Acad. Wetensch. Amsterdam*, 1922, **25**, 188—198).—A number of samples of soil (peat, clay, and sand) taken from nine new wells in the Amsterdam district have been examined for the presence of the sulphate reducing organism *Microspira desulfuricans* by placing small portions in a solution containing 100 tap-water, 0.5 sodium lactate, 0.1 asparagine, 0.5 hydrated magnesium sulphate, and 0.001 hydrated ferrous sulphate at 25°. In every case, after two to twenty days the reduction of the sulphate was evident by the formation of ferrous sulphide. Consequently the grey colour of the sand and the blue to bluish-black colour of the clay point to the sulphate reduction occurring at depths from 10 metres to 34.50 metres. The bacteria have been isolated and counted and shown to be facultative anærobic organisms. The transformation of sulphate into ferrous sulphide by *Microspira desulfuricans* explains the partial or total absence of sulphuric acid from deep dune water.

J. F. S.

JOURNAL

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THE CHEMICAL SOCIETY.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN
BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Refraction of Light and Atomic Structure. Refraction Equivalents of Ions. JARL A. WASASTJERNA (*Öfvers. Finska Vet.-Soc.*, 1921, **63**, [A], No. 4, 18 pp.; from *Chem. Zentr.*, 1921, iii, 759).—Cuthbertson's rule for the relation between the refraction equivalents of atoms and their position in the periodic system is applicable to the refraction equivalents of the ions of the alkali and alkaline-earth metals. It follows that the outer electron sheath of an alkali metal contains only one electron which in salt formation passes over to the acid half, which thereby becomes negative. In the case of alkaline-earth metals the outer sheath contains two electrons which go over to the negative atom or group. The next sheath in the alkali and alkaline-earth metals is identical with that in the preceding member of the horizontal series which is nearer to the nucleus on account of increased attraction. Numerical values are given for the refraction equivalent of positive and negative ions. G. W. R.

The Molecular Refraction of Substances of Higher Melting Point and the Calculation of the Corresponding Refractive Exponents to the Temperature of Comparison, 20°. FRITZ EISENLOHR (*Ber.*, 1921, **54**, [B], 2857—2867).—Difficulties are experienced in calculating the refractive values of substances of higher melting point above 20°, since values calculated from the

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Lorentz-Lorenz expression increase perceptibly with increasing temperature, whereas those calculated according to Gladstone-Dale decrease to about a corresponding extent. The only expression for the molecular refraction which is nearly independent of the temperature is that of Eykman, $(n^2-1)M/(n+0.4)d$, but this has never become popular with chemists. If a and b are the factors for the conversion of the Lorentz-Lorenz and Gladstone-Dale to the Eykman values, the expressions $n^2-1/n+0.4=a(n^2-1)/(n^2+2)$ and $n^2-1/n+0.4=b(n-1)$ are obtained, whence $a=n^2+2/n+0.4$ and $b=n+1/n+0.4$. For a given interval of temperature, for example 10° , it is found that the alteration in $\log a \times \log b$ is approximately constant and independent of the value of the refractive index; for the given temperature interval, $\log a = -0.00033$ and $\log b = +0.00024$. The latter value cannot be regarded as completely independent of the magnitude of the refractive index if this varies greatly from the normal value ($n=1.45$) and, for this case, a modified table of corrections is given, but, in general, the values quoted are sufficiently accurate. A number of examples are quoted showing the method of calculating the refractive index from one temperature to another over considerable intervals of temperature; in general, the observed and calculated values are in excellent agreement, but cymene affords an exception. A small number of other substances also do not behave in accordance with Eykman's formula. The substances appear to have a very appreciable vapour tension at the atmospheric temperature and to pass at a comparatively low temperature into a region in which there is no longer a perfectly uniform change of refractive index with the temperature. For safety, it is advisable to restrict observations to a region which does not embrace more than one-third of the temperature of ebullition as usually expressed. H. W.

Optical Properties of Solutions. A Theory of the Structure of the Molecules of Electrolytes. JARL A. WASASTJERNA (*Acta Soc. Sci. Fennicae*, 1920, **50**, No. 2, 129 pp.; from *Chem. Zentr.*, 1921, iii, 758—759).—The refractive indices and densities of aqueous solutions of a number of organic salts, sodium chloride, potassium chloride, and oxalic acid were determined for two different temperatures and for three different wave-lengths at each temperature. From the results obtained certain conclusions were drawn as to the influence of dissociation on the optical properties of electrolytes. The number of valency electrons in each atom may be directly calculated from Eisenlohr's atomic refraction constant and the results are in agreement with Drude's valency theory. A new interpretation of the Lorenz-Planck dispersion formula is given leading to a working hypothesis whereby the selective photoelectric effect can be calculated as well as, in certain cases, the alteration in refraction and dispersion due to ionisation. It is shown that the temperature coefficient of molecular refraction for dissolved salts is always negative by the Newton-Laplace formula, variably positive and negative by the Gladstone-Dale formula, and negative by the Lorentz-Lorenz formula. It is

further shown that the additive character of specific refractive power is satisfied by the Gladstone-Dale formula. For the determination of the molecular refraction of dissolved salts, strong solutions should be used and the values extrapolated for 100%. The optical properties of salt solutions can be simply explained by assuming that the ions occur ready formed in the molecules of strong electrolytes whilst the molecules of weak electrolytes cannot be thus polarised.

G. W. R.

Notes of Spectrography. E. VON ANGERER (*Physikal. Z.*, 1921, 22, 521—523).—A description of various modifications of apparatus and technique used by the author in spectroscopic work. The points included refer to (a) the iron arc, (b) the mercury reference spectrum, (c) the reproduction of a wave-length scale, and (d) an ultra-violet monochromatic light filter.

J. F. S.

The Origin of Band Spectra. YUTAKA TAKAHASHI (*Proc. Phys. Math. Soc. Japan*, 1921, [3], 3, 20—28, 30—33).—It is possible to deduce a formula representing a system of band spectra from the oscillation of the atoms in a molecule if, with Bohr and Sommerfeld, the quantum relations $A_1 - A_2 = h\nu$ and $\int_L p_i dq_i = nh$ are accepted for the conditions of the radiation and the stationary state. A simple Deslandres formula $\nu = A + B(n_1^2 - n_2^2)$ where $B = h/8\pi^2 I_0$ is arrived at. If the angular momentum of the molecular rotation is not a complete multiple of $h/2\pi$ the formula becomes $\nu = A \pm B(n + \epsilon)^2$, where $\epsilon < 1$ as observed in many cases. The theoretical values of A and B in the last equation are found to be of the same order of magnitude as the observed ones for band spectra of nitrogen and oxygen. In the low potential discharge in hydrogen, Fulcher isolated two triplet bands. It is shown that these bands can be represented by the author's formula by taking suitable values for the constants.

CHEMICAL ABSTRACTS.

The Changeable Fine Structure of the Balmer Series. E. GEHRCKE and E. LAU (*Physikal. Z.*, 1921, 22, 556—557).—A change in pressure brings about a change in the intensity relationship of the two components of the Balmer series, which is a series of doublets. The intensity change is most noticeable in the case of H_α and least in the case of H_γ . Using a long tube of 2 cm. bore the ratio I_k/I_l , on changing the pressure from 0.1 mm. to 0.01 mm., increases by 50% for H_α , 11% for H_β , and 5% for H_γ . The ratio I_k/I_l is that of the intensity of the short wave-length component to the intensity of the long wave-length component. The change of the intensity relationship is nearly inversely proportional to the square of the series number. The bore of the tube has a controlling influence on the intensity relationship, thus, in a 5 cm. long tube of 1.5 mm. bore the longer wave-length component is stronger, but both components are faint. The appearance of the lines is unchanged on changing the bore from 5 mm. to 0.1 mm.

J. F. S.

Spectrum of Bromine Vapour ; Zeeman Effect. G. RIBAUD (*J. phys.*, 1917, 7, 205—208).—The emission spectrum of bromine

vapour was studied with the aid of a Geissler tube discharge. If a Geissler tube is placed perpendicularly to the field of an electromagnet, and strong fields are used, the apparent resistance of the tube becomes extremely high, and the discharge requires, therefore, a very high potential; moreover, the lines obtained are much broadened and difficult to measure. The tube is consequently introduced along the axis of the pole-pieces. Twenty-six lines in the region λ 4014 to λ 5332 were studied in a field of 21800 gauss. The values of $\Delta\lambda/H\lambda^2$ for the majority of the lines are grouped about the values 1.05×10^{-4} and 1.23×10^{-4} . Normal separation was not observed for any of the lines, but the lines λ 4766, 4785, and 4816 have a separation very nearly double the normal (cf. A., 1912, ii, 1114; Kimura, A., 1921, ii, 140, 141).

CHEMICAL ABSTRACTS.

Excitation of the Enhanced Spectrum of Magnesium in a Low Voltage Arc. PAUL D. FOOTE, W. F. MEGGERS, and F. L. MOHLER (*Phil. Mag.*, 1921, [vi], **42**, 1002—1015).—A vacuum arc is described in which the electronic-atomic collisions take place at any desired definite velocity of the electrons. The neutral magnesium atom is shown to absorb quanta of the following values, which may be emitted as equivalent quanta of radiation: 46.9 volts, producing *L*-radiation; 22.8 volts (probably), producing double ionisation and resulting in the simple enhanced and the arc spectra; 7.61 volts, producing simple ionisation and resulting in the arc spectrum; 2.70 volts resulting in the single line spectrum. The simply ionised magnesium atom absorbs quanta as follows: 14.97 volts, producing double ionisation and resulting in the simple enhanced spectrum; 4.4 volts resulting in the single-line enhanced spectrum. With high current density other quanta may be absorbed corresponding with fundamental lines of the subordinate series. J. F. S.

Band Spectra of Isotopes. L. GREBE and H. KONEN (*Physikal. Z.*, 1921, **22**, 546—549).—The wave-lengths of the higher members of the band spectrum of uranium-lead and ordinary lead have been compared. The chosen wave-lengths lie between λ 4257.690 and 4281.458 Å.U. Eighteen lines have been compared, and it is shown that the wave-length of the line corresponding with uranium-lead is on the average 0.055 Å.U. shorter than that for ordinary lead. This figure agrees so far as its order is concerned with the assumption that the diatomic molecules are the carriers of the band spectrum. J. F. S.

Wave-lengths of Lines in the Iron Arc from Grating and Interferometer Measurements, λ 3370—6750. CHARLES E. ST. JOHN and HAROLD D. BABCOCK (*Astrophys. J.*, 1921, **53**, 260—299).—One thousand and twenty-six lines were measured with an accuracy of ± 0.001 Å. Manipulative details receive special consideration in this paper. CHEMICAL ABSTRACTS.

Determination of the Terms of the Cyanogen Bands. A. KRATZER (*Physikal. Z.*, 1921, **22**, 552—555).—A theoretical

paper in which the relationships of the violet cyanogen bands are investigated and the values obtained theoretically are compared with the experimental and empirical values of Heurlinger (*Z. Physik.*, 1920, i, 82). It is shown that the zero lines of the violet cyanogen bands are expressed by the formula $\nu = 25797.83 + n_1(2143.88 - n_1 \times 20.25) - n_2(2055.64 - n_2 \times 13.25)$, in which n_1 and n_2 are the quantum numbers. A comparison of the zero values calculated by this equation with the empirically deduced values of Heurlinger shows in most cases an astonishingly good agreement between the two sets of wave-lengths. The whole of the line systems of the violet bands of cyanogen may be calculated by the theoretically deduced formula. $\nu = \nu_e + B_1^{n_1} + n_1 \nu_1^{\circ}(1 - n_1 u_1 x_1) - n_2 \nu_2^{\circ}(1 - n_2 u_2 x_2) \pm 2mB_1^{n_1} + m^2(B_1^{n_1} - B_2^{n_2})$, where $\nu_e + B_1^{\circ} = 25797.83$; $\nu_e = 25795.91$; $\nu_1^{\circ} = 2143.88$; $\nu_1^{\circ} u_1 x_1 = 20.25$; $2B_1^{n_1} = 3.841 - 0.0044n_1$; $\nu_2^{\circ} = 2055.64$; $\nu_2^{\circ} u_2 x_2 = 13.25$ and $2B_2^{n_2} = 3.705 - 0.035n_2$. It now becomes possible to differentiate between the red cyanogen bands and the so-called nitrogen bands, since, as was shown by Heurlinger, the red cyanogen bands and the violet cyanogen bands have a common end term.

J. F. S.

The Absorption Spectrum of Hydrogen Chloride. WALTER F. COLBY and CHARLES F. MEYER (*Astrophys. J.*, 1921, **53**, 300—309).—The hydrogen chloride absorption band extending from 3.16 to 3.70 μ was observed by the use of apparatus similar to that described by Imes (*Astrophys. J.*, 1919, **50**, 251—276). The compensation chamber was found to be superfluous. The absorption chambers, 16 to 60 cm. in length, could be heated to incipient redness. The experiments confirmed results of Paton showing that heating increases the number of observable lines but does not change the wave-length. The wave numbers for 28 lines were tabulated and an equation was derived to represent them. The law of spacing is not parabolic, as has been supposed, but a cubic term is found to be necessary.

CHEMICAL ABSTRACTS.

An Absorption Band Spectrum for Water in the Region of Wave-lengths of Several Decimetres. RICHARD WEICHMANN (*Physikal. Z.*, 1921, **22**, 535—544).—The method of the parallel wire system is so modified that it may be used for the determination of the refractive indices of liquids and gives results with an error of only 0.5%. An exciter has been constructed by means of which a practically monochromatic radiation up to $\lambda = 12$ cm. and of a sufficient intensity can be produced. The resonance curve has a perfectly smooth course and a decrement which in general does not exceed 0.04. The width of the spectrum lines is therefore not much greater than $\Delta\lambda = 1$ mm. In the spectrum of water over the range $\lambda = 65$ cm. to $\lambda = 27$ cm., three bands of anomalous dispersion are found, which at the same time are three absorption bands. The width of the two outside bands is approximately $\Delta\lambda = 3$ cm. The middle band is sharper and has a width of 0.5 cm. These results indicate that it is probable that water possesses a true absorption spectrum in the region of long wave-lengths, which is

a continuation of the usual long wave-length absorption spectrum of water.

J. F. S.

Action of Electrical Fields on Absorption Lines (*D*-Lines of Sodium Vapour). R. LADENBURG (*Physikal. Z.*, 1921, 22, 549—552).—The effect of electric fields of 100,000 volt/cm. on the *D* lines of sodium has been investigated. The sodium light was produced in a quartz capillary filled with a mixture of neon and helium, and was examined in a Lummer-Gehrcke spectroscope. It is shown that no resolution of the absorption lines occurs, but that probably the *p* and *s* components are displaced unequally in the same sense. It is shown that two fundamentally different kinds of electrical action on spectrum lines must be differentiated, (1) the symmetrical, relatively strong Stark effect, which is proportional to the field strength, and (2) the unsymmetrical effect, which is proportional to the square of the field strength and occurs when the influenced electron together with the Coulomb's force act, and in comparison with which the external field is to be regarded as small.

J. F. S.

Effect of a Strong Electrical Field on the Absorption Lines of Sodium Vapour. R. LADENBURG (*Naturwiss.*, 1921, 9, 667; from *Chem. Zentr.*, 1921, iii, 993).—The Stark effect has only been observed with emission spectra of gases under the influence of canal rays. Using a strong electrical field (150,000—200,000 volts/cm.) and a Lummer-Gehrcke interference spectrometer, a marked asymmetrical effect on the absorption lines of sodium vapour in the yellow was observed, and a displacement in the red of 0.02 Å.

G. W. R.

Width of the Absorption Bands of the Rare Earths. KARL F. HERZFELD (*Physikal. Z.*, 1921, 22, 544—546).—A mathematical paper, in which the width and the influence of temperature on the width of the absorption bands of the rare earths is considered. The width is shown to be due to a Stark effect, which is brought about by the penetration, due to the vibration, into the electric fields of the neighbouring ions. This view is in keeping with the dependence of the width on the temperature and leads to widths for the bands which are of the correct dimensions. It is shown that observations on the width of the bands at very low temperatures will furnish information on the existence of an energy zero point. The strength of the electric field in water is estimated as of the order 5×10^7 volts/cm.

J. F. S.

Spectroscopy of Uranium and some Rare Earths. G. MEYER and GREULICH (*Physikal. Z.*, 1921, 22, 583—585).—The minimum concentration of solutions of salts of uranium, cerium, lanthanum, didymium, and thorium which may be detected spectroscopically has been ascertained. The illumination was produced in three ways: (1) sparks from a transformer of 10,000 volts were passed from a platinum wire to a bundle of platinum wires moistened with the solution, (2) a syringe mixture of the salt solution with

phosphoric acid was placed in the platinum electrodes of a Miethe extra current apparatus, and (3) hollow carbon arc carbons were filled with the residue obtained on evaporating the solution to dryness. The following gives the minimum concentrations (c) in mg./c.c. and the wave-lengths of the lines visible at this concentration: cerium, λ 3940.89, 4166.75; $c=0.01$; lanthanum, λ 3949.22; $c=0.006$; didymium, Nd λ 4061.27, 4325.80; Pr λ 4206.81, 4429.41; $c=0.01$; thorium, λ 4391.30, 4382.10; $c=0.01$; uranium, λ 4090.28, 5919.61, $c=5.0$. It is thus seen that the minimum concentration of uranium is approximately 500 times greater than that of the other metals. Experiments were made to ascertain the influence of other salts on the amount of the elements in question which could be detected. The value of $G=U/(U+M)\times 100$ has been determined, in which U and M represent the amounts of uranium and the other element. It is shown that the presence of cerium, lanthanum, didymium, and thorium has very little effect on the visibility of the uranium lines; in all cases the value of G approximates to unity. In the case of fifteen other elements examined with uranium, it is shown that G has a considerable value. It is also shown that a knowledge of the value of $G=U/(U+Fe)\times 100=7$ gives a means of estimating the amount of uranium in a solution of a uranium salt. The method consists in adding an iron salt to the solution until the persistent uranium lines just vanish. In the case of a solution of uranium sulphate containing 15.8 mg./c.c., there was found, using this method, 15.4 mg./c.c. The influence of the addition of salts of iron, nickel, chromium, manganese, potassium, sodium, calcium, cobalt, lithium, aluminium, magnesium, uranium, cerium, didymium, and thorium on the persistence of the spectrum lines obtained from solutions of cerium, lanthanum, didymium, and thorium salts was also investigated. The values $100Ce/(Ce+M)$; $100La/(La+M)$; $100Di/(Di+M)$, and $100Th/(Th+M)$ vary between 0.5 and 1.0 for all cases except those in which sodium to cerium, of the above list, have been added. It therefore follows that the rare earths are detectable in much smaller quantities in mixtures than is uranium.

J. F. S.

Absorption of Ultra-violet Light. THOS. H. DURRANS (*Perf. Essent. Oil Rec.*, 1921, **12**, 370—371).—The ultra-violet absorption spectra of eugenol, *isoeugenol*, methyl*isoeugenol*, anethole, methylchavicol, and anisole were examined. *isoEugenol* absorbs more strongly than eugenol, and methylation of the phenolic group still further increases the absorption, an $N/10,000$ solution being opaque in thicknesses greater than 20 cm. The absorptive power of anethole is remarkable, 10 cm. of $N/10,000$ solution or 0.25 mm. of pure anethole completely stopping ultra-violet light of a wave-length of less than about 27 Å.U. The substitution of the propenyl side-chain by the allyl radicle, or its complete removal, causes an enormous diminution of the absorptive power. The paper is illustrated by photographs of the absorption spectra of the substances examined.

G. F. M.

Absorption of Light by Solutions. HARALD LUNELUND (*Ofvers. Finska Vet.-Soc.*, 1916—1917, 59, No. 21, 21 pp.; from *Chem. Zentr.*, 1921, iii, 810).—Working with aqueous solutions of "brilliant safranin," "tartrazine," "crystal-ponceau," and "rose Bengal" with and without addition of sulphuric acid, it was shown that the extinction coefficient, ϵ , calculated from the formula $I' = I \cdot 10^{-\epsilon d}$, agrees with Beer's law, according to which the extinction coefficient is proportional to the concentration. Using the König-Martens spectral photometer, it is shown that in aqueous solutions of safranin a marked maximum absorption occurs for λ 519 μ . By addition of sulphuric acid the colour changes to green through violet, and the absorption maximum changes to λ 622 μ . G. W. R.

A Theory of Chromo-isomerism of Solid Compounds. HOWARD J. LUCAS and ARCHIE R. KEMP (*J. Amer. Chem. Soc.*, 1921, 43, 1654—1665).—See this vol., i, 30.

Hydrated Boric Acid as the Basis of Systems Capable of [Showing] a High Phosphorescence. E. TIEDE, P. WULFF, and A. RAGOSZ (*Physikal. Z.*, 1921, 22, 563).—When boric acid is mixed with certain organic substances, particularly aromatic and heterocyclic substances, and partly dehydrated by melting, it is found on cooling that the mixtures are strongly phosphorescent. These substances after illumination by ultra-violet light emit a phosphorescent glow of a colour which varies with the organic substance and in the best cases persists for two to three minutes after the exciting light is removed. J. F. S.

Destruction of Phosphorescent Zinc Sulphides by Ultra-violet Light. LEONARD B. LOEB and LLOYD SCHMIEDESKAMP (*Proc. Nat. Acad. Sci.*, 1921, 7, 202—207).—Three different samples of phosphorescent zinc sulphides were exposed in very thin layers to the action of ultra-violet light from a mercury arc. In each case there was a marked decrease in phosphorescent intensity (measured by a phosphoroscope) with increase of time of ultra-violet illumination. The reduction of intensity was accompanied in each case by a darkening in colour. Exposure to chlorine restored to some extent the original colour and ability to phosphoresce. Some points of similarity with the destruction of phosphorescence by the bombardment of α -particles are discussed. G. W. R.

Linear Polarisation of the Blue Light from the Focus of the Lilienfeld Röntgen Tube. H. SEEMAN (*Physikal. Z.*, 1921, 22, 581—582).—It has been shown by Lilienfeld and Rother (*ibid.*, 1920, 21, 249, 360) that the light from the point of convergence of the Lilienfeld tube is almost completely linear polarised in the sense that the vibrations of the electric vector are at right angles to the plane of the anti-cathode which is inclined generally at 45° to the direction of the cathode rays. The present paper shows that this phenomenon can be observed without special apparatus

in full daylight by means of a Nicol prism held before the eye. The phenomenon is not observed in Coolidge or Müller electron tubes because of the very intense white light. J. F. S.

Studies on the Dependence of Optical Rotatory Power on Chemical Constitution. IV. Aryl Derivatives of Bisimino-camphor. BAWA KARTAR SINGH, MAHAN SINGH, and JIWAN LAL (T., 1921, 119, 1971—1976).

Negative Optical Anomalies. GERVAISE LE BAS (*Chem. News*, 1921, 123, 271—272).—From a study of certain thiophen derivatives, it is shown that substitution α 2 in position 3 can reduce the negative anomaly of sulphur to zero. Substitution on both sides of the sulphur atom practically neutralises the negative anomaly. The full substitution of one ethenoid group or substitution on one side of the molecule reduces the negative anomaly to half its value. Chlorine and bromine have lost their usual positive anomalies for substitution in these cases. W. G.

Mechanism of the Photochemical Chlorine-Hydrogen Gas Reaction and the Question of the Damping of the Velocity [of Reaction] of Chlorine Activated by Light. RUDOLF GÖHRING (*Z. Elektrochem.*, 1921, 27, 511—518).—The paper opens with an account of the principal investigations on the photochemical reactions between hydrogen and chlorine which have been carried out in the last twenty years. The possible reactions which may occur photochemically in a mixture of chlorine, hydrogen, and a little oxygen after the reaction $\text{Cl}_2 + L = 2\text{Cl}$ are considered. From a large number of possible combinations of reactions two sets are picked out, which both conform to Bodenstein's empirical reaction equation. The Bodenstein equations are theoretically deduced. The light absorption by chlorine has been measured for several wave-lengths and the fraction of light absorbed from the radiation of an Osram lamp has been calculated. It is shown that the number of quanta absorbed by 1 c.c. per sec. is approximately 2×10^{11} . The number of collisions calculated for the gas theory and the number of absorbed quanta are compared with reaction velocity calculated by Bodenstein. It is shown that for $1h\nu$ the number of molecules of hydrogen chloride formed is 5×10^5 . Inserting the collision number and the measured reaction velocity in the equations deduced does not lead to any contradiction of the initial assumptions. The time required for damping of the activity of chlorine activated by light is calculated, and it is shown that theoretically no effect was to be expected in the experiments of Bodenstein and Taylor (A., 1916, ii, 463), although under other definite conditions an effect might have been observed. J. F. S.

The Decomposition of Ozone by Light of the Visible Spectrum. ROBERT OWEN GRIFFITH and WILLIAM JAMES SHUTT (T., 1921, 119, 1948—1959).

Verification of the Photochemical Equivalent Law with Photographic Dry Plates. J. EGGERT and W. NODDACK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1921, 631—635).—Dry plates

of various kinds have been illuminated with light of wave-length $407.8\mu\mu$ for measured periods of time and the amount of metallic silver formed by the absorption of a measured amount of light energy has been ascertained. It is shown that for a given type of dry plate (Agfa reproduction) the ratio N/Q , where N is the number of silver atoms formed by an amount of light energy Q quanta is constant and equal to 3.0%, that is, the production of one atom of silver requires 3% of the light energy striking the plate. The light absorption by the non-illuminated plate has been directly measured and is shown to be about 12—15%. A further experiment shows that about one hundred times as many quanta are absorbed as are silver nuclei formed. This indicates that about 100 quanta must act on a single particle before it can be reduced by the developer. The results point definitely to the conclusion that not every absorbed quantum produces a silver particle, but, in the case of moderate illumination, every silver particle corresponds with one and only one absorbed quantum. This is in keeping with the experimental result that the number of developed nuclei is proportional to the amount of absorbed light.

J. F. S.

Photochemistry of Silver Compounds. FRITZ WEIGERT and W. SCHÖLLER (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1921, 641—650).—Experiments have been carried out in silver chloride emulsions with the object of ascertaining the mechanism of the photographic copying process. It is shown that silver chloride is, of itself, neither light sensitive, nor does it furnish a noticeable quantity of the silver which constitutes the photographic positive. The colloidal metallic silver, which is present as an impurity in very small amounts in fresh unilluminated emulsions, is the only light sensitive substance present. The colouring of the emulsion layers therefore commences very slowly and after a while accelerates itself for a short time and then the rate of colouring decreases since the photographic yield in such solid systems is smaller with increasing quantities of silver. This behaviour is represented by an S-shaped curve which is obtained by plotting the amount of silver formed as ordinates against the time of illumination. The strong colouring in systems rich in silver acts in the same sense, since the silver behaves as a harmful light filter. The fact, that in this case the substance, which is light sensitive, is produced by the process itself, shows that the photochemical process takes place in molecules other than those which actually absorb the light. Since the system is solid the transmission of energy from the absorbing molecules to the reacting molecules cannot take place through collisions as in gaseous systems. It is therefore probable the energy transmission occurs by means of electrons. In a single atom, as, for example, the absorbing silver atom, no process other than the separation of an electron can occur through the absorption of an energy quantum. The electron is absorbed by the surrounding silver salts with the production of a photo-electric effect.

J. F. S.

Action of Ultra-violet Light on Colloidal Platinum.

ELLWOOD B. SPEAR, P. F. JONES, A. S. NEAVE, and M. SHLAGER (*J. Amer. Chem. Soc.*, 1921, **43**, 1385—1391).—A number of experiments on the coagulating action of ultra-violet light on platinum sols of various concentrations have been carried out at 20—22°. It is shown that ultra-violet light will precipitate colloidal platinum from solutions which contain no electrolytes other than carbon dioxide or constituents of the hard glass containers. Thus a solution containing 0.038 gram of platinum per litre was half coagulated in ten hours by ultra-violet light, whilst in the absence of ultra-violet light coagulation was not complete in two years. Coagulation by electrolytes is greatly accelerated by ultra-violet light. Thus a solution containing 0.038 gram of platinum was half coagulated in seven minutes by a solution of sodium chloride containing 4.25 millimols per litre when the action took place in ultra-violet light, but when no ultra-violet rays were employed sixty-four minutes were necessary to accomplish the same change. The action of ultra-violet light is greater in dilute solutions than in concentrated solutions of the colloids. J. F. S.

The Action of Light of Short Wave-lengths on some Organic Acids and their Salts. FRANS MAURITS JAEGER (*T.*, 1921, **119**, 2070—2076).

Photochemistry of the Retina. FRITZ WEIGERT (*Z. Elektrochem.*, 1921, **27**, 481—487).—The processes occurring in the retina are considered and an hypothesis of the action is advanced on the basis of experiments on the velocity of bleaching of layers of collodion containing dyes by polarised light. The velocity of bleaching of layers of collodion containing cyanine by linear polarised light has been examined spectro-photometrically and dichrometrically. It is shown that the velocity of bleaching of a freshly-prepared layer is much greater than that of an already partly bleached layer of the same extinction. It is also shown that layers of dyes resemble very strongly the photochlorides. J. F. S.

Phototropy and Photoelectric Effect. PATRICK H. GALLAGHER (*Bull. Soc. chim.*, 1921, [iv], **29**, 961—976; cf. *A.*, 1921, i, 715).—The author has applied the method of Padoa and Amaduzzi (cf. *A.*, 1912, ii, 227) in a modified form to a study of photo-electric effects in relationship to phototropy in the case of a number of aldehyde-amines. Phototropic compounds show photo-electric fatigue on exposure to the light from a mercury lamp much more slowly than other substances. The results seem to indicate that in phototropic transformations there is a liberation of electrons. An electron so liberated will take up a new position in the molecule or will remain at some distance from the molecule in a state of forced equilibrium. Its intervention in the photo-electric effect will be secondary. The relationship between phototropy and phosphorescence and fluorescence is considered. W. G.

Passage of α -Rays through Materials. H. RAUSCH VON TRAUBENBERG and K. PHILIPP (*Physikal. Z.*, 1921, **22**, 587—588).—The range of α -rays in liquids and gases has been investigated. The range of the α -ray in water is found to be 60μ . In the case of gases, carbon monoxide, carbon dioxide, methyl bromide, methyl iodide, chlorine, hydrogen chloride, and ammonia have been investigated and results obtained which agree with the results obtained by Bragg by the ionisation method. In the case of liquids, the range was measured by immersing a Sidot screen in the liquid until it just fluoresced and measuring the thickness of the liquid layer with a horizontal microscope. The range in gases was obtained by passing the beam of rays parallel to the horizontal side of a glass wedge containing the gas and placing in the path of the rays a Sidot screen at a small angle to the horizontal. By observing the boundary of dark and light on the screen, the range may be deduced. Taking oxygen as standard, it is shown that the stopping power of the gases varies as \sqrt{Z} . It is shown that the stopping power of compounds is not strictly additive as Bragg has stated, and it is now shown that the stopping power of hydrogen varies in different compounds, thus H_2 , 0.200 per atom; but in the compounds C_2H_2 , C_2H_4 , C_2H_6 , CH_4 , 0.187; NH_3 , 0.173; and HCl , 0.16.
J. F. S.

Collisions of α -Particles with Hydrogen Nuclei. J. CHADWICK and E. S. BIELER (*Phil. Mag.*, 1921, [vi], **42**, 923—940).—The relationships which hold in the collisions between α -particles and hydrogen nuclei have been investigated. The angular distribution of the hydrogen particles projected by α -particles of mean range 6.6 cm. has been determined up to an angle of 66° . The distribution for α -rays of mean ranges 8.2, 4.3, and 2.9 cm. has been obtained over a smaller range of angle. It is shown that the number of hydrogen particles projected within these angles by α -rays of high velocity is greatly in excess of that given by forces varying as the inverse square of the distance between the centres of the two nuclei. The variation in the number of hydrogen particles projected within a given angle with the velocity of α -rays has been observed over a wide range. It is shown that for α -rays of high velocity the variation is in the opposite direction to that given by the inverse square law; for α -rays of range less than 2 cm. and velocity less than 1.26×10^9 cm. per sec., however, the collision relation is about the same as that given by the inverse square law. The experimental collision relation is compared with those calculated by Darwin for various models of the α -particle, and the conclusion is drawn that the α -particle behaves in these collisions as an elastic oblate spheroid of semi-axes about 8×10^{-13} and 4×10^{-13} cm., moving in the direction of its minor axis. Outside this surface, the force varies approximately as the inverse square of the distance from the centre of the spheroid. J. F. S.

Recoil of Hydrogen Nuclei from Swift α -Particles. A. L. MCAULAY (*Phil. Mag.*, 1921, [vi], **42**, 892—904).—An account of

work undertaken to ascertain the number of atoms recoiling at various angles from an homogeneous α -ray beam, from thorium-*C* and radium-*C* respectively with the object of obtaining data bearing on the nature of the collisions, the size of the colliding particles, and similar quantities. The experimental method was similar in principle to that already described (*ibid.*, 1920). An experiment made to determine the relation between the α - and γ -ray activity of thorium-*C* is described. J. F. S.

The Oxidising Properties of certain Radioactive Elements.

PIERRE LEMAY and LÉON JALOUSTRE (*Compt. rend.*, 1921, **173**, 916—918).—The bromides of mesothorium, radiothorium, thorium-*X*, and radium were found to be catalysts of certain oxidation reactions. Their action is not due to the intermediate formation of ozone but to α -radiation, and, for the small amounts of material used, it is the same for the four elements. W. G.

Scattering of β -Rays by Thin Metal Sheets. H. GEIGER and W. BOTHE (*Physikal. Z.*, 1921, **22**, 585—587).—The scattering of β -rays by thin metal sheets has been measured (*a*) in the region of small scattering angle ($\phi=15^\circ$ or less) and (*b*) in regions of large scattering angle ($\phi=60^\circ$ or more). It is shown that there is a fundamental difference between the two types of scattering. In the region of smaller angles, the observed angle is produced by the superposition of many individual small scattering angles through which the β -ray is bent as it passes the individual atoms (multiple scattering), whilst in the region of larger angles the superposition plays a subordinate rôle; each scattering angle is produced by a single collision of a β -ray with a single atom. This is relatively rare, for it is only brought about when the path of the electron lies very close to the nucleus of the atom (individual scattering). In the case of β -rays from radium-*(B+C)*, it is shown that for the very thinnest layers (under 0.01 mm.) the scattering is less than that demanded by the square root law, but for thicker layers this law is confirmed. There is an inverse proportionality between mv^2 and the probable scattering angle, if the uncertain measurements for β -rays of high velocity are left out of account.

J. F. S.

Excitation of γ -Radiation by α -Particles from Radium Emanation. F. P. SLATER (*Phil. Mag.*, 1921, [vi], **42**, 904—923).—A hard γ -radiation is emitted when α -particles from radium emanation impinge on metals such as lead and tin. The radiation differs but little in quality when the radiator is changed from one of high atomic number to one of low atomic number. The coefficients of absorption in lead are 1.8 cm.^{-1} for lead and 2.1 cm.^{-1} for tin. The intensity obtained is very small, and only a small fraction of the impinging α -particles can be effective. For the same absorption conditions the intensity is about 50% greater for the lead radiation than for the tin radiation. It appears to be emitted fairly uniformly in all directions, but differs in all other respects from the characteristic radiations, and is probably emitted from

the nuclei of the atoms in the radiator after direct collision with the α -particles. No hard radiation is emitted by the disintegration of the radium emanation nucleus in the ordinary course of radioactive transformation. Elements of high atomic number when bombarded by α -particles emit two well-defined types of radiation, corresponding roughly with their characteristic K and L radiations. Tin, an element of medium atomic number, emits one type, within the range of the experiments, of quality roughly the same as its L radiation. The quantity of radiation emitted by any element is so small that a very small fraction of the impinging α -particles can cause radiation. Radium emanation emits, under the conditions of the experiments, no soft radiation on disintegration.

J. F. S.

Excitation of Soft Characteristic X-Rays. O. W. RICHARDSON and C. B. BAZZONI (*Phil. Mag.*, 1921, [vi], **42**, 1015—1019).—A development of work previously published by the authors (A., 1917, ii, 521). The thermionic radiation from a tungsten wire has been allowed to fall on targets of carbon, molybdenum, copper, and tungsten and in all cases an emission of radiation has been detected. In the case of carbon and molybdenum, the critical potential at which radiation sets in has been determined with considerable exactitude. In the case of carbon, the target was prepared on a copper disk from india-ink, and the thermionic current was kept constant by reducing the temperature of the filament as the operating voltage was increased. Although the pressure was of the order 10^{-8} — 10^{-9} mm., a radiation effect was present at 220 volts which may have been due to residual gas as it was independent of the voltage above 220 volts. A radiation occurs at 286 volts. If it be admitted that the radiations are soft X-rays excited according to the same laws as hard X-rays and the quantum relation is applied, it is found that the wave-length of the shortest member of the group lies between 42.7 and 44.3 Å.U. and is probably close to 43.4 Å.U. Extrapolating from K_{β} for aluminium and using Moseley's relation, it is found that K_{β} for carbon should have the wave-length 45.5 Å.U. This makes it practically certain that the radiation is the K series of carbon. In the case of molybdenum, radiation is obtained at 356 volts, which corresponds with the wave-length 34.8 Å.U. Calculating from Vegard's empirical relation, the M_{α} line of molybdenum should be 35.2 Å.U., which indicates that the radiation is the M series of molybdenum.

J. F. S.

Scattering of Röntgen Rays by Anisotropic Liquids. E. HÜCKEL (*Physikal. Z.*, 1921, **22**, 561—563).—The scattering of Röntgen rays by *p*-azoxyanisole, *p*-azoxyphenetole, dianisylideneazine, cholesteryl propionate and cholesteryl benzoate as solid, clear-liquid, and turbid-liquid crystals has been photographed with the object of ascertaining whether or no the liquid crystals possess a space lattice. Several of the photographs are reproduced in the paper, and show that the turbid liquids do not consist of

regions built up on a space lattice, and, further, that in the suspended liquids there is no noticeable amount of material built up on a space lattice. It is not impossible, however, that small quantities of crystals are suspended in the liquid, since the interference bands which they would produce are too weak to be visible. It is shown that the term anisotropic liquids must be used in place of that of liquid crystals, for the word crystal implies a space lattice. If this is not adopted it will be logical to term as crystals a gas with molecules which carry electric dipoles in an electric field, also paramagnetic gases in a magnetic field. Consequently, it is to be taken that anisotropic liquids possess a more or less ordered arrangement of their molecules on account of their electrical and magnetic characteristics. J. F. S.

A Precision Röntgen Spectrograph. H. SEEMANN (*Physikal. Z.*, 1921, 22, 580—581).—A Röntgen spectrograph is described which is designed to measure lines of the hardest spectrum region. Using rock salt, reflecting crystal measurements may be made beyond 1 Å.U., and also in the softest technical Röntgen spectrum by using a gypsum reflecting crystal, measurements may be obtained beyond 3 Å.U. The instrument is designed for both the camera and window methods of measurement. J. F. S.

Fine Structure of Röntgen Spectra. ADOLF SMEKAL (*Physikal. Z.*, 1921, 22, 559—561).—A theoretical discussion of the fine structure of Röntgen spectra in which it is shown that if the sum of the quanta of an electron layer is k , that is, the layer is k -quantal, then the number of energy levels belonging to the layer is $2k-1$. According to Bohr, the O -layer of the heaviest elements is tri-quantal and the P -layer is di-quantal; it follows that there must be $5O$ and $3P$ energy levels. Wentzel has shown by means of his principle of selection that the O -layer is actually tri-quantal. J. F. S.

The Existence of a New Radioactive Emanation in the Springs of Bagnoles-de-l'Orne and its Surroundings. P. LOISEL (*Compt. rend.*, 1921, 173, 1098—1101).—In studying the gases dissolved in the water of a large number of springs in the region of Bagnoles-de-l'Orne, a curve of activity was obtained which could not be explained by the presence of any known emanation. The curve showed at first a decreasing activity, then a rise to a maximum, followed by a decrease. The results indicate the presence of a new, simple, radioactive substance, to which the author provisionally gives the name *emilium*. W. G.

Radioactivity and Atomic Constitution. LISE MEITNER (*Naturwiss.*, 1921, 9, 423—427; from *Chem. Zentr.*, 1921, iii, 847).—A discussion of the subject of isotopes in relation to atomic transformations. From a formula connecting the number of nuclear constituents with the number of helium nuclei and the number of electrons, four possible types of atomic disintegration of radioactive elements are deduced. G. W. R.

Adsorption of Radium by Barium Sulphate. FRANK E. E. GERMANN (*J. Amer. Chem. Soc.*, 1921, **43**, 1615—1621).—From experiments on the adsorption of radium, from a radium barium chloride solution, containing 22.79×10^{-10} gram of radium per c.c., by barium sulphate, it is shown that Kroeker's adsorption law is true in the case of the adsorption of a radioactive substance. The adsorption law of Freundlich is found to be equally true in the case of a radioactive substance. Consequently, it follows that the laws which apply to the adsorption of easily weighable masses also apply with an equal degree of accuracy to masses of the order 5×10^{-8} gram adsorbed by 1 gram of adsorbent. The relationship existing between adsorption taking place during precipitation and that taking place on a solid precipitate of definite surface area has been discussed. J. F. S.

The Radioactivity of Mineral Springs. II. ERICH EBLER and A. J. VAN RHYN (*Z. anorg. Chem.*, 1921, **119**, 135—144; cf. A., 1911, ii, 1049).—Borings for thermal water undertaken by the town of Heidelberg in 1913 provided an opportunity for studying the relationship of radium to radium emanation content and the influence of depth and geological considerations on the radioactivity of the water. The waters from these borings were also compared with those from other springs. In the Heidelberg waters the radium emanation content was constant at about 10^{-10} "Curie" per litre, and was independent of the depth of the boring down to 600 m. The granite springs of Löwenbrunnen show a higher and the New Red Sandstone springs of Felsenmeer a lower emanation content, in agreement with the known relatively high radium content of granite and the low radium content of sandstones. The radium salt content of the water from the Heidelberg borings was of the order 10^{-12} gram per litre, but rose at a depth of 590 m. to $0.97 \cdot 10^{-10}$, of the same order as that in the Max spring at Bad-Dürkheim (*loc. cit.*). This observation supports the view that the radium content increases with the depth of the spring. The granitic water of Löwenbrunnen does not show a high radium salt content corresponding with its high emanation content. It is important when comparing different waters to measure both radium and radium emanation content, as these may vary independently of each other. E. H. R.

The Adsorption of Radioactive Substances. II. ERICH EBLER and A. J. VAN RHYN (*Ber.*, 1921, **54**, [B], 2896—2912; cf. A., 1911, ii, 957).—The view has been expressed previously (*loc. cit.*) that the colloidal condition does not exercise a directive influence on the behaviour of colloids towards radio-elements, but that this depends on the chemical nature of the substances, the reactions which occur being expedited by the increased surface. Thus, the adsorption of radioactive material by silica or, more precisely, by its hydrate, is due to the formation of sparingly soluble silicates which owe their origin to the acidic nature of the hydrate. The discordant results obtained by many observers

are due to the fact that the acidity of the solution plays an important part, since acid has a de-adsorbent action probably in accordance with the scheme: $\text{RaSiO}_3 + 2\text{HCl} = \text{RaCl}_2 + \text{H}_2\text{SiO}_3$. In addition, the silicic acid and its gels which have been used are very ill-defined products which, owing to the number of factors affecting their condition, are frequently not reproducible. In this connexion it is pointed out that the statement of Horovitz and Paneth (A., 1915, ii, 305) that the separation of silica during the estimation of radium in minerals is of no importance is only true within certain limits, since if free acid is not present in considerable quantity, the precipitate carries down radium.

The adsorptive power of charcoal for radioactive material appears difficult to explain in the light of the hypothesis outlined above. It is pointed out, however, that the varieties of charcoal employed never consist of pure carbon. In a series of experiments the adsorptive power of blood and animal charcoal towards uranium-*X* has been compared with that of pure charcoal in differing degrees of fineness (prepared by the carbonisation of pure sugar, extraction of the residue with water, and ignition of the product at bright redness). It is found that the selective adsorption of uranium-*X* by pure carbon is very much less than that of the impure varieties. An active preparation is obtained, however, when pure charcoal is mixed with the residues prepared by extracting blood or animal charcoal with water or dilute acid and subsequent evaporation of the extracts to dryness. The adsorptive power of impure charcoal, therefore, appears to be due to the impurities contained in it.

The adsorption of radium by barium sulphate has been examined further. This so-called "precipitation" of radium sulphate is not, in reality, a precipitation in the usual sense since, on account of the small concentration of radium, the solubility product $L = K \cdot C_{\text{Ra}} \cdot C_{\text{SO}_4}$ is seldom attained. It is shown that co-precipitation of radium sulphate with barium sulphate from solutions containing radium and barium is only complete when the barium is completely precipitated. An exact distribution of radium between the solid and liquid phase does not appear to occur.

H. W.

The Adsorption of Thorium-*B* and Thorium-*C* by Ferric Hydroxide. JOHN ARNOLD CRANSTON and ROBERT ALEXANDER BURNETT (T., 1921, 119, 2036—2044).

Excitation of Atoms to Emission of Light by Electronic Collisions. IV. Behaviour of Individual Members of a Series. R. SEELIGER (*Physikal. Z.*, 1921, 22, 610—613; cf. A., 1921, ii, 143, *Z. Physik.*, 1920, i, 355; 1921, 5, 182, 7, 93).—An examination of the spectra of helium, hydrogen, mercury, and neon produced by collisions with electrons shows that two kinds of series are produced, the one, which shows the regular behaviour, namely, that the optimal velocity increases with increasing member number, and the intensity maximum is displaced toward

the cathode with increasing member number, and the other, where the opposite behaviour is observed. To the first belong the Balmer series of hydrogen and both subsidiary triplet series of mercury, whilst to the second belong, the series of neon and helium.

J. F. S.

Entropy of Electron Gas. RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 1592—1601).—It is shown that considerable simplification in expression and thought can be achieved by treating electrons as atoms of a chemical substance. This substance, which may be regarded as a gas "*plus que parfait*," owing to the very considerable force of repulsion between electrons, will not deviate appreciably in behaviour from a perfect monatomic gas if the concentration is low enough and the temperature high enough so that the effects produced by the repulsive force between the electrons can be neglected in comparison with the effect produced by their thermal agitation. It is shown with a reasonable certainty that the entropy of electron gas may be calculated from the theoretical equation, $S = 5/2R \log_e T - R \log_e p + 3/2R \log_e M + S_1$, which is found to apply to the monatomic gases. Using this equation, the entropies of 1 mol. of electron gas in equilibrium with metal filaments at 2000° are found to be: tungsten 53.3, tantalum 52.3, molybdenum 51.0. The entropy may also be calculated from the heat of vaporisation of the electron gas by the equation $S = \Delta H/T$, in which ΔH is the heat absorbed when 1 mol. of electrons is reversibly evaporated at T . The following values are obtained: tungsten, $\Delta H = 107270$ cal., $S = 53.6$; tantalum, $\Delta H = 107970$ cal., $S = 54.0$; molybdenum, $\Delta H = 109770$, $S = 54.9$.

J. F. S.

Thermal Ionisation of Metallic Vapours. RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 1630—1632).—Making use of work recently published on the entropy of electron gas (see preceding abstract) it is shown that further information on the thermal ionisation of metallic vapours may be obtained. Thus assuming that a metallic vapour can ionise into a positive ion and an electron thus: $R = R^+ + E^-$, it is shown that $\Delta F = EQ - 5/2RT \log_e T + (5/2R - 3/2R \log_e M_E - S_1)T$ which connects the free energy with the heat content and the entropy and is of the same form as the well known free energy equation $\Delta F = \Delta H_0 - \Delta C_p T \log_e T + IT$. The ionisation constant is given by the equation $\log_e K_p = -EQ/RT + 5/2 \log_e T - (5/2 - 3/2 \log_e M_E - S_1/R)$, or, putting in the numerical values of the constants $Q = 96540$ coulombs, M_E (the molecular weight of electron gas) $= 5.44 \times 10^{-4}$ gram. $S = -3.2$ cal./degree and $R = 1.985$ cal./degree the equation becomes: $\log_e K_p = -5040E/T + 2.5 \log T - 6.69$, where E is the ionisation potential in volts. Using the above formulæ, the author calculates the ionisation of calcium in the sun. Taking the ionisation potential as 6.1 volts, the partial pressure of un-ionised calcium vapour as 4 atms., and the temperature as 5500° abs., it is found that the partial pressure of the calcium ion or electron gas is 0.07 atm., corresponding with 1.7% ionisation.

J. F. S.

New Detectors of High Frequency Vibrations. W. HEIKE (*Z. anorg. Chem.*, 1921, **118**, 255—263).—An account of experiments made with the object of discovering an artificial detector for use as a substitute for pyrites in wireless telegraphy. Preparations of zinc arsenide, ZnAs_2 , containing crystals of zinc antimonide, ZnSb , proved specially sensitive. The zinc-arsenic alloys are discussed in the succeeding paper (this vol., ii, 60).

E. H. R.

Conductivity of Solutions of Ternary Electrolytes in Propyl Alcohol. CHARLES A. KRAUS and JOHN EGBERT BISHOP (*J. Amer. Chem. Soc.*, 1921, **43**, 1568—1575).—The electrical conductivity of anhydrous calcium nitrate and magnesium nitrate hexahydrate in anhydrous propyl alcohol and magnesium nitrate hexahydrate in mixtures of propyl alcohol and water has been determined at 18° for a series of concentrations. The present results are compared with those of Schlamp (A., 1894, ii, 376) on lithium and calcium chlorides and it is shown that his results indicate that the calcium chloride must have been hydrated. Neither the present work nor that of Schlamp supports the view that ternary salts ionise in this solvent according to a binary process. The specific conductivity of anhydrous propyl alcohol at 18° is 1.7×10^{-7} .

J. F. S.

The Theory of Electrolytic Ions. XXVI. How is the Limiting Value of the Molecular Conductivity of Strong Electrolytes Determined? RICHARD LORENZ (*Z. anorg. Chem.*, 1921, **118**, 209—222; cf. A., 1921, ii, 158, 481, 482, 483).—A graphic method for determining the limiting molecular conductivity μ_0 of univalent electrolytes is described, based on Herz's theory of ionic conductivity (A., 1921, ii, 482). According to this theory, the conductivity of a single ion is expressed by the equation $B(\lambda_0 - \lambda) = \psi(\omega)$, where B is a constant and $\omega = A[S]^\frac{1}{2}$, where A is another constant and S is the concentration. The ionic conductivity λ of the theory is identical with the molecular conductivity, μ . The graphic method described depends on the fact that, by means of the constants A and B , the $[S]^\frac{1}{2}$ -conductivity curve of any substance can be transformed to coincide with a "universal conductivity curve." The molecular conductivities as ordinates are plotted against $[S]^\frac{1}{2}$ as abscissæ on a prescribed scale, and by a simple geometric process the curve obtained is transformed into a form of the universal curve. By comparing this derived curve with a series of standard curves printed on transparent paper on the same scale, the values of μ_0 and of the constant B can be read off on the ordinate axis.

E. H. R.

Concentration and Potential Fall at Boundary Surfaces. H. FREUNDLICH (*Z. Elektrochem.*, 1921, **27**, 505—511).—A theoretical paper in which the change in concentration and the *E.M.F.* at the boundary surfaces of two liquids is considered. It is shown that the concentration of saponin or amyl alcohol in the foam produced at the air-water interface is due to the lowering of the

surface energy at the interface. All cases of adsorption are shown to be fundamentally due to the same cause. The case of adsorption on crystal faces is particularly considered, and although in this case the adsorption is held to be due to residual affinity, it is shown that here the phenomenon is molecular-kinetic, whilst with the surface tension a thermodynamic function is employed. In the case of surface tension, the mean value of a large number of molecules is considered, whilst with crystal surfaces when considering the residual valencies individual molecules only are concerned. The *E.M.F.* existing at interfaces and the changes effected by the introduction of foreign non-electrolytes is considered.

J. F. S.

The Normal Potential of Silver. I. M. KOLTHOFF (*Z. anorg. Chem.*, 1921, **119**, 202—212).—The electrolytic potential of silver was measured in silver nitrate solutions varying in strength from 0.001 to 0.1*N* at 18° against a normal calomel electrode. The mean value found for the silver potential was -0.7887 volt against the normal hydrogen electrode. Potassium nitrate, up to a concentration of 1.0*N*, has no measurable effect on the potential of the silver electrode. From measurements with a silver-silver bromide electrode in solutions of potassium bromide from 0.001 to 0.5*N*, the solubility product of silver bromide at 18° was found to be 4.1×10^{-13} . The concentration of bromine ions can be calculated from the equation $\log [\text{Br}] = (-\pi - 0.34852)/0.0576$. In presence of sulphates in solution, the silver electrode becomes "nobler"; the same is true of the mercury electrode. E. H. R.

Some Phenomena in the Electromotive Behaviour of certain Metals. NIL RATAN DHAR (*Z. anorg. Chem.*, 1921, **118**, 75—80).—If the potential difference between a metal and a solution of one of its salts increases with increasing dilution, it is to be expected, by extrapolation of Nernst's formula, that the potential difference would be still greater when the metal is in contact with water or a solution of a neutral electrolyte. Conversely, if the *E.M.F.* decreases as the dilution increases, it should be still less in water or a solution of a neutral electrolyte. A large number of measurements were made to test these theoretical deductions. The metals magnesium, zinc, and aluminium gave each a smaller *E.M.F.* in water or a neutral electrolyte than in a solution of its own salt, instead of greater, as was to be expected. Similarly, nickel and tin, by giving greater *E.M.F.* in water or neutral electrolytes, behaved in a manner contrary to what was expected. Only the metals antimony, copper, and silver, which have small solution tensions, behaved in the way indicated by theoretical considerations. A large number of measurements were made of the *E.M.F.* given by pairs of the above metals in water and potassium chloride solution respectively.

E. H. R.

Electromotive Behaviour of Aluminium. A. SMITS (*Z. Elektrochem.*, 1921, **27**, 523—526).—Polemical. An answer to the criticism of Gunther-Schulze (*A.*, 1921, ii, 535) to the author's

paper (A., 1920, ii, 579) in connexion with anodic polarisation and passivity. The author maintains his former position. J. F. S.

Electromotive Behaviour of Aluminium. III. A. SMITS and C. J. DE GRUYTER (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **24**, 86—91; cf. A., 1920, ii, 579; 1921, ii, 371).—A continuation of previous work (*loc. cit.*). The influence of mercury on the potential of aluminium immersed in a solution of aluminium sulphate has been investigated. The aluminium electrode was placed in a solution of aluminium sulphate and small quantities of a mercury salt were added at intervals, and the potential was measured repeatedly. The influence of oxygen on the process was prevented by a stream of nitrogen which was continuously bubbled through the solution. It was found that the potential of the aluminium at first became less negative, reached a minimum, after which it rose to a strongly negative value which increased to a maximum. The maximum value was maintained for some time and then fell to a value which was close to the mercury potential. Up to the point where the maximum was observed, the aluminium electrode was grey in colour, but during the last stage it became lustrous, due to a coherent film of mercury. The changes are considered in connexion with the three-phase equilibrium of the four component system $\text{Al}^{+++}\text{—Hg}^{++}\text{—anion—H}_2\text{O}$. J. F. S.

Electrochemical Investigations of Gold-Copper Mixed Crystals. RICHARD LORENZ, W. FRAENKEL, and M. WORMSER (*Z. anorg. Chem.*, 1921, **118**, 231—253).—In connexion with the study of discharge and decomposition potentials, experiments were made in which a series of gold-copper alloys were used as anodes in an electrolytic cell. For studying the discharge potentials, $N/10$ -sodium hydroxide was used as electrolyte, with a copper cathode, and the cell was charged for a short time, about two minutes, with an *E.M.F.* of about 4 volts. The discharge potential was then plotted against time. With pure copper and with alloys containing less than 0.2 atom of gold, a distinct arrest occurred in the curve, whilst alloys with 0.2 atoms of gold and upwards behaved like pure gold, giving a smooth discharge curve. The charging, or decomposition, potentials were studied, using as electrolytes first a solution containing sodium hydroxide and ammonia, and then copper sulphate. In the former case, copper or an alloy with 0.1 atom of gold showed an early rise of current with *E.M.F.*, followed by a fall to zero and then a steady rise starting at about 0.7 volt. With 0.2 atom or more of gold, no current passed until the *E.M.F.* reached 1.05 volts, and the current increased steadily with the *E.M.F.* Using copper sulphate as electrolyte, the decomposition potential rose steadily with the gold content of the alloy up to about 0.25 atom of gold, and from 0.35 atom of gold upwards was indistinguishable from that of pure gold. This is in agreement with Tammann's observations on the limiting composition in gold-copper alloys (A., 1920, ii, 672). It is shown experimentally that

changes in the resistance of the cell during the experiments have no appreciable influence on the results obtained, and it follows that the maximum and minimum in the decomposition potential curves and the arrest point in the discharge potential curves for copper and the alloys less rich in gold have a common cause.

E. H. R.

Metallographic Investigations on the Cathodic Deposition of Metals on Aluminium and Chromium. S. KYROPOULOS (*Z. anorg. Chem.*, 1921, **119**, 299—304).—The cathodic deposition of copper, silver, chromium, and nickel on aluminium and chromium was studied. Copper and silver from nitrate solution, with a current density of 0.01 to 0.1 amp. per sq. cm., are deposited on tempered aluminium principally on the intercrystalline boundaries and to a very limited extent on the crystal faces, whilst chromium and nickel are deposited more freely in isolated spots on the crystal faces. With chromium and nickel, a higher current intensity favours deposition on the crystal faces of the aluminium. From cyanide solution copper may be deposited on the crystal faces when the current intensity is high; on pressed aluminium it is deposited along the gliding lines. It is noteworthy that deposition on the crystal faces is favoured under conditions such that production of hydrogen at the cathode is possible. Resistance to copper deposition is most clearly shown by passive chromium, deposition occurring only on isolated spots of non-passive metal or impurity. Under conditions which destroy the passivity of the chromium, such as hydrogen evolution at the cathode, deposition occurs on the crystal faces of the chromium.

E. H. R.

Electrolysis of Aqueous Solution of Cerous Salts. A. B. SCHIPTZ (*Z. Elektrochem.*, 1921, **27**, 521—523; cf. A., 1921, ii, 589).—After a short account of the work which has previously been carried out on the electrolysis of solutions of the rare earth salts, and of that on the cerium alloys, experiments are described on the electrolysis of concentrated solutions of mixtures of cerous and ferrous chlorides to which various additions had been made. The electrolysis took place between a platinum spiral which served as anode and a platinum gauze covered with lead dioxide which served as cathode. The solutions, which were used warm, contained 30 grams of lactic acid neutralised by sodium or potassium hydroxide, and 5—10 grams of sodium chloride in 400 c.c. of water to which was added cerous chloride (7.0—3.5 grams) and ferrous chloride (4.5 grams). The electrolysis was effected with a current density of 0.4—2.0 amp./sq. cm. and yielded in all cases a black, powdery deposit which was metallic and contained about 62% of cerium. Whether or no it contained oxygen could not be ascertained because of the difficulty of drying the substance without oxidation. The deposit corresponds with the iron-cerium alloy, Ce_2Fe_3 , prepared by Vogel (A., 1912, ii, 557). The electrolysis of cerous chloride in the presence of chloride of mercury, nickel, platinum, zinc, or aluminium gave deposits which contained no

cerium. The addition of potassium lactate to solutions of cerous chloride raises the overvoltage by 0.15 volt. J. F. S.

Biochemical and Electrochemical Oxidation of Organic Compounds. FR. FICHTER (*Z. Elektrochem.*, 1921, **27**, 487—494).—A general discussion of electrolytic and biochemical oxidation of organic substances in which a number of similarities in the two processes are indicated. J. F. S.

Magnetism and the Constitution of Atoms. PIERRE WEISS (*Rev. sci.*, 1920, **58**, 645—659).—A review of work already published (see A., 1911, ii, 91, 183, 250, 367, 694; 1915, ii, 737).

CHEMICAL ABSTRACTS.

Behaviour of Substances near the Absolute Zero. WILLIAM R. FIELDING (*Chem. News*, 1921, **123**, 97—99).—The results previously obtained by the author (A., 1920, ii, 732; 1921, ii, 487) are applied in the present paper to several substances in the neighbourhood of the absolute zero. Making use of the specific heat of lead determined by Kammerlingh Onnes and Keesom over the range 46° Abs.—14° Abs., the author has determined the specific heat over the range 14° Abs.—0° Abs. by three methods and finds that by plotting the specific heat curve the specific heat appears to be zero at 6° Abs., by plotting the specific heats against the absolute temperatures the values 10° Abs., $s=0.0053$, 2° Abs., $s=0.0012$ and 1° Abs., $s=0.00005$ are obtained, whilst applying Debye's law (atomic heat= kT^3) leads to values which demand that the molecule of lead must change from Pb_8 to $Pb_{(3000-4000)}$. Similar calculations are made for water, copper, and carbon, and the absolute molecular weight is calculated for the absolute zero. The values recorded are, water 540, lead 1456, and copper 9450. If the values of p , the number of single molecules in the complex molecule, are plotted, it becomes possible to obtain by extrapolation the values for other elements. The values of p are shown to be periodic, thus, iodine 6.3, bromine 6.6, chlorine 14, and fluorine 24 all at 0° Abs. In the case of mercury, p is slightly greater than 2. The number of atoms in the benzene, naphthalene, and anthracene polymerides at the absolute zero are respectively 84, 100, and 132. J. F. S.

The Properties of Organic Liquids. W. HERZ (*Z. anorg. Chem.*, 1920, **118**, 202—206).—The relation $T_c/d_c \sqrt{n} = \text{const.}$, where n is the number of atoms in the molecule, has been found to hold for 27 non-associated organic liquids and to have a value approximately equal to 450. When this is combined with the formula $n = T_c/0.9p_c$ (A., 1920, ii, 285), the relation $T_c p_c/d_c^2 = \text{const.}$ is obtained, which should have a value of about 225×10^3 . This relation was verified for the above 27 liquids, with the exception that acetylene and carbon dioxide give respectively high and low values. It was shown previously (A., 1920, ii, 736) that the relation $d_c = M/9.24z$, where z is the total of the valencies of the atoms in the molecule (C=4, N=3, O=2, H=1), also holds for

non-associated liquids. With the first equation above, this gives $T_c z / M \sqrt{n} = 48.7$, which has been verified for a number of aliphatic liquids. In the case of aromatic liquids, the relation holds if the valency of carbon is taken as 3. From Trouton's rule $M.L/T_c = 14$, it follows that $Lz/\sqrt{n} = 686$, and this is also found to hold for a number of fluids, but aniline and dimethylcyclohexane give high values. Finally, from the relation $L = 0.666 p_c / d_c$, it follows that $p_c z / d_c \sqrt{n} = 1030$, and this relation is also satisfactorily verified in most cases, but acetylene gives a high value. It is pointed out that these relations can only be tested for relatively simple substances, of which the critical data do not differ widely. Not improbably complications may arise when data are available for other types of substance.

E. H. R.

General Improvement of the Equation of Condition: Special Equation of Condition for Hydrogen. LÉON SCHAMES (*Physikal. Z.*, 1921, **22**, 630—634).—A theoretical paper in which the constants a and b of van der Waals's equation are considered on the basis of a perfectly rigid atom. A general equation of condition is evolved, and taking account of the compressibility of the atoms the equation $pv(1 - b/v) + a_0/v(\alpha - v_0/v) = RT$ is deduced for hydrogen.

J. F. S.

Joule-Thomson Effect for Air. FREDERICK G. KEYES (*J. Amer. Chem. Soc.*, 1921, **43**, 1452—1470).—The Joule-Thomson coefficients of air have been calculated from the author's equation of state for air based on the measurements of pressure, volume, and temperature by Amagat (*Proc. Nat. Acad. Sci.*, 1917, **3**, 323), and have been compared with the coefficients as measured by Joule and Thomson, by Noell, and by Hoxton. The measurements of Joule and Thomson accord well with the calculations except at zero degrees, whilst the recent careful measurements of Hoxton (*Physical Rev.*, 1919, **13**, 438) exceed the calculated values between 0° and 100° by about 15%. The value of the ice-point absolute temperature (273.36) deduced from the Chappuis 1000 mm. constant-pressure expansion coefficient for air, corrected by means of the Hoxton Joule-Thomson coefficients is too large, due to the fact that the Chappuis expansion coefficient is too small and the Joule-Thomson values too large. The calculated expansion coefficient and the Hoxton and Joule-Thomson coefficients lead to $T_0 = 273.197$. The value $T_0 = 273.135$ is, on the other hand, shown to be substantially correct in that this value is the mean value obtained by graphically extrapolating the measured constant volume and constant pressure expansion coefficients of air, nitrogen, hydrogen, and helium measured at various ice-point pressures. The value 273.135 is also the mean of T_0 as deduced from the same data by means of the equations of state for the respective gases. The pressure coefficient at zero of the Joule-Thomson coefficient as obtained by Hoxton is shown to be much larger than that obtained by other observers. The pressure coefficient given by Vogel and Noell (8.8×10^{-4}) is twice that calculated from the equation

(4.5×10^{-4}) for low pressures, but agrees approximately with that calculated for high pressures, by means of the equation of state. The Bradley and Hale average pressure coefficient to 200 atmospheres at 0° is shown to be 7.3×10^{-4} , whilst the average value over this range calculated by the equation of state is 7.1×10^{-4} . The Joule-Thomson coefficient itself at one atmosphere, as given by Vogel and Noell, is 0.277° , and from Bradley's work 0.268° . The equation gives 0.261° . An explanation of the discrepancies in the observed Joule-Thomson numbers is suggested which assumes that at the low pressure surface of the plug a temperature drop is superposed on the Joule-Thomson temperature change due to the momentary persistence of the fine gas streams issuing from the pores of the plug and their subsequent expansion. It is shown that this effect would produce a large apparent pressure coefficient, since the specific effect of the velocity-persistence-effect is shown to vary inversely as the pressure. The value of the measured Joule-Thomson effect at 0° and one atmosphere pressure is given as 0.303 by Hoxton, whilst that deduced from the high pressure measurements of Bradley and Hale is 0.268 , as compared with 0.261 calculated by the equation of state. The Joly constant-volume specific heats of air are considered, and it is shown that a correction is required to compensate for the increased specific heat of the copper sphere used by Joly to contain the air. The corrected Joly values are shown to be independent of pressure, which fact confirms the validity of the form of the air equation of state employed. As a further consequence, it is pointed out that at low pressures the Joule-Thomson effect must vary inversely with the absolute temperature. Another important consequence is that the constant volume air thermometer scale reads directly on the absolute scale and therefore requires no correction. J. F. S.

Simple Methods for the Determination of Melting Points and Critical Temperatures. The Melting Point of Arsenic. W. HEIKE (*Z. anorg. Chem.*, 1921, **118**, 254).—In a paper under the above title, Rassow (A., 1921, ii, 164) quotes the author's determination of the melting point of arsenic, 830° . The author points out that later work gave a value 814.5° , which is more trustworthy (A., 1916, ii, 248). E. H. R.

Theory of Concentrated Solutions. Separation of Solids from Organic Mixtures. J. TIMMERMANS (*Bull. Soc. chim. Belg.*, 1921, **30**, 276—290; cf. A., 1909, ii, 388).—From a study of experimental data in the literature relating to the freezing points of binary organic mixtures, it is concluded that deviations from the behaviour of ideal mixtures cannot in all cases be accounted for by assuming combination between the components or polymerisation, as suggested by Dolezalek and others (A., 1909, ii, 22; also Ikeda, A., 1908, ii, 932). It is necessary to take into account also certain physical factors, in the sense of van der Waals's theory, in particular for systems of limited mutual solubility. A provisional scheme of classification of binary organic liquids is based on these chemical and physical factors.

Freezing-point data respecting numerous binary mixtures containing benzene as the crystallising component were compared with the ideal curve obtained by plotting T and C from the thermodynamic equation: $\log_e C = Q(T_0 - T)/2T_0T$, in which Q is the molecular heat of fusion of the component which separates, C is the number of molecules of the latter per 100 molecules of the mixture, T is the temperature at which this component separates, and T_0 is the solidifying point of the same substance in the pure state (cf. Washburn, "Introduction to the Principles of Physical Chemistry," 1915, ch. 14). Experimental data for many of the mixtures agreed well with the curve, especially where the two components were closely related and not of widely different chemical character. Deviations from the curve in the direction of the axis of composition might reasonably be attributed to combination between the components, but deviations in the other direction could not in all cases be due entirely to polymerisation, and it is shown that they are to be expected if mixed crystals separate or if the components are not completely miscible in all proportions (cf. Kohnstamm, A., 1911, ii, 93). Similar considerations apply also to boiling-point curves, but abnormalities are here more frequent than with freezing-point curves. In many cases where the boiling-point curve is convex towards the axis of composition (cf. Dolezalek, *loc. cit.*), the assumption of polymerisation sufficient to account for the abnormality appears inadmissible (for example, for carbon tetrachloride, benzene, toluene, etc.), and here again the results may be due to the existence of a range of immiscibility. This explanation was verified in a number of cases, the suspected mixtures separating into two liquid phases when their temperature was lowered sufficiently, by means of liquid air or solid carbon dioxide.

J. H. L.

The Temperature of the Vapour Arising from Boiling Saline Solutions. GEORGE HARKER (*J. Roy. Soc. New South Wales*, 1920, **54**, 218—226; cf. Sakurai, T., 1892, **61**, 495).—Experiments with solutions of calcium chloride boiled in a hypsometer either by direct flame or by steam blown in, the only jacketing of the vapour column being by the slightly cooled issuing vapour, indicate that the vapour coming from a boiling solution has a higher temperature than the vapour from the boiling pure solvent.

W. G.

A Simple Receiver for Fractional Distillation under Diminished Pressure. E. J. WILLIAMS (*Chem. News*, 1921, **123**, 265—266).—A simple receiver for fractional distillation under reduced pressure, working on the principle of that of Lothar Meyer, is figured and described. It is constructed with a small distillation flask, a small wide-necked tap funnel, and an adapter.

W. G.

The Separation of Miscible Liquids by Distillation. ARTHUR FELIX DUFTON (T., 1921, **119**, 1988—1994).

Temperature Correction in Bomb Calorimetry. N. H. ENGSTRÖM (*Tekn. Tidskr. Kemi Berg.*, 1921, **51**, 18—21).—A formula is evolved for the correction of temperature in bomb calorimetry. This formula is for general use where the tedious calculations by the application of the classical equation of Regnault-Pfaundler is not absolutely necessary. It is given as follows: $k = (1-n)v_1 - v$. The order and significance of the letters are the same as in the Regnault-Pfaundler equation. This new formula was tested by a large number of determinations and its error falls within the limits ± 0.001 — 0.003° . The error was seldom as high as $\pm 0.003^\circ$.
CHEMICAL ABSTRACTS.

Constitution and Heats of Combustion. F. OTTO H. BINDER (*Chem. Zeit.*, 1921, **45**, 1114—1116; cf. A., 1921, ii, 241, 435).—In continuation of the method previously described (*loc. cit.*) for calculating the heat of combustion of a substance from its constitutional formula, the author has worked out from a consideration of a large number of hydrocarbons the average value of the following: Hydrogen atom attached to carbon 55560, carbon-carbon linking 16258, one carbon valency 24495, compared with 24240, the value obtained by calorimetric experiments on wood charcoal. The heat of combustion of a compound accordingly equals $cH \times 55560 + y \times 24240 + z \times 34170$, where cH is the number of carbon valencies bound to hydrogen, y the number not bound to either hydrogen or oxygen, and z the number of free carbon valencies. From consideration of hydrogen cyanide, cyanogen, and acetonitrile, a mean value for one carbon-nitrogen valency of 35301 cal. is obtained.
G. F. M.

Absolute Value of the Energy of the Linkings between the Atoms of Compounds. M. PADOA (*Gazzetta*, 1921, **51**, ii, 239—245).—The method of calculation used by Fajans (A., 1920, ii, 354) is substantially that employed by the author (A., 1919, ii, 96), who, however, assumed the value 42 Cal. for the heat of sublimation of diamond and graphite indicated by Thomsen's results, whereas Fajans, on the basis of relationships established by Grüneisen between the heat of sublimation of a solid monatomic element and the ratio of atomic heat to the coefficient of thermal expansion, concluded that the heat of sublimation of carbon is at least 275 Cal. per gram-atom. In spite of the large difference between these two values, both authors conclude that the energy of the linkings between the carbon atoms is almost the same in diamond and in aliphatic hydrocarbons. It seems probable that neither of the above two values is the correct one, and the author considers 150 Cal. to be more nearly the truth; Kohn (A., 1921, ii, 302) arrives at values similar to this. Steiger's results (A., 1920, ii, 355, 735) are also discussed.

Taking the value 150 Cal. for the heat of sublimation of 1 gram atom of carbon and 81.3 Cal. for the heat of dissociation of 1 gram molecule of hydrogen, the energy of the C-C linking is calculated for the aromatic and aliphatic hydrocarbons previously considered.

The results show that the energy of the linking increases from simpler to more complex compounds. The differences of the values referred to graphite and to diamond vary from 5 to about 7% and are small considering that the side of the hexagon is 6.2×10^{-8} cm. in benzene and 1.45×10^{-8} cm. in graphite.

The energy of the simple linking in ethane is 69.9 Cal., that of the double linking in ethylene, 2×59.65 Cal., and that of the triple linking in acetylene, 3×53.33 Cal. The heat of combustion of acetylene (3 mols.) being 938.4 Cal. and that of benzene vapour 783.3 Cal., the difference between the three triple linkings and the nine simple linkings is 155.1 and that between one triple linking and three simple linkings hence 51.7 Cal.; the numbers just given for ethane and acetylene lead to the value 49.7 Cal. The absolute values of the double and triple linkings are, therefore, positive and unsaturated hydrocarbons all highly exothermic when formed from the free atoms. These considerations have been extended to various endothermic reactions, such as the formation of hydrogen telluride, the formation of cyanogen from carbon and nitrogen, the formation of nitrous and nitric oxides, the results indicating that, in all probability, all compounds must be formed from free atoms with generation of heat.

T. H. P.

Compressibility of Benzene, Liquid and Solid. THEODORE W. RICHARDS, EDWARD P. BARTLETT, and JAMES H. HODGES (*J. Amer. Chem. Soc.*, 1921, **43**, 1538—1542).—The compressibility of liquid benzene has been determined at 20°, solid benzene at 0°, and toluene at 0° and 20°, using a steel piezometer previously described (Richards and Bartlett, A., 1915, ii, 229). It is found that the compressibility of solid benzene at 0°, $(\Delta v / \Delta P_{v_0})_T$, is 0.0000305 over a pressure range 100 to 500 megabars. Incidentally, the compressibility of liquid toluene at 0° over the same pressure range was found to be 0.0000618. A new determination of the compressibility of liquid benzene at 20° confirmed satisfactorily the previous determination made in a glass piezometer (Richards and Shipley, A., 1916, ii, 376), giving the value 0.00007207 for the same range. The compressibility of solid benzene is shown to be less than half that of liquid benzene at the same temperature. Thus another case, supporting the majority of those investigated, is found in which the solid shows a much smaller compressibility than the liquid (A., 1915, ii, 518). No interpretation of this result is offered at present.

J. F. S.

Relative Volumes of the Chemical Elements. HAWKSWORTH COLLINS (*Chem. News*, 1921, **122**, 76—77, and **123**, 95—97).—A continuation of previous work (A., 1921, ii, 168). In the first part, a table is given of the relative volumes and the densities of a number of organic compounds, the latter quantity is compared with the experimentally determined values. The calculated results are based on the hypothesis previously put forward by the author. In the second part, a further long list is given. It is shown that the experimental facts obtained from the examination of 76 mole-

cules demonstrates that one relative volume of hydrogen is 15.25 at 15° whether, Cl, Br, I, NH_2 , NO_2 , SH, C_2H_3 , C_2H , CO_2Me , CO_2Et , CO_2Pr , CO_2H or $-\text{OH}$ be displaced; in this case $-\text{OH}=13.29$. In a further series of 24 compounds, the relative volume of hydrogen is 12.22 at 15° for the same replacements, $\text{OH}=10.21$. The methyl group has a volume 31.67 at one end of a chain and 28.64 at the other end. When an atom of hydrogen the volume of which is 15.25 is displaced by methyl, the volume of the latter is 31.67, and when the displacement occurs with hydrogen 12.22, the volume of the methyl is 28.64. The two valencies of carbon concerned are distinguished by the fact that one (first position) has hydrogen with a volume 15.25 and the other (second position) has hydrogen with a volume 12.22.

J. F. S.

Atomic and Molecular Volumes at the Absolute Zero. II.

W. HERZ (*Z. anorg. Chem.*, 1921, **119**, 221—224).—In a previous paper it was shown by Lorenz and Herz (*A.*, 1921, ii, 536) that the molecular volumes of alkali salts reduced to absolute zero are smaller than the sums of the volumes of the constituent atoms, similarly reduced according to the law of corresponding states. The inquiry has been extended to a number of simple inorganic compounds other than salts. In the hydrogen compounds the molecular volume is smaller than the sum of the atomic volumes, but the difference becomes smaller with increasing molecular weight. In the halogen acids, for example, these differences are, HF, 7.52; HCl, 3.09; HBr, 1.09; HI, 0.01. In the trihaloids of the elements of the fifth group, however, the molecular volume is greater than the sum of the atomic volumes. The molecular volumes are also calculated from the dielectric constant by the Clausius-Mossotti equation $\gamma = D - 1/D + 2.M/d$. The values obtained are sometimes greater and sometimes smaller than the actual molecular volumes. The divergences may be due to association in the liquids.

E. H. R.

Surface Tensions and Densities of Liquid Mercury, Cadmium, Zinc, Lead, Tin, and Bismuth.

THORFIN R. HOGNESS (*J. Amer. Chem. Soc.*, 1921, **43**, 1621—1628).—The densities of liquid zinc, cadmium, tin, lead, and bismuth have been determined at various temperatures and the following values obtained: zinc $d=6.59-0.00097(t-419)$, lead $d=10.71-0.00139(t-327)$, cadmium $d=8.02-0.00110(t-320)$, bismuth $d=10.07-0.00125(t-269)$, and tin $d=7.01-0.00074(t-232)$. The surface tension for mercury and the above-named molten metals has been determined by the Cantor drop pressure method for a series of temperatures. The values of the surface tension may be calculated by the following equations: mercury $r=467-0.043(t+39)-0.000386(t+39)^2$, bismuth $r=378-0.063(t-269)$, cadmium $r=630-0.065(t-320)$, lead $r=444-0.077(t-327)$, tin $r=531-0.080(t-232)$, and zinc $r=758-0.090(t-419)$. It is shown that there is no appreciable difference between the surface tensions of mercury in dry air, hydrogen, and a vacuum.

J. F. S.

Relationship of the Internal Friction of Organic Liquids to other Properties. W. HERZ (*Z. Elektrochem.*, 1921, **27**, 518—521).—In the case of a large number of simple non-associated organic liquids an approximately constant relationship exists between the surface tension and the critical pressure. This relationship is $\gamma_s : p_c \simeq 1.6 \times 10^4$, in which γ_s is the surface tension at the boiling point and p_c the critical pressure. Between the surface tension and the internal friction (η_s), both at the boiling point, the approximate relationship $\gamma_s : \eta_s \simeq 6 \times 10^3$ exists. It is also shown that the two expressions, $M\gamma_s/T_s d_s = \text{const.}$ and $Ld_s/\gamma_s = \text{const.}$, both hold for non-associated organic liquids, where M is the molecular weight, L the latent heat of vaporisation, and d_s the density at the boiling point T_s . In the case of the former equation, the constant value varies between 6.7×10^4 and 11.3×10^4 , whilst in the latter the value is between 2.0×10^4 and 3.2×10^4 . Two relationships connecting the internal friction and the critical temperature respectively with the molecular refractivity are deduced. These have the form $\eta_s MR/T_c = \text{const.}$ and $\eta_s MR/T_s = \text{const.}$, where MR is the molecular refractivity. The constant in the first case varies between 1.1×10^{-4} and 1.7×10^{-4} and in the second case between 1.6×10^{-4} and 3.2×10^{-4} . If n is the number of atoms in a non-associated liquid, the quantity $\eta_s n/T_s$ is constant and has a value between 0.86×10^{-4} and 1.39×10^{-4} . Finally, it is shown that $V_c \eta_s/T_s$ and $V_c \eta_s/T_c$ are both constant for the same class of organic liquid. In the first case the value varies between 9.0×10^{-8} and 12.6×10^{-8} , and in the second case between 5.8×10^{-8} and 8.0×10^{-8} . J. F. S.

Theory of Brownian Movement. GUSTAV JÄGER (*Sitzungsber. K. Akad. Wiss. Wien*, 1919, [2a], **128**, 1271, 1298; from *Chem. Zentr.*, 1921, iii, 833).—Stokes's law is held to be inapplicable in the case of Brownian movement. It is shown from consideration of mechanical examples that if this law holds, osmotic pressure must be exerted as a continuous force and the consequences of Einstein's equation for Brownian movement and the calculation of molecular size from diffusion are justified. The distribution of energy for particles of any number of molecules may be obtained from Maxwell's law directly by gradual building up of groups from molecules. The velocity of particles relative to the liquid medium, including their Brownian movement, is only to a small degree dependent on their mass. G. W. R.

Influence of Water-content on the Adsorption-capacity of an Active Charcoal. HEINRICH HERBST (*Biochem. Z.*, 1921, **118**, 103—119).—The highest adsorption is obtained with dry charcoal. For practical purposes 10% of water is not harmful, since the presence of water has a catalytic effect. H. K.

Absorption of Gases by Crystals. R. SEELIGER and K. LAPKAMP (*Physikal. Z.*, 1921, **22**, 563—567).—Partly or completely dehydrated zeolites have the power of absorbing gases in large quantities. The absorption of a mixture of neon and helium,

nitrogen, oxygen, methane, nitric oxide, carbon dioxide, acetylene, hydrogen, and ammonia by dehydrated chabasite ($\text{CaAl}_2\text{Si}_4\text{O}_{16}\cdot 6\text{H}_2\text{O}$) has been examined at 0° under a series of pressures from 0° to 760 mm. It is shown that, with the exception of hydrogen, the amount of gas absorbed is greater the higher the critical temperature of the gas. The following volumes of gases in c.c./gram of chabasite at 0° and 760 mm. are absorbed. Neon 25% + helium 75%, 4.10; nitrogen, 6.89; oxygen, 8.32; methane, 15.18; nitric oxide, 25.67; carbon dioxide, 39.60; acetylene, 56.46; hydrogen, 82.22, and ammonia, 180.59. The adsorption curves can be approximately reproduced by the formula $v = \alpha p^{1/n}$, in which α and $1/n$ are constants. All gases except nitric oxide, ammonia, and impure acetylene can be entirely removed from the crystals by lowering the pressure. The results do not indicate whether the absorbed gases are adsorbed according to the usual conception of the term, or whether they enter into the structure of the crystal lattice. In favour of the pure adsorption are the qualitative character of the adsorption isotherm, the connexion between the critical temperature and the amount of absorption, and the effect of reducing the pressure. Further, the connexion between $1/n$ and the critical temperature also indicates a pure adsorption. On the other hand, the large absorption of hydrogen and the difficulty experienced in removing nitric oxide, ammonia, and impure acetylene from the crystals point to the view that the absorbed gases enter into the crystal lattice in the position occupied by the water before dehydration.

J. F. S.

Graphic Deductions with regard to the Dissociation of Weak Electrolytes. N. SCHOORL (*Rec. trav. chim.*, 1921, 40, 616—620).—An expression is deduced from Ostwald's dilution law which gives approximately correct values for the degree of ionisation of weak electrolytes. Such approximation is depicted graphically in contrast with the calculated values.

H. J. E.

The Redissolution of a Salt during the Isothermal Evaporation of a Solution. ETIENNE RENGADE (*Compt. rend.*, 1921, 173, 1080—1081; cf. A., 1921, ii, 93).—A reply to Raveau (cf. A., 1921, ii, 682).

W. G.

Formulae for the Solubility of certain Salts in Aqueous Ethyl Alcohol and Water. W. D. TREADWELL (*Helv. Chim. Acta*, 1921, 4, 982—991).—Attempts are described to devise a mathematical expression for the diminution of the solubility of a salt in water by the addition of alcohol on the assumption that the solvent action is exerted by the water alone, and that its extent is lessened by its dilution with the alcohol. Consideration is confined for the present to substances which are almost insoluble in absolute alcohol. In these circumstances, the solubility is expressed by the equation $h = L_0 C_w^k$, in which L_0 is the solubility of the salt in pure water, C_w the concentration of the water in the solvent, and k a proportionality factor of the approximate order, 1. The results calculated from this formula ($k = 0.88$) are in harmony with the experimental data for the solubility of potassium chlorate in

mixtures of alcohol and water at the atmospheric temperature, at 30°, and at 40°. The influence of temperature, therefore, is manifest essentially in the alteration of the value, L_0 . Within certain limits of alcoholic concentration, similar observations are made with potassium nitrate, but, in this case, the value of k does not appear to be so independent of the temperature. At 14.5°, the solubility of potassium chloride is represented satisfactorily by the expression when $k=0.93$, but at 30° and 40° a distinct specific action of the alcohol is observed which causes a variation in the value of k with varying alcoholic content of the solution. This specific action is also in evidence in the cases of sodium chloride, etc., more noticeably, of ammonium sulphate.

The remarkable independence of the value of k of the temperature in the case of potassium chlorate and, to a more limited extent, in that of potassium nitrate points to the conclusion that alcohol behaves merely as an inert diluent. L_0 may therefore be expressed as a function of the temperature and replaced by the expression aK^n in which a and n are empirical constants and K is the ionisation product of water $\times 10^{14}$. The solubility of potassium chlorate in any mixture of alcohol and water between 12° and 40° is given by the expression: $L=8.4 \times K^{0.482} C_w^2 \times 0.88 = 7.4 \cdot K^{0.482} \times C_w^2$. That of potassium nitrate, sodium chloride, potassium chloride, potassium sulphate, and lead nitrate can be calculated satisfactorily if a constant value is given to n , but, in the case of sodium chloride a distinct linear variation of the exponent is noticeable which, if taken into consideration, permits a very exact calculation of the observed values. The solubility of non-ionised mercuric chloride cannot be calculated accurately if n is assumed to be constant.

H. W.

Application of Ideal Solution Equations to Dilute Aqueous Solutions. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1921, **43**, 1391—1396).—A theoretical paper in which it is shown that the present method of applying the fundamental ideal solution equation to dilute aqueous solutions, particularly in the vapour pressure and freezing-point depression equations, leads to certain incompatibilities, which have been pointed out and discussed. It is also shown that the discrepancy disappears when due notice is taken of the fact that the vapour pressure of water at the ordinary temperature must be ascribed practically entirely to its uni-molecular fraction, the shift in the equilibrium $(H_2O)_g \rightleftharpoons gH_2O$ on addition of a solute counterbalancing the effect of the association on the molecular fraction. Some fundamental errors in the present application of ideal osmotic pressure and freezing-point depression equations to dilute aqueous solutions have also been pointed out and corrected.

J. F. S.

Factors Affecting the Stability of Additive Compounds in Solution and their Influence on Ionisation Equilibria. I. JAMES KENDALL and PAUL M. GROSS (*J. Amer. Chem. Soc.*, 1921, **43**, 1416—1426).—In an earlier paper (Kendall, Booge, and Andrews, *A.*, 1918, ii, 36, 37), it is postulated that the formation of solvent-

solute complexes is a pre-requisite to ionisation in solutions. On this assumption, it should be possible to predict the degree of dissociation in any given solution from (a) the stability of the complexes with respect to their components, and (b) the instability of the complexes with respect to their ionisation products. The first of these points has been dealt with in detail in previous papers (*loc. cit.*), and the rules formulated have here been extended to the association of pure liquids. In the present communication the study of the second point—the factors affecting the ionic disintegration of solvent-solute complexes in solution—has been commenced. These generalisations are shown to be in excellent qualitative agreement with the experimental data of earlier investigators. A more stringent test of their validity is furnished by careful conductivity determinations on specially selected systems (*cf.* following abstract). The connexion between the ionisation hypothesis presented here and the views of Abegg and Bodländer, on the one hand, and of Werner, on the other, has been shortly examined and some points of difference have been indicated.

J. F. S.

Compound Formation and Specific Conductivity in Solutions of the Types, Acid-Ester, Acid-Ketone, and Acid-Acid. JAMES KENDALL and PAUL M. GROSS (*J. Amer. Chem. Soc.*, 1921, **43**, 1426—1439).—Complete specific conductivity-composition curves have been produced for fourteen systems of the types, acid-ester, acid-ketone, and acid-acid, at 25°. The substances employed are all liquids, and the specific conductivity of these was taken as the test of purity. It is shown that this property is far more sensitive to small amounts of impurities than the melting point or boiling point; the specific conductivity at 25° is found for the substances named to be: ethyl acetate, $<1 \times 10^{-9}$; ethyl benzoate, $<1 \times 10^{-9}$; benzyl benzoate, $<1 \times 10^{-9}$; acetone, 5.8×10^{-8} ; acetophenone, 5.5×10^{-8} ; acetic acid, 2.4×10^{-8} ; propionic acid, $<1 \times 10^{-9}$; monochloroacetic acid, 1.4×10^{-6} (60°); trichloroacetic acid, 6.2×10^{-9} (60°), and formamide, 4×10^{-6} . These results are from one-third to one-six hundred and twentieth of the previous best values. The conductivities of solutions of the above-named types are, in general, considerably in excess of those of the pure components, and increase uniformly with increasing diversity in character (that is, in the positive or negative nature of the constituent radicles) of their components. The results obtained have been correlated with those derived from freezing-point measurements on similar systems, and the validity of the fundamental relationships between compound formation and ionisation in solutions (see preceding abstract) has been confirmed. The maximum specific conductivity in no case corresponds with a composition of the system which is the same as that of an isolated compound. The following compounds have been isolated: $\text{CCl}_3 \cdot \text{CO}_2\text{H} \cdot \text{CH}_3 \cdot \text{CO}_2\text{Et}$, m. p. -27° ; $\text{CCl}_3 \cdot \text{CO}_2\text{H} \cdot \text{C}_6\text{H}_5 \cdot \text{CO}_2\text{Et}$, m. p. -23° ; $\text{CCl}_3 \cdot \text{CO}_2\text{H} \cdot \text{C}_6\text{H}_5 \cdot \text{CO}_2 \cdot \text{C}_7\text{H}_7$, m. p. 11.9° ; $\text{CCl}_3 \cdot \text{CO}_2\text{H} \cdot \text{COMePh}$, m. p. 26° ; $\text{H} \cdot \text{CO} \cdot \text{NH}_2 \cdot 2\text{CH}_3 \cdot \text{CO}_2\text{H}$, m. p. -8° .

J. F. S.

Prediction of Solubility in Polar Solutions. JAMES KENDALL, ARTHUR W. DAVIDSON, and HOWARD ADLER (*J. Amer. Chem. Soc.*, 1921, **43**, 1481—1502; cf. preceding abstracts).—The various factors inducing deviations from the ideal solubility curve in polar solutions have been critically discussed, and it has been shown that the predominant disturbing factor is additive compound formation between the components of the solution. In previous papers (*loc. cit.*) it has been shown that the extent of such compound formation in any series is dependent on the diversity in character of the constituent radicles of the components, the basis of the diversity being the relative position of the variable radicles in the *E.M.F.* series. Ionisation, furthermore, has been found to increase uniformly with compound formation. These generalisations have been employed to predict solubility relationships in systems of various types. It has been shown that: (a) for a given solute in a series of different solvents, increasing solubility and increasing compound formation proceed in parallel, (b) for a series of different solutes of high melting point in a given solvent, increasing solubility and increasing compound formation also proceed in parallel at low temperatures. Illustrations of these rules for non-aqueous and aqueous solutions have been presented which indicate their agreement with the facts of experiment. A general discussion of solubility relationships in systems of increasingly complex nature (for example, $RX-HX$; $RX-H_2O$; $RX-R'X-H_2O$) has been made, and the rules deduced for the simpler types of systems have been found to be applicable, to a limited extent, to the more complex types. For example, (a) salts of a very weak base exhibit increasing hydrate formation and increasing solubility in water as the acid radicle X diverges from OH' ; salts of a very weak acid show the same behaviour as R diverges from H . (b) The increase in the solubility of a sparingly soluble salt in water on addition of a second salt containing a common ion, due to complex salt formation, is dependent on the diversity of the variable radicles.
J. F. S.

Solubilities of Acids in Aqueous Solutions of other Acids. JAMES KENDALL and JAMES C. ANDREWS (*J. Amer. Chem. Soc.*, 1921, **43**, 1545—1560; cf. preceding abstracts).—Solubility curves have been produced for hydrogen sulphide, boric acid, benzoic acid, and salicylic acid in aqueous solutions of hydrogen chloride of a series of concentrations and also for the same acids, except hydrogen sulphide in aqueous solutions of nitric acid. The changes of the specific conductivity of the solvent acids, due to the presence of the weaker acids in solution, has also been investigated. The results obtained, together with those of previous investigators, have been critically discussed in connexion with the rule established previously (*loc. cit.*), that compound formation between acids in pairs increases in extent with increasing diversity of acidic strength. The predicted and observed solubility curves for systems of various types have been compared, and satisfactory agreement, in general, has been obtained. The conductivity results also fall into line in

most cases. Certain abnormalities, however, do appear in particular systems, which are probably to be explained by the water entering into the equilibria in some as yet undefined way. J. F. S.

The Influence of Pressure on Spontaneous Crystallisation. MEINHARD HASSELBLATT (*Z. anorg. Chem.*, 1921, **119**, 353—364).—Experiments were made to determine the influence of pressure on the number of nuclei developed during spontaneous crystallisation at different temperatures (cf. Tammann, A., 1898, ii, 330). Experiments were made with betol, piperine, and papaverine, and it was found that increased pressure, up to 1000 kilos. per sq. cm., had the same effect on nuclei formation as on melting point. At 1000 kilos. the m. p. of betol is raised from 93° to 122.9° , and the temperature of spontaneous crystallisation was raised by a closely corresponding amount. In the case of piperine, the temperature of maximum formation of nuclei was raised from 35° to 70° by increasing the pressure from 1 to 1000 kilos. per sq. cm., and in the case of papaverine from 40° to 60° . The form of the curve showing the variation of number of nuclei with temperature was similar at both pressures. The maximum number of nuclei is doubled at the higher pressure in the case of piperine, but in the case of papaverine it is about the same at 1 kilo. and 1000 kilos. per sq. cm. E. H. R.

Crystallisation Velocity under High Pressure. MEINHARD HASSELBLATT (*Z. anorg. Chem.*, 1921, **119**, 325—352).—The conditions determining crystallisation velocity at normal pressure have been recorded by Tammann (A., 1898, ii, 425; 1899, ii, 272, 548). For examining the effect of pressure on crystallisation velocity, a modified form of an apparatus described by Tammann was used ("Kristallisieren und Schmelzen," p. 165). The substances studied were thymol, phenyl salicylate, benzophenone, apiole, calcium nitrate tri- and tetra-hydrates, cadmium nitrate tetrahydrate, mixed crystals of calcium and cadmium nitrates, guaiacol, form-anilide, benzoic anhydride, *m*-iodonitrobenzene, and benzylaniline. In general, the effect of pressure, up to 2000 kilos. per sq. cm., was remarkably small. In two cases there was an increase in crystallisation velocity of 43% and 18% respectively, but in most cases a slight fall, the greatest being 49% at 1000 kilos. per sq. cm. As the increased pressure has also the effect of raising the melting point considerably, for instance by 27.4° at 1000 kilos. in the case of phenyl salicylate, and the crystallisation temperature limits are raised proportionately, it can be concluded that the real effect of pressure alone is always to decrease the maximum crystallisation velocity. The influence of other substances on the crystallisation velocity of benzophenone was not appreciably affected by pressure. E. H. R.

Recrystallisation Produced by Annealing. PAUL GAUBERT (*Compt. rend.*, 1921, **173**, 1089—1092).—From a study of the behaviour of crystals of vanillin at a temperature slightly below their melting point and of substances like paraffin wax or cetin, which

give malleable crystals in the neighbourhood of their melting point, it is shown that recrystallisation is, as a rule, only possible if the crystals are sufficiently malleable for certain mechanical actions to modify their crystalline system. There is then produced, as it were, a slow polymorphic transformation, with, however, this difference, that in hammer-hardened substances there may remain some intact crystals which will act as nuclei to start the recrystallisation.

W. G.

Crystal Structure and Atomic Constitution. I. P. NIGGLI (*Z. Kryst. Min.*, 1921, **56**, 12—45; from *Chem. Zentr.*, 1921, iii, 833—834).—A discussion of the bearing of crystal structure on atomic constitution in the light of existing crystallographic data. Crystal symmetry with a known arrangement of atoms in the lattice implies also a certain minimal symmetry in the structure of the component atoms. A volume effect must follow from the actual effective size of atoms, as, for example, in the series formed by the carbonates of calcium, magnesium, ferrous iron, nickel, and cobalt, all of which have the calcite structure. From a consideration of published crystallographic data, the univalent metallic elements may be arranged in two series, namely, a principal series, lithium, sodium, potassium, rubidium, and caesium and a subsidiary series, copper (univalent), silver, and gold (univalent). Molecular volume does not increase continuously with electron number but shows periodicity. Similar results are given by bivalent and tervalent metallic elements. With higher valencies the periodicity in molecular volumes tends to disappear (cf. Bragg, A., 1920, ii, 537).

G. W. R.

Crystal Structure and Atomic Constitution. II. P. NIGGLI (*Z. Kryst. Min.*, 1921, **56**, 167—190; from *Chem. Zentr.*, 1921, iii, 834—835).—A continuation of an earlier discussion (see preceding abstract) of the relations between crystal structure and atomic constitution. The theories of Kossel, Vegard, Lewis, Langmuir, Lacombe, and Kohlweiler imply certain assumptions as to atomic structure. The periodicity in atomic volumes already noted is related to the arrangement of electrons in the atom. Whilst crystal form is connected with chemical constitution, isomorphism in its widest sense is a geometrical rather than a chemical effect. A comparison of the volume relationships in series of crystalline "isosteric" compounds permits a comparison of the effective sizes of atoms of differing valency, whereby it appears that atomic size diminishes with increase of valency.

G. W. R.

Investigation of Crystal Space Lattices by means of Röntgen Rays: a Simple Röntgen Tube. WALTER GERLACH (*Physikal. Z.*, 1921, **22**, 557—559).—The lattice constant, a , has been determined for magnesium oxide, calcium oxide, strontium oxide, and barium oxide. In all cases the substances are shown to be regular and belong to the sodium chloride type. The values of a recorded are MgO, 4.204; CaO, 4.762; SrO, 5.100; BaO, 5.47. Making use of the Debye-Scherrer method, it is shown that

the ions of magnesia are both bivalent. The lattice of fluorspar has been redetermined and the structure put forward by Bragg confirmed. The lattice constant is found to be $a = 5.452 \text{ \AA. U.} \pm 0.2\%$. Various forms of silicon have been examined and shown to be crystallographically similar. The lattice is of the diamond type and has the constant $a = 5.400 \times 10^{-8} \text{ cm.} \pm 0.2\%$. The transport of anti-cathode material towards the cathode has been considered. It is shown that after using a Siegbahn-Hadding tube for a prolonged period a deposit of the anti-cathode material is found on the cathode in the form of small crystals. In the case of aluminium cathodes, the crystals were well-formed cubes of 1 mm. edge. In the case of copper cathodes the transport of material takes place in the ionic form, and is not in any way to be regarded as a distillation. The amount of material transported is in accordance with the dimensions of the ionic stream.

A Röntgen tube is described in which a portion of the outside wall serves as the metallic hemisphere constituting the cathode, whilst the anti-cathode is situated at the geometrical centre of the hemisphere. The Röntgen rays pass through a number of holes in the cathode which is rendered air-tight by suitable cements.

J. F. S.

The Theory of Resistance Limits in Mixed Crystals. G. MASING (*Z. anorg. Chem.*, 1921, **118**, 293—308).—It has been held by Tammann (A., 1919, ii, 398) that the existence in binary mixed crystals of resistance limits to the attack of chemical agents which react with one constituent but not with the other provides a proof that the two kinds of atom in the mixed crystals are regularly distributed on a space lattice. The author shows that, making certain assumptions, it can be proved by the mathematical laws of probability that resistance limits will occur if the atoms are irregularly distributed on the space lattice. The limits calculated are not the same as those found experimentally, but they depend on certain simple arbitrary assumptions made with respect to the manner in which the solvent attacks the mixed crystals, and these may be insufficient. The work is only intended to show that the mere existence of resistance limits is no proof of the regular distribution of the atoms in the mixed crystals.

E. H. R.

Coagulation of Colloids by Electrolytes. HUMPHREY D. MURRAY (*Chem. News*, 1921, **123**, 277—279).—A general review of the work within recent years on the coagulation of colloids by electrolytes.

J. F. S.

Kinetic and Static Coagulation Measurements of Suspensoids. FRIEDRICH VINCENZ VON HAHN (*Z. Elektrochem.*, 1921, **27**, 501—505).—A general discussion of the various kinetic and static methods of measuring the coagulation of suspensoids with the object of ascertaining the suitability or otherwise of these methods for determining the relative stability of the sols. A new method of determining the stability by coagulation is described.

The apparatus consists of a long U-tube consisting of a narrow tube and a wide tube; the wide tube terminates at its lower end in a tap and extends slightly beyond the cross-piece joining the two tubes which is closed by a tap. In making a determination, the tap is closed and the wide limb filled with water and the narrow tube with the sol, both to the same height. The tap is now opened, and the levels adjust themselves; if now a portion of the disperse phase owing to coagulation reaches the continuation of the longer tube, the density of the sol is changed and the meniscus commences to move. The time which must elapse before this movement of the meniscus begins is characteristic of the stability of the sol. Two other, rather more sensitive, methods based on the same principles are described. J. F. S.

The Equilibrium in the Reduction of Nickel Chloride by Hydrogen. E. BERGER and G. CRUT (*Compt. rend.*, 1921, 173, 977—979).—Within wide limits the equilibrium of the reversible reaction $\text{NiCl}_2 + \text{H}_2 \rightleftharpoons \text{Ni} + 2\text{HCl}$, is determined accurately by the formula $29642/4.571T - 1.75 \log T - 0.006T^2/4.571 + \log p + \log [\alpha^2/(100 - \alpha)] = K$, taking the heat of reaction from left to right as -30700 cal. at 15° and the value of K as 5.93 . The equilibrium concentrations are the same in whichever direction the reaction proceeds. W. G.

An Explanation of Liesegang's Rings. HUGH MCGUIGAN (*Science*, 1921, 54, 78—80).—When a minute drop of silver nitrate solution is placed on a gelatin gel containing potassium dichromate, there is an immediate formation of a circle of silver chromate about which is a sharply demarcated zone of influence from which the chromate has been removed. The Liesegang ring formation when a larger drop of silver nitrate is used is explained as follows: Silver chromate is formed and a clear zone results in the gelatin by the attraction of the chromate to the silver. Beyond this zone of influence, the chromate is fixed and remains so unless an attraction force is exerted. The silver nitrate now wanders on through the ring into the clear zone until it is sufficiently close to the chromate gelatin to exert an attraction which again draws the chromate and forms another ring and clear zone. At the same time the chromate exerts a "pull" on the silver and the ring is formed where the forces are balanced. Again it may be presumed that to start the chromate moving will require a greater force than to keep it moving after the movement has commenced; consequently the second ring is separated from the first. With each succeeding ring the concentration of the silver is less and this also will operate to remove the succeeding rings farther apart. As a requisite for ring formation the precipitate formed must be permeable to the liquid solution used, in this case silver nitrate.

CHEMICAL ABSTRACTS.

Preparation of Nitroanisole from Nitrochlorobenzene. A. V. BLOM (*Helv. Chim. Acta*, 1921, 4, 1029—1035).—The action of *o*- or *p*-nitrochlorobenzene on sodium methoxide in the presence

of methyl alcohol has been studied and by a combination of different titrations it has been possible to determine the rate of formation of each component of the change (cf. A., 1921, ii, 497). Below 70°, the reducing action of intermediately formed alkoxide is so slight as to be practically negligible. The yields of nitrophenol ethers and the rate of reaction depend, not only on temperature and time, but also on the quantity and composition of the solvent. Accelerating factors increase the yield of ethers if they do not also accelerate the subsidiary reactions. High alcoholic concentration and a minimum amount of solvent are favourable in this respect. The use of temperatures higher than 70° or of a large excess of alkali is disadvantageous on account of the increased production of dichloroazoxybenzene or nitrophenol. The possibility of the hydrolysis of the ether formed need not be taken into account, and the whole of the alkali may therefore be added at the commencement of the operation. H. W.

The Theory of Reaction Velocities. N. R. DHAR (*Z. anorg. Chem.*, 1921, **119**, 177—178).—In criticising Lewis's theory, Lindemann (A., 1920, ii, 743) states that the inversion of sucrose by acids, which should proceed 10^{13} times as fast in sunlight as in the dark, is not accelerated at all by light. The author has found that a solution of sucrose in tropical sunlight is completely inverted even in absence of acids, whilst in presence of hydrochloric acid the inversion is distinctly accelerated by sunlight. These observations therefore confirm the theory of Lewis in a qualitative manner. Reactions which have a large temperature coefficient are those most sensitive to light. E. H. R.

Rates of Hydrolysis of the Rare Earth Carbonates and the Serial Order of the Rare Earth Elements. PAUL H. M.-P. BRINTON and C. JAMES (*J. Amer. Chem. Soc.*, 1921, **43**, 1446—1451).—The relative rates of hydrolysis of the carbonates of ytterbium, thulium, yttrium, dysprosium, terbium, gadolinium, europium, samarium, neodymium, praseodymium, lanthanum, and cerium have been determined. An equivalent quantity of the carbonate of each of the earths was dissolved in a definite quantity of water and treated with the theoretical quantity of sodium carbonate and boiled. The carbon dioxide evolved was collected during half-hour periods and measured, and from the results the percentage hydrolysis calculated. In the case of lanthanum and cerous carbonate anomalous behaviour is displayed inasmuch as the whole of the carbon dioxide is evolved in the first half-hour and consequently on plotting percentage hydrolysis against the time of boiling they give horizontal line curves, whilst the curves for the other elements are slowly rising curves, slightly convex to the time axis. The curves place the elements, with the exception of the two named, in the order of their basicity. The position thus assigned to yttrium agrees with the solubilities of its compounds, whilst previous determinations of basicity have not done so. The increasing order of basicity of the ten elements concerned

is given as: ytterbium, thulium, yttrium, dysprosium, terbium, gadolinium, europium, samarium, neodymium, and praseodymium. A short discussion on the serial order of the rare earth elements is given.

J. F. S.

The Explosion of Acetylene and Nitrogen. I. WILLIAM EDWARD GARNER and KICHIMATSU MATSUNO (T., 1921, 119, 1903—1914).

Velocity of Decomposition of Mono- and Di-substituted Malonic Acids. AUGUST L. BERNOULLI and HEINRICH JAKUBOWICZ (*Helv. Chim. Acta*, 1921, 4, 1018—1029).—In extension of the work of Bernoulli and Wege (A., 1919, ii, 503), the rate of decomposition of malonic, diallylmalonic, diethylmalonic, phenylmalonic, benzylmalonic, ethylmalonic, tartronic, mono- and dichloromalonic, and dibromomalonic acid has been measured at a variety of temperatures.

The relative effect of the different substituents as established by Bernoulli and Wege (*loc. cit.*) at 100° is found to be maintained at all temperatures investigated. As mono-substituents, bromine, chlorine, and hydroxyl accelerate the decomposition of malonic acid in order of decreasing effect. The temperature curves of the mono-substituted acids diverge from one another with increasing temperature, without, however, intersecting. The temperature curves of the di-substituted malonic acids (from 80° upwards) remain parallel to one another and to that of malonic acid so that the latter behaves as "symmetrically di-substituted." Two similar substituents depress the rate of decomposition greatly, even when the latter is accelerated by the same substituent acting singly. The retarding action becomes more marked with increase in mass of the substituent; this is particularly noticeable with dibromomalonic acid. The effect of substitution in the case of di-substitution is the result of two component actions, (a) a specific effect which is obvious in the case of mono-substitution, and (b) a symmetry effect which depends on the mass and not on the electrochemical character of the radicle or atom.

H. W.

Influence of Neutral Salts on the Hydrolysis of Ethyl Formate. ALEXANDER BERNARD MANNING (T., 1921, 119, 2079—2087).

The Maximum Stability of Esters of Carboxylic Acids. KARL GUSTAV KARLSSON (*Z. anorg. Chem.*, 1921, 119, 69—96).—Experiments were made to determine the influence of hydrogen-ion concentration on the stability of methyl acetate and ethyl acetate. The experiments were carried out at 85.55° and 75.40°. The ester was heated in aqueous solution in presence of a "buffer" salt (sodium acetate) in a sealed quartz tube for a known time. The hydrogen-ion concentration was determined by direct measurement before and after the experiment and the amount of hydrolysis was determined by titration with barium hydroxide solution. The velocity constant was calculated from the usual unimolecular equation. In the case of methyl acetate, the lowest velocity con-

stant, that is, the greatest stability, was found at 85.55° with $P_H=4.70$, and in the case of ethyl acetate, $P_H=5.1$. The presence of neutral salts, sodium chloride, or potassium nitrate had no effect on the position of the point of maximum stability. The curves obtained by plotting the velocity constants as ordinates against the P_H values descend to a minimum at the P_H representing maximum stability, but they are not symmetrical about this point, rising more steeply on the alkaline side. It follows that H- and OH-ions cannot have the same hydrolytic activity (cf. Wijs, A., 1893, ii, 364; 1894, ii, 82). What function the reaction velocity is of the H- and OH-ions cannot yet be determined. Neutral salts increase the reaction velocity in alkaline solution, that is, when P_H is high, by increasing the acidity, but on the acid side of the point of maximum stability they have much less effect.

E. H. R.

Preparation and Hydrolysis of Benzyl Esters. E. H. VOLWILER and E. B. VLIET (*J. Amer. Chem. Soc.*, 1921, **43**, 1672—1676).—The comparative rates of hydrolysis of certain benzyl esters were determined in order to obtain a basis for the correlation of chemical properties and physiological action. The rates of hydrolysis of these benzyl esters increase in the following order: salicylate, benzoate, stearate, cinnamate, acetate, succinate, and fumarate. The rate of hydrolysis of the benzyl group in benzyl aceto-oxybenzoate is of the same order as in benzyl salicylate.

W. G.

The Influencing of Catalysts and Specifically Active Catalysts. KARL W. ROSENMUND and FRITZ ZETZSCHE (*Ber.*, 1921, **54**, [B], 2885—2888; cf. A., 1921, ii, 320, 392, 393).—A reply to the criticism of Abel (A., 1921, ii, 542).

H. W.

Catalytic Action at Solid Surfaces. VII. Influence of Pressure on the Rate of Hydrogenation of Liquids in the Presence of Nickel. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1921, [A], **100**, 240—252; cf. A., 1921, ii, 582; 1920, ii, 608).—The influence of pressure on the rate of absorption of hydrogen by pinene, ethyl cinnamate, ethyl linoleate, linolein, linolenin, geraniol, terpineol, oleic acid, citral, and carvone in the presence of nickel has been investigated. The results fall into three definite groups: (i) *Normal*. In the absence of substituent groups of the type mentioned below and in the presence of sufficient nickel (generally as long as at least 0.1% of nickel is present) the ethylenic union is hydrogenated at a rate which is in almost exact proportion to the absolute pressure of the hydrogen. To this group belong ethyl cinnamate, ethyl linoleate, and pinene. (ii) *Subnormal*. At very low concentrations of catalyst (for example, 0.01—0.02% of nickel calculated on the organic compound) the increase in the rate of hydrogenation becomes less than proportional to the increase in pressure. The compounds which absorb hydrogen most readily are in general more prone to show the sub-normal effect when the concentration of the catalyst is diminished, and it

is especially marked in the case of multi-ethylenic compounds such as derivatives of linoleic or linolenic acid or citral, although at low concentrations of catalyst it is also shown by ethyl cinnamate. (iii) *Abnormal*. If the unsaturated compound contains another group which has affinity towards nickel (but is not open to hydrogenation), it is found that increase in hydrogen pressure causes an increase in the rate of hydrogen absorption in greater than simple proportion to the altered concentration of the hydrogen. This is observed with unsaturated alcohols and carboxylic acids; the carboxyl group tends to produce the nickel salt and hydrogen, although at 180° the equilibrium is moving in the direction of reduction, whilst with the alcohol there is a tendency toward dehydration. On the other hand, unsaturated aldehydes and ketones show a normal reduction with increase in the hydrogen concentration. In general, an increase of the hydrogen concentration causes a directly proportionate increase in the rate of hydrogenation, provided that there are no disturbing factors; the increase of hydrogenation becomes abnormally large if other groups active toward nickel, but not open to hydrogenation, are also present. The nature of the unsaturated organic compound has a determining influence on the effect of the hydrogen concentration.

J. F. S.

Catalysis of the Mutarotation of Dextrose by Metals.

WILLIAM EDWARD GARNER and DOUGLAS NORMAN JACKMAN (T., 1921, **119**, 1936—1948).

Oxidation Catalysis. I. L. KARZAG (*Biochem. Z.*, 1921, **117**, 69—86).—A group of colouring matters was subjected to the action of hydrogen peroxide under various experimental conditions in the presence of iron, copper, cobalt, manganese, nickel, and platinum salts. The conclusion is drawn that the first four metals named have a two-fold action, like that of catalase and oxydase respectively, whilst the two latter have only an oxydase-like action.

H. K.

Magnitude of Atoms. THEODORE W. RICHARDS (*J. Amer. Chem. Soc.*, 1921, **43**, 1584—1591).—A theoretical paper in which it is pointed out that the contraction suffered during combination, taken in connexion with the compressibilities of the elements combined, makes possible an approximate estimate of the bulk occupied by the several constituents in a compound. Calculations are made of the diameters of the atoms of the halogens and the alkali metals in the alkali haloids when the following values in Ångström units are obtained: (a) in chlorides, chlorine, 2·8; lithium, 2·3; sodium, 2·9; potassium, 3·5; rubidium, 3·8; caesium, 3·8; (b) in bromides, bromine, 3·1; lithium, 2·4; sodium, 2·9; potassium, 3·5; rubidium, 3·8; caesium, 3·7; (c) in iodides, iodine, 3·4; lithium, 2·6; sodium, 3·1; potassium, 3·7; rubidium, 3·9; caesium, 3·8. These values lie about half-way between the values obtained by Bragg and Landé. Emphasis is placed on the importance of considering the compressing effect of the affinities concerned in

making any comparison of atomic volume. A series of volumes of the individual halogen and alkali metal atoms in alkali haloids is given in the paper.
J. F. S.

Analysis of the Atomic Structure. A. DAUVILLIER (*Compt. rend.*, 1921, **173**, 1077—1079; cf. A., 1921, ii, 669).—A table is given showing the number of internal electrons and the number of quanta for each layer in the heavy atoms, and these data are discussed. A periodic table is given illustrating the author's theory of electronic structure of the elements, and from it, it is shown that the chemical analogy of the different elements depends, not only on the number of superficial corpuscles, but also on the sub-jacent electronic layer. The table enables the transformations that will be observed in the X-spectrum of the light elements to be foretold.
W. G.

Langmuir's Theory of the Arrangement of Electrons in Atoms and Molecules. CHARLES R. BURY (*J. Amer. Chem. Soc.*, 1921, **43**, 1602—1609).—A theoretical paper in which an alternative has been suggested to the fourth postulate in Langmuir's arrangement of electrons in atoms and molecules (A., 1919, ii, 328). This avoids the necessity of postulating cells in the structure of the atom, and leads to different structures for the elements of higher atomic weights than that of neon. It is claimed that the application of Lewis and Langmuir's octet hypothesis of valency to these structures gives a better explanation of the chemical properties of the higher elements than can be obtained from Langmuir's structures.
J. F. S.

Motion of Electrons in Gases. J. S. TOWNSEND and V. A. BAILEY (*Phil. Mag.*, 1921, [vi], **42**, 873—891).—An account is given of the method of finding the velocities of electrons in gases, and the application of the results to determine some properties of gaseous molecules. The paper also contains the results of a large number of experiments which have been made on the motion of electrons in hydrogen, nitrogen, and oxygen with ranges of forces and pressures similar to those used in experiments with air.
J. F. S.

New Type of Sodium Lamp for Polarimetry. HAROLD A. FALES and JACQUES C. MORRELL (*J. Amer. Chem. Soc.*, 1921, **43**, 1629—1630).—A sodium lamp for use in all cases where a continuous sodium flame is required is described. The lamp consists of a small alundum thimble supported by nickel or nichrome wire in the flame of a Méker burner. The molten sodium chloride contained in the thimble slowly percolates through the pores of the thimble, so that the flame is continuously fed by sodium chloride vapour.
J. F. S.

Rotary Burner with Fixed Gas Connexion. GEORG LOCKE-MANN (*Z. angew. Chem.*, 1921, **34**, 594—595).—A modification of the rotary burner previously described (A., 1921, ii, 447) enables an ordinary Teclu burner with a non-flexible gas connexion to be

used. The burner tube is fitted into the hub of the horizontal pulley, and is continued on the upper side by a tube bent four times at right angles and jointed in the central vertical limb, so that the upper portion can be twisted round to bring the gas outlet to any desired distance from the axis of rotation of the pulley. A fitting is also provided to fix on the top of the burner tube to give an oblique instead of a vertical flame.

G. F. M.

Inorganic Chemistry.

Molecular Volumes, Physical Properties, and Molecular Models of the Halogens. F. A. HENGLEIN (*Z. anorg. Chem.*, 1921, **118**, 165—171).—It has been shown by Biltz (A., 1921, ii, 437, 487) that there is a linear relation between the molecular volumes of the halogens and of their compounds. It is now shown that there is likewise a linear relation between the atomic volumes of the halogens at their boiling points and others of their physical properties including melting point, boiling point, critical point, latent heat of fusion or of evaporation, and normal potential; also between the molecular volumes of the halogen acids at the boiling point and many other of their physical constants. Owing to the close similarity in structure of the different halogen atoms, their properties are determined principally by the atomic radius. In contrast with most groups of the periodic system, the molecule of a halogen element has an especially simple structure; it can be represented diagrammatically by two cubes having a common edge, with the valence electrons situated at the corners.

E. H. R.

The Catalytic Formation of Hydrogen Chloride from Hydrogen and Chlorine without Explosion. BERNHARD NEUMANN [with BERGDAHL, BROY, and KARWAT] (*Z. angew. Chem.*, 1921, **34**, 613—620).—All non-explosion methods for the synthesis of hydrogen chloride gas yield a product contaminated with chlorine. Hoppe, who first suggested the use of metallic chlorides as catalysts to this reaction employed the chlorides of aluminium, tin, and zinc in concentrated solution at a temperature of 130°. A repetition of his work has shown that, under the most favourable conditions and with a very slow current of gas not more than 70% conversion is obtained. The reaction is favoured by an increase of concentration and of temperature, but a practical limit is set to the latter by the point at which evaporation becomes rapid. The author has used solid chlorides and higher temperatures. The hydrogen and chlorine were generated electrolytically in separate cells in the same electric circuit, passing into a mixing flask containing water and thence to a quartz tube in the shape of a pipette filled

with granules of quartz impregnated with the selected chloride and heated. The emerging gases were absorbed in a 10-bulb potash tube. The mixed gases were shielded from light and drawn through the apparatus by uniform slight suction, fluctuation of pressure being a source of explosions. With a low gas velocity, a complete conversion was effected by magnesium chloride at 300°, by calcium chloride at 305°, by aluminium chloride (which at this temperature is almost entirely decomposed) at 350°, and by quartz unimpregnated by any salt at 380°. Conversion was improved by warming the mixing flask to 50°, with the effect of adding 1 mol. of water to each mol. of hydrogen chloride, this temperature being an optimum. The dilution of the gases with oxygen had at 380° no influence on the reaction. The reactions $\text{Cl}_2 + \text{H}_2\text{O} = \text{ClOH} + \text{HCl}$, $\text{ClOH} + \text{H}_2 = \text{H}_2\text{O} + \text{HCl}$ are considered to occur, removal of the hydrogen chloride generated being facilitated by the partly dissociated chlorides.

C. I.

Sulphate-free Sulphites for Standard Sulphur Dioxide Solutions. S. LANTZ SHENEFIELD, FRANK C. VILBRANDT, and JAMES R. WITHROW (*Chem. and Met. Eng.*, 1921, **25**, 953—955).—Pure sodium sulphite heptahydrate was prepared by passing carefully purified sulphur dioxide into a solution of sodium carbonate to saturation, adding the requisite amount of sodium carbonate to transform the resultant sodium hydrogen sulphite into the normal sulphite, and cooling the solution to 0°, whereby a crystalline meal of the heptahydrate was obtained. All the operations were carried out in the absence of oxygen and the damp crystals were found to be free from sulphate. They were placed in a desiccator over sulphuric acid and sodium pyrogallate was used as oxygen absorbent. Although every precaution was taken to exclude air leakage, the crystals after one week contained 7.52% of sodium sulphate decahydrate. Similar oxidation occurred in the preparation of pure dry calcium sulphite, and the opinion is expressed that in both cases this is due to autoxidation of the salt. It is concluded that the validity of all investigations in the literature based on the preparation of sulphate-free sulphite for use as a sulphur dioxide standard is doubtful.

A. R. P.

Polythionic Acids and Polythionates. E. H. RIESENFELD and G. W. FELD (*Z. anorg. Chem.*, 1921, **119**, 225—270).—A method has been devised for estimating the proportions of tri-, tetra-, and penta-thionates together in solution with sulphite, thiosulphate, and sulphate, and the method has been applied to the study of the formation and stability of the polythionates. The hexathionic acid described by Debus (T., 1888, **53**, 278) does not exist. The total polythionic acids can be determined by treatment in neutral solution with a mercuric salt, when four equivalents of sulphuric acid are produced for each molecule of polythionate, for instance: $2\text{S}_5\text{O}_6^{''} + 2\text{Hg}^{''} + 4\text{H}_2\text{O} = 2\text{HgS} + 4\text{SO}_4^{''} + 8\text{H}^+ + 4\text{S}$. The acid can then be titrated. Alternatively, the polythionates can be oxidised with bromine in alkaline solution; the whole of the sulphur is oxidised to sulphate and is precipitated and weighed

as barium sulphate. The trithionate is estimated by boiling the solution with an excess of copper sulphate, when the following reaction occurs: $\text{S}_3\text{O}_6'' + \text{Cu}^{++} + 2\text{H}_2\text{O} = \text{CuS} + 2\text{SO}_4'' + 4\text{H}^+$. The copper sulphide is filtered, ignited, and weighed as copper oxide. When boiled with excess of alkali, the polythionates form thiosulphate and sulphite thus: $2\text{S}_3\text{O}_6'' + 6\text{OH}' = \text{S}_2\text{O}_3'' + 4\text{SO}_3'' + 3\text{H}_2\text{O}$; $2\text{S}_4\text{O}_6'' + 6\text{OH}' = 3\text{S}_2\text{O}_3'' + 2\text{SO}_3'' + 3\text{H}_2\text{O}$; $2\text{S}_5\text{O}_6'' + 6\text{OH}' = 5\text{S}_2\text{O}_3'' + 3\text{H}_2\text{O}$. The sulphite and thiosulphate formed are estimated by titration with iodine. By applying three of these reactions, data can be obtained from which to calculate the proportions of tri-, tetra-, and penta-thionate present.

The interaction between hydrogen sulphide and sulphur dioxide was studied by leading a current of the former, as gas, into an aqueous solution of the latter at 0° , until a definite ratio of the reacting substances was present in solution. The total polythionate was estimated after sixty hours. The optimum ratio for polythionate formation was $2\text{SO}_2 : 1\text{H}_2\text{S}$. On the other hand, with the ratio $2\text{H}_2\text{S} : \text{SO}_2$, all the sulphur was precipitated in the elementary form. Evidence was obtained that, immediately after the preparation of a solution in the ratio $2\text{SO}_2 : \text{H}_2\text{S}$, an intermediate compound is formed which can be precipitated at a low temperature as the barium salt; in solution, this changes to barium thiosulphate. The proportion of tri- and tetra-thionic acids formed (determined after fourteen days) depends on the sulphur dioxide concentration, the formation of tetrathionic acid being favoured by low concentration. The proportion of pentathionic acid is, however, practically constant. These results are contrary to those obtained by Heinze (A., 1919, ii, 334). The sulphuric acid which is always formed reaches a maximum near the commencement of the reaction; it must therefore be formed from the intermediate compound, not by oxidation of the polythionic acids.

Of the three polythionic acids, the tetrathionic acid is the least stable and decomposes relatively quickly into tri- and pentathionic acids. The trithionic acid decomposes more slowly with formation of sulphur dioxide, whilst pentathionic acid decomposes only in the course of months with separation of sulphur. The order of stability is the same in neutral as in acid solution; in alkaline solution all the polythionates decompose quickly into thiosulphate and sulphite.

The phenomena observed are explained on the assumption that the above intermediate compound is a hydrate of the unknown sulphur monoxide, SO . This is stable in acid solution for a time, but in neutral or alkaline solution quickly forms thiosulphate. In acid solution, it slowly polymerises to pentathionic acid. By combination with sulphurous acid it forms tri- and tetra-thionic acid: $3\text{SO} + \text{H}_2\text{SO}_3 = \text{H}_2\text{S}_4\text{O}_6$; $\text{SO} + 2\text{SO}_2 + \text{H}_2\text{O} = \text{H}_2\text{S}_3\text{O}_6$. By hydrogen sulphide, it is reduced to sulphur. E. H. R.

The Preparation of Hydrogen Selenide from Metallic Selenides. L. MOSER and E. DOCTOR (*Z. anorg. Chem.*, 1921, 118, 284—292).—The selenides of magnesium, aluminium, iron,

and zinc were prepared in a similar manner to the corresponding tellurides (this vol., ii, 48) by passing selenium vapour over the heated metal in a vacuum. The aluminium and magnesium compounds were also prepared by direct combination of the metal with selenium in a crucible, starting the reaction between the mixed components with a burning magnesium wire. All the products were considerably contaminated with metal except aluminium selenide, which, prepared by the latter process, was practically pure. Aluminium selenide, Al_2Se_3 , forms a light brown powder, unstable in air, and magnesium selenide, MgSe , is very similar. Zinc selenide, ZnSe , is citron-yellow and iron selenide, FeSe , is black and metallic; both are stable in air.

Hydrogen selenide was prepared in an apparatus similar to that used for hydrogen telluride, by dropping the metallic selenide slowly into acid. The best results were obtained using aluminium or magnesium selenide. The gas was liquefied at the temperature of a solid carbon dioxide-ether mixture and by revaporisation was obtained pure. It is not decomposed by daylight in the liquid or gaseous form, but is sensitive to ultra-violet light. Dry oxygen has no action on the dry gas, but in presence of moisture decomposition is rapid.

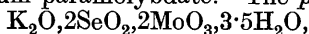
E. H. R.

Selenious Acid and Heteropolyselenites. ARTHUR ROSENHEIM and LEONHARD KRAUSE (*Z. anorg. Chem.*, 1921, **118**, 177—192).—A large number of heteropolyselenites with vanadates and molybdates have been described by Prandtl and others (A., 1907, ii, 477; 1912, ii, 167; 1916, ii, 333), who described numerous well-crystallised salts which, however, had variable compositions according to the conditions of preparation. These compounds have been re-examined with a view to determine whether they may not have a semi-colloidal constitution similar to that of the periodates (A., 1919, ii, 508). Experiments were first made to determine the state of aggregation of selenious acid in aqueous solution. Depression of the freezing point of water indicated slight association, which has a tendency to decrease with time. The dissociation was determined by the hydrogen-ion concentration method and from the electrical conductivity, the results obtained being $4.85 \cdot 10^{-3}$ and $3.45 \cdot 10^{-3}$ respectively. These results are taken to be consistent with the presence of associated $(\text{H}_2\text{SeO}_3)_2$ molecules in solution.

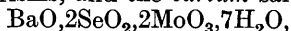
The method of estimating selenious acid by heating with potassium iodide and hydrochloric acid and distilling the iodine over into potassium iodide was improved by the addition of phosphoric acid to the hydrochloric acid. This prevents the formation of selenium iodide, which may be the cause of low results. It was also found that selenious acid may be accurately titrated with sodium hydroxide; the best indicators are, for the formation of NaHSeO_3 , *p*-nitrophenol, and for complete neutralisation to Na_2SeO_3 , thymolphthalein.

Lithium selenite forms the hydrate $4\text{Li}_2\text{SeO}_4 \cdot 3\text{H}_2\text{O}$; its solubility has a negative temperature coefficient.

Molybdoselenites.—The composition of molybdoselenites was found to depend on the ratio of molybdate to selenious acid in the solution from which they were precipitated. When less than 1 mol. of selenium dioxide was present to 1 mol. of molybdate, the potassium and barium salts corresponded with $2R_2O, 2SeO_2, 5MoO_3, xH_2O$ and the ammonium salt with $3(NH_4)_2O, 2SeO_2, 8MoO_3, 6H_2O$. With more than 1 mol. of selenium dioxide per mol. of molybdate in solution, salts were obtained in which the proportion of base was variable, but the ratio $SeO_2 : MoO_3$ was always very nearly 1 : 1. The ammonium salt, $2(NH_4)_2O, 5SeO_2, 5MoO_3, 8H_2O$, white, microscopic prisms, was obtained by adding 15 mols. of selenium dioxide to a saturated solution of ammonium paramolybdate. The potassium salt,



forms microscopic prisms, and the barium salt,



a white, crystalline precipitate.

Vanadioselenites.—Vanadioselenious acid has the composition $4SeO_2, 3V_2O_5, 10H_2O$. An extensive series of experiments showed that, as the concentration of selenious acid in the mother-liquor increased from zero to 5*N*, the ratio of SeO_2 to V_2O_5 in the solid phase increased from 4 : 3 to 5·5 : 3. Similar behaviour was shown by the ammonium vanadioselenites having the approximate formula $3(NH_4)_2O, 12SeO_2, 8V_2O_5$. It is concluded that the variable composition of the vanadic acid compounds is due to the formation of adsorption compounds, although in the case of the molybdic acid compounds this is not so clearly demonstrated. E. H. R.

The Preparation of Hydrogen Telluride from Metal Tellurides. L. MOSER and K. ERTL (*Z. anorg. Chem.*, 1921, **118**, 269—283).—A new method for preparing metal tellurides was devised which consisted in distilling tellurium at a low pressure (8 mm.) over the hot, finely divided metal. In this way the tellurides of magnesium, $MgTe$, aluminium, Al_2Te_3 , iron, $FeTe$, and zinc, $ZnTe$, were prepared. The aluminium compound was obtained in an almost pure state; it is a blackish-brown, lustrous, amorphous substance, decomposing in the air with formation of tellurium hydride. The other tellurides were all more or less contaminated with excess of the respective metal. Magnesium telluride forms a brown, sintered mass, iron telluride is grey and metallic, and zinc telluride is pale brown. The last two are stable in air. For the preparation of hydrogen telluride a special apparatus was designed, in which the powdered metallic telluride was dropped very gradually into acid in an atmosphere of nitrogen. Aluminium telluride proved the most suitable substance from which to generate the gas, and hydrochloric acid the best acid to use. The yield of gas obtained under the best conditions was more than 80% of the theoretical. The gas was liquefied by passing through a tube immersed in a mixture of solid carbon dioxide and ether. In the liquid state hydrogen telluride is very sensitive both to daylight and ultra-violet light, but the dry gas is quite stable in light. The dry gas is, however, immediately oxidised by oxygen. E. H. R.

The Preparation of Telluric Acid. JULIUS MEYER and HANNS MOLDENHAUER (*Z. anorg. Chem.*, 1921, **119**, 132—134).—Telluric acid can be prepared in a pure state and in almost theoretical yield by oxidation of tellurium tetrachloride with chloric acid. Tellurium (10 grams) is boiled with 10 c.c. of nitric acid and 3 c.c. of hydrochloric acid until completely dissolved. To the hot solution is added gradually a concentrated solution of 9 grams of chloric acid and the solution is boiled until no more chlorine is evolved. A slight excess of chloric acid is added to avoid formation of any explosible chlorine oxide. The solution is filtered through asbestos and concentrated by distillation in a vacuum on the water-bath, thereby removing chlorine. The telluric acid can be crystallised out by the addition of concentrated nitric acid, collected, and finally freed from chlorine and nitrogen oxides by drying in a vacuum. It is obtained as a crystalline, snow-white powder, readily soluble in water, having the composition H_6TeO_6 .
E. H. R.

Vapour Pressures of Ammonia-Salt Solutions. R. O. E. DAVIS, L. B. OLMSTEAD, and F. O. LUNDSTRUM (*J. Amer. Chem. Soc.*, 1921, **43**, 1580—1583; cf. this vol., ii, 56).—Vapour pressure curves have been constructed for the following solutions: $\text{Ca}(\text{NO}_3)_2$ 22.48%, NH_3 19.18%, H_2O 58.34%; NaI 32.34%, NH_3 16.06%, H_2O 51.60%; NH_4CNS 77.84%, NH_3 22.16%; NH_4NO_3 33.7%, NH_3 18.82%, H_2O 47.48%; CaCl_2 12.9%, NH_3 22.9%, H_2O 64.2%; $\text{Ca}(\text{NO}_3)_2$ 55.8%, NH_3 25.77%, H_2O 18.43%; NH_3 28.15%, H_2O 71.85%; NaI 64.88%, NH_3 26.02%, H_2O 8.20% over the temperature range -16° to 40° . It is shown that solutions of ammonium nitrate in ammonia and ammonium thiocyanate are very corrosive to iron and steel, the calcium chloride-ammonia solution is less corrosive, and calcium nitrate-ammonia, and sodium iodide-ammonia solutions show no immediate corrosive action. Calcium nitrate-ammonia solutions seem to be the most promising of these solutions for practical use as an absorbent for ammonia in the synthetic ammonia process.
J. F. S.

The Action of Metals, such as Copper and Zinc, on an Aqueous Solution of Ammonium Nitrite. N. R. DHAR (*Z. anorg. Chem.*, 1921, **119**, 174—176).—The action of a solution containing ammonium nitrite on copper was attributed by Hofmann and Buhk (A., 1921, ii, 43) to the hydrolysis of the nitrite with formation of free nitrous acid. The observation that the metal is attacked even in presence of urea, however, renders this explanation improbable. Further, solutions of other nitrites such as zinc nitrite, which are hydrolysed as much as ammonium nitrite, do not attack copper. The activity of the ammonium nitrite is probably related to its instability and ready decomposition into nitrous oxide and water.
E. H. R.

The Structure of Pyrophosphoric Acid. III. D. BALAREFF (*Z. anorg. Chem.*, 1921, **118**, 123—130; cf. A., 1915, ii, 446; 1917, ii, 467).—In previous papers it has been shown that there is a good

deal of evidence in favour of the unsymmetrical structure of pyrophosphoric acid. The synthesis of the pyro-acid by combination of the ortho- and meta-acids in sulphuric acid would give added support to the hypothesis of an unsymmetrical structure, but attempts in this direction were not successful, even in acid containing 15% of free sulphuric anhydride.

The change of colour of the salt $\text{NaAg}_3\text{P}_2\text{O}_7$ from white to yellow on heating has been attributed to its decomposition into NaPO_3 and Ag_3PO_4 , but it is now shown that this does not occur, the colour change being probably due to some physical change in the salt.

No evidence as to the structure of the pyro-acid could be gained from a study of the dehydration of dihydrogen phosphates of alkali metals. The potassium salt heated at 244° loses water and changes to the acid pyrophosphate, $\text{K}_2\text{H}_2\text{P}_2\text{O}_7$; the rubidium salt behaves in the same way. The sodium salt loses water very slowly at 180° and in the course of about one hundred and seventy-eight hours becomes completely converted into $\text{Na}_2\text{H}_2\text{P}_2\text{O}_7$. The products of further dehydration at a higher temperature depend on the water vapour pressure. In moist air at 305° , only soluble metaphosphate is formed, whilst in dry air at 330° about 75% of the metaphosphate formed is insoluble.

Phosphoryl bromide dehydrates orthophosphoric acid to pyrophosphoric acid, but not to the meta-acid. The action is a complex one, and depends on the temperature and proportions of the interacting substances.

A dilute solution of an alkali pyrophosphate, after prolonged boiling, shows the presence of orthophosphate, proving that hydration occurs slowly.

E. H. R.

Iso- and Heteropoly-acids. XVII. Polyborates in Aqueous Solution. ARTHUR ROSENHEIM and FELIX LEYSER (*Z. anorg. Chem.*, 1921, **119**, 1—38).—An attempt was made to prepare simple and complex polyborates with the object of comparing these with salts of other acids such as telluric, antimonie, periodic, plumbic, and stannic acids, which show semi-colloidal properties. Methods for the quantitative estimation of boric acid were examined. The polarimetric method, depending on the influence of boric acid on the optical rotation of tartaric acid, is of limited application on account of the disturbing influence of salts or other substances present in solution. Titration with sodium hydroxide in presence of mannitol, using phenolphthalein as indicator, gives trustworthy results. Free boric acid in the presence of borate can be detected by boiling a sample of the substance for some minutes with dry acetone, filtering, evaporating the filtrate on a watch glass, moistening with a few drops of methyl alcohol, and igniting, when the characteristic flame coloration is given if free boric acid is present.

An investigation of the equilibrium in the system $\text{Na}_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 0° confirmed the existence of the three salts, $\text{Na}_2\text{O}, \text{B}_2\text{O}_3, 8\text{H}_2\text{O}$, $\text{Na}_2\text{O}, 2\text{B}_2\text{O}_3, 10\text{H}_2\text{O}$, and $\text{Na}_2\text{O}, 5\text{B}_2\text{O}_3, 10\text{H}_2\text{O}$. Sodium pentaborate can readily be crystallised from solutions containing Na_2O

and B_2O_3 in the ratio 1 : 5, but sometimes only crystals of borax are obtained, probably because the pentaborate is metastable at ordinary temperatures and borax is the less soluble salt. Potassium pentaborate, $K_2O, 5B_2O_3, 8H_2O$, is a well-defined, characteristic salt, separating from solutions in which the ratio $B_2O_3 : KOH$ is 3 : 1 or higher. Its solubility is very low, not much greater than that of potassium perchlorate. Potassium monoborate crystallises with $8H_2O$ at 0° , with $2.5H_2O$ at 30° . Rubidium pentaborate is very similar to the potassium salt, but crystallises with $10H_2O$. Thallium pentaborate, like the potassium salt, crystallises with $8H_2O$, but is more soluble than the latter. Guanidine forms a diborate crystallising in elongated prisms with $4H_2O$ and a pentaborate with $8H_2O$.

Experiments on the dehydration of pentaborates showed that, in the general formula $R_2O, 5B_2O_3, xH_2O$, two molecules of water are probably constitutively combined. Conductivity experiments indicated that in dilute aqueous solution the pentaborate anion is hydrolysed into the diborate anion and boric acid. In presence of great excess of boric acid this hydrolysis is prevented, and the specific conductivity of sodium pentaborate at 0° appears to be 85% of that of sodium diborate. Experiments on the hydrogen-ion concentration of solutions containing varying ratios of NaOH to B_2O_3 confirm the existence of a pentaborate ion in concentrated solution.

The pentaborate ion appears to form complex anions with a number of metals. Whilst borax solution immediately precipitates zinc or cadmium hydroxide from a solution of a salt of the metal, sodium pentaborate does not. Cobaltous hydroxide dissolves in sodium pentaborate solution to form a red solution in which, although alkalis do not readily precipitate it, the cobalt is in the kation. When this solution is oxidised with hydrogen peroxide, however, some cobaltic oxide is precipitated and a yellow solution is formed containing a complex cobalt anion. Nickel, chromium (Cr'''), manganese (Mn''), and copper also appear to form complex anions. A very small quantity of a copper compound was isolated, having approximately the composition $2Na_2O, 4CuO, 12B_2O_3, 50H_2O$.
E. H. R.

The Atomic Weight of Carbon. E. MOLES (*Anal. Fís. Quím.*, 1921, 19, 255—259).—The value 12.005 for the atomic weight of carbon given by Richards and Hoover (A., 1915, ii, 96) is held to be based on an erroneous value for the atomic weight of sodium. The value 12.000 is claimed to be more exact. G. W. R.

The Oxidising Properties of Carbon Suspensions. F. FEIGL (*Z. anorg. Chem.*, 1921, 119, 305—309).—The oxidising effect of blood charcoal was studied in a qualitative manner by boiling solutions of different oxidisable substances with a suspension of the charcoal. In acid solution, hydrogen sulphide was oxidised to sulphuric acid, potassium iodide to iodine, mercurous salts to mercuric, oxalic acid to carbon dioxide. In alkaline solu-

tion, potassium iodide was oxidised to iodate, alkaline sulphides and sulphites to sulphate, cuprous and cupric sulphides to copper sulphate, cobalt sulphide to sulphate, potassium chromite to chromate. Sodium thiosulphate was unacted on in alkaline or neutral solution, and sodium nitrite was unaffected in alkaline solution. A quantitative study of the oxidation of tervalent chromium to chromate was made, after a method had been devised for removing from the solution a product, formed by the interaction of the charcoal and potassium hydroxide, which liberates iodine from potassium iodide. This was accomplished by boiling with potassium permanganate and removing the excess with hydrogen peroxide. The experiments showed that the proportion of chromate formed increased with the proportion of charcoal used, but that, with a constant quantity of charcoal, the amount of chromate formed increased with the quantity of chromium salt taken. Different charcoals varied widely in their oxidising power, but the differences seemed to bear no relation to the ash content.

E. H. R.

Aqueous Carbonic Acid Solutions. E. WILKE (*Z. anorg. Chem.*, 1921, **119**, 365—379).—The dissociation constant of carbon dioxide solutions was measured by the conductivity method, using a solution through which the gas was being continuously circulated. When an ordinary saturated solution was used, without circulation, the conductivity was found to increase during measurement, probably through electrolytic changes caused by the current. Even with the greatest precautions, variable results were obtained, confirming the observations of earlier workers. It was observed that, by contact with the metal electrodes (gold), even without passage of current, the conductivity gradually increased. In three hours the dissociation constant $K \cdot 10^7$ increased from 3.07 to 4.5. Light seemed to have an effect in the same direction. For measuring the hydrogen-ion concentration, a special hydrogen electrode was used consisting of a palladium capillary into which hydrogen was forced at a pressure of 20 atm. The hydrogen-ion concentration was determined in presence of sodium, potassium, and barium chloride. In these solutions carbon dioxide has the character of a strong acid, increasing with the concentration of salt. The hydrogen-ion concentration increases more rapidly than the total carbon dioxide concentration. The observations can be explained on the assumption that a solution of carbon dioxide in water contains orthocarbonic acid, H_4CO_4 , which, containing no ketonic oxygen, is a very weak acid. In concentrated salt solutions it is dehydrated to form the strong acid $CO(OH)_2$.

E. H. R.

Behaviour of Amorphous Carbon and Sulphur at High Temperatures. Carbon Sulphides. J. P. WIBAUT (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, **24**, 92—101).—The action of sulphur on amorphous carbon at high temperatures has been investigated. Pure sugar charcoal has been heated with sulphur at temperatures from 400° to 1000° under reduced pressure for

prolonged periods of time. A slow evolution of hydrogen sulphide, due to the small amount of hydrogen present in the carbon, is observed and a carbon-like substance containing 1.98% of sulphur obtained. This substance yields no sulphur to toluene, even after prolonged boiling, and the residue after this treatment contained 2.03% of sulphur. Prolonged heating in a vacuum at temperatures up to 1010° did not reduce the sulphur content nor was any volatile compound obtained. Prolonged shaking with bromine water oxidised 9% of the sulphur to sulphuric acid, and heating in a current of hydrogen at temperatures up to 750° removes 77% of the sulphur as hydrogen sulphide; this reaction is exceedingly slow and must be regarded as an action between a sulphur compound and hydrogen and not as an action between hydrogen and sulphur vapour. This was further proved by the fact that heating in nitrogen did not reduce the sulphur content. The author considers that a solid carbon sulphide is formed which bears a strong resemblance to coal coke (cf. Stock and Praetorius, A., 1913, ii, 46). A further sulphide containing 3.5% of sulphur has been obtained by heating carbon purified by chlorine with sulphur. This substance has similar properties to the compound containing 2.0% of sulphur. J. F. S.

The Deviations from the Gas Laws of Carbon Disulphide.

ALFRED SCHULZE (*Z. anorg. Chem.*, 1921, **118**, 223—230).—A number of observations on the properties of carbon disulphide vapour indicate that it is associated to a small extent. The increase of pressure observed when carbon disulphide and ether vapours are mixed at constant volume at 80° under atmospheric pressure indicates association of the former to the extent of 0.14%, whilst vapour density determinations by Dumas's method give results corresponding with 2% association. Compressibility experiments at 80° showed 0.5% more association at 2 atmospheres than at 1 atmosphere pressure. The PV curves at 78.82° and 130.48° show that the amount of association decreases with increasing temperature, but at constant temperature increases with increasing pressure. It is probable that in the liquid phase association is more considerable. E. H. R.

New Theory of the Constitution of Hydroxides, particularly those of the Basic Metallic Oxides. FR. TIEMANN (*Chem. Zeit.*, 1921, **45**, 1125).—To furnish an explanation for a number of phenomena in organic, inorganic, and electrolytic processes which are not in consonance with existing ideas, the author proposes a new theory of the constitution of the hydroxides of the pronounced electropositive metals. It is suggested that these compounds do not contain hydroxyl groups, but are to be regarded merely as true hydrates of the corresponding oxides, that is to say that sodium and calcium hydroxides, for example, are not correctly represented by the formulæ NaOH and Ca(OH)_2 but are actually $\text{Na}_2\text{O}\cdot\text{H}_2\text{O}$, and $\text{CaO}\cdot\text{H}_2\text{O}$, a molecule of water being closely associated with the metallic oxide similarly to the "water of

crystallisation" of salts. This applies to all the elements of groups I and II of the periodic system, whilst the constitution of the hydroxides of those of groups III and IV (aluminium, zinc) will depend on the electrochemical conditions under which they are produced. Only the hydroxides of the metalloids and non-metals are to be regarded invariably as true hydroxyl derivatives. With increasing basicity of the oxides the associated water molecules become increasingly firmly bound exactly as in the case of the increasingly basic character of salts containing associated water. So the dehydration of the hydroxides of calcium, strontium, and barium is effected with increasing difficulty in the order named.

The sucrosates are cited to illustrate the application of the theory. If calcium hydroxide is regarded as a hydroxyl compound, the chemical character of sucrose or dextrose is quite incompatible with the idea of a "neutralisation" of hydroxide, looked on as a generator of hydroxyl ions. There can therefore only be a question of the displacement of the associated water by the sugar, and the sucrosates must be formulated $C_{12}H_{22}O_{11} \cdot 2CaO$, $C_6H_{12}O_6 \cdot CaO$, etc. The isomerism of the hydroxides of tin and aluminium is also explained by reference to the theory, *e.g.* $Al(OH)_3$ and $Al_2O_3 \cdot H_2O + 2H_2O$ can both exist as individual substances, and either one or the other will be produced according to the conditions of the reaction. The non-appearance of hydrogen peroxide, derived from the union of two hydroxyl groups, during electrolysis of a metallic hydroxide is explained by the new theory as due to the absence of hydroxyl groups. The electrolysis actually is that of, say, $Na_2O \cdot H_2O$, the associated water taking no part in the process. There takes place simply a direct fission into metal and oxygen which are liberated at their respective poles. An assumption of the appearance of hydroxyl ions in any electrolytic process is quite unjustified.

G. F. M.

Preparation of Alcoholic Potassium Hydroxide Volumetric Solution. S. T. McCALLUM (*J. Ind. Eng. Chem.*, 1921, **13**, 943).—A solution which does not darken in colour when kept is prepared by dissolving potassium hydroxide in methyl alcohol (purified wood spirit); the solution must be filtered through glass-wool to remove insoluble potassium carbonate, etc., before it is used.

W. P. S.

Existence of Tetra-hydrated Sodium Sulphate in Mixed Crystals with Sodium Chromate. THEODORE W. RICHARDS and W. BUELL MELDRUM (*J. Amer. Chem. Soc.*, 1921, **43**, 1543—1545).—It is shown that crystals of the tetrahydrate of sodium chromate, $Na_2CrO_4 \cdot 4H_2O$, dissolve sodium sulphate as $Na_2SO_4 \cdot 4H_2O$, a form of sodium sulphate otherwise unknown, to the extent of somewhat less than half the quantity corresponding with the same weight of sodium chromate in the supernatant liquid. When sodium sulphate was in large excess, no crystallisation could be induced by "seeding" the saturated mixture with the crystals of the mixed tetrahydrate above the transition temperature of sodium

sulphate, and below this temperature only crystals of the decahydrate could be formed. Thus under these conditions the tetrahydrate is so much more soluble than the phases containing more sodium sulphate as to be incapable even of metastable existence.

J. F. S.

Ammonium Radicles. III. Ammonium. HANS HEINRICH SCHLUBACH and FRITZ BALLAUF (*Ber.*, 1921, **54**, [B], 2825—2834; cf. A., 1920, i, 822 and this vol., i, 15).—The authors' experience with tetraethylammonium leads them to expect that the ammonium radicle would be extremely sensitive to rise in temperature and that there is no hope of isolating it by the electrolyses of solutions of ammonium salts in liquid ammonia on account of the impossibility of avoiding the thermal effect of the current, and that the only prospect of success lies in displacement reactions effected at a low temperature. They find that when well-cooled ammonium chloride is added to a solution of potassium in liquid ammonia at -70° in the apparatus described previously for the preparation of tetraethylammonium, decolorisation of the solution takes place before the calculated volume of hydrogen has been evolved, the deficit amounting to as much as 65%; according to Moissan, the whole of the hydrogen is evolved by the time the solution becomes colourless. The deficit cannot be attributed to the solubility of hydrogen in liquid ammonia since this is shown to be too small to account for the observed effect, and it appears therefore that colourless ammonium is actually present in the solution. This conclusion is supported by the observation that the remainder of the hydrogen is evolved rapidly when the solution is cautiously warmed at about -40° . Repetition of Moissan's experiment shows that the non-observation of the production of ammonium is due to operation in too concentrated solution and consequent decomposition of the radicle by the heat liberated during the reaction. When a solution of potassium (1.8%) is added to a solution of ammonium chloride (1%) in liquid ammonia at -70° , a violent reaction is observed and each drop of added solution is immediately decolorised, formation of ammonium and its conversion into the colourless form appearing to occur instantaneously; tetraethylammonium and ammonium, therefore, stand to one another in the same relationship as triphenylmethyl to methyl. In spite of the violence of the reaction, the yields of ammonium by this method are good and readily reach 50%; the influence of concentration is, however, again apparent, and it is to be expected that an improvement in yield would be observed with more dilute solutions.

The behaviour of ammonium towards the reagents used with tetraethylammonium is described. Corresponding with the rapid isomerisation to the colourless form, the equilibrium is here greatly displaced in the direction of the latter, and it is probable that dissociation and consequent reaction only occur in close proximity to the temperature of decomposition. A reaction with dimethylpyrone could not be observed. Iodine, on the other hand, appears

to react immediately with ammonium, but the quantitative examination of this change could not be completed on account of the experimental difficulties involved. H. W.

Vapour Pressure of the System, Lithium Nitrate : Ammonia. R. O. E. DAVIS, L. B. OLMSTEAD, and F. O. LUNDSTRUM (*J. Amer. Chem. Soc.*, 1921, **43**, 1575—1580).—The solution of ammonia in lithium nitrate has been studied with the object of finding an absorbent for ammonia in the synthetic production of this gas. The use of ammonium nitrate (Kurilov, A., 1898, ii, 156) and ammonium thiocyanate (Foote and Hunter, A., 1920, ii, 246) suffers from the serious drawback that the liquids produced, when these salts adsorb ammonia, attack metals rapidly. A large number of salts have been tested as to their suitability for this purpose, and of these lithium nitrate alone forms a liquid with ammonia in the absence of water, whilst calcium nitrate tetrahydrate liquefies in the presence of a little water. The ammonia contained in 1 c.c. of the lithium nitrate solution saturated at 24° is equivalent to 26.0 c.c. of 0.95*N* sulphuric acid, whilst that for the calcium nitrate solution under identical conditions is 18.5 c.c. of 0.95*N* acid. Vapour pressure measurements have been made for the solution 36.34% ammonia, 63.66% lithium nitrate, and for several other mixtures containing 6.06—58.66% of water. The solutions of ammonia in lithium nitrate have no action on machine steel, iron wire, and nichrome wire after several months' contact, but nickel steel shows a slight action after several months. The results show that a solution of lithium nitrate in ammonia with a small percentage of water should be a good absorbent for the removal of ammonia from mixtures of nitrogen, hydrogen, and ammonia. The absorption could be effected at 0° and a large proportion of the ammonia released either by a small increase of temperature or by reduction of the pressure. J. F. S.

The Reaction between Persulphates and Silver. GEOFFREY ISHERWOOD HIGSON (T., 1921, **119**, 2048—2055).

Silver Bromate. J. H. REEDY (*J. Amer. Chem. Soc.*, 1921, **43**, 1440—1445).—In an earlier paper (A., 1915, ii, 733) it was shown that the electrode $\text{Ag}|\text{AgBrO}_3|0.1\text{N}\text{KBrO}_3$ only reached a steady value (0.631 volt) after being kept for five days, if the bromate was prepared by the action of bromine on silver nitrate solution, but if it was obtained by double decomposition of silver nitrate and potassium bromate, the correct value was at once obtained. Investigation now shows that silver bromate is dimorphous, existing as tetragonal bi-pyramids and as hair-like crystals. The tetragonal crystals are stable at temperatures below 98.5° (the transition point) and the fine, hair-like crystals are stable above this temperature. Difference of solubility of the two forms explains the irregular behaviour of the electrode mentioned above. The solubility of silver bromate has been determined at temperatures from 25° to 90° and the following values have been found: 25°, 0.196; 35°, 0.269; 45°, 0.371; 55°, 0.497; 65°, 0.648; 75°, 0.832; 85°, 1.055

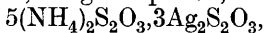
and 90° , 1.325, the solubilities being expressed in grams per 100 grams of water. The solubility curve indicates 98.5° as the transition temperature, a value which is confirmed by a dilatometric measurement of this quantity. Dry silver bromate melts at $308-310^{\circ}$ and is stable toward heat and light, but in the presence of water it darkens slowly at the ordinary temperature and rapidly at high temperatures. If a little impurity, such as dust, is introduced into heated silver bromate decomposition occurs with explosive violence. Silver bromate crystals absorb a considerable quantity of air which is slowly evolved at high temperatures.

It is shown that silver bromate may be used as a standard in iodometry. The method of use consists in placing 1 gram of bromate with an excess of potassium iodide in 150 c.c. of water in a 250 c.c. flask; this is heated on a water-bath to effect double decomposition. The contents of the flask are cooled and made up to 250 c.c. Samples of 25 c.c. are withdrawn, acidified with dilute hydrochloric acid, and titrated with sodium thiosulphate. Arsenious oxide gives a result about 0.2% higher than silver bromate, but after recrystallising the arsenious oxide from hydrochloric acid this figure was reduced to 0.05%. This indicates that whilst silver bromate may have a somewhat higher oxygen equivalent than arsenious oxide, this defect is fully compensated by its greater definiteness. J. F. S.

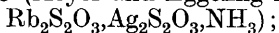
Alkali Silver Thiosulphates and their Ability to Add Ammonia. ERIK JONSSON (*Ber.*, 1921, 54, [B], 2556—2564).—Additive compounds of alkali silver thiosulphate and ammonia have been described previously by Schwicker (A., 1889, 942) and by Meyer and Eggeling (A., 1907, ii, 347), who, however, do not record analyses of their products. A repetition of their work has given somewhat different results. The ability to form additive compounds seems to depend on the presence of unused subsidiary valencies of the silver atom and is most marked in compounds of the type $K_2S_2O_3 \cdot Ag_2S_2O_3$; it is scarcely noticeable in the case of the salts $2M_2S_2O_3 \cdot Ag_2S_2O_3$ and $5M_2S_2O_3 \cdot 3Ag_2S_2O_3$. The existence of colourless and yellow alkali silver thiosulphates (cf. Meyer and Eggeling, *loc. cit.*) is confirmed, but it appears doubtful whether their isomerism is explicable by assigning the respective formulæ $AgS \cdot SO_2 \cdot OK$ and $KS \cdot SO_2 \cdot OAg$, since their behaviour towards ethyl iodide indicates that the silver is attached to the sulphur atom in each case. Conversion of the colourless into the yellow modification can be effected frequently by cautious warming with water, but too drastic treatment leads to the formation of silver sulphide, sulphur dioxide, and sulphate. It appears, therefore, that the yellow compounds are intermediate products in the decomposition of the colourless salts, and the transformation is possibly explained by such a scheme as: $KO \cdot SO_2 \cdot SAg \rightarrow KO \cdot S \cdot SO_2 \cdot Ag$.

The following individual substances are described: the salt, $2K_2S_2O_3 \cdot Ag_2S_2O_3$, colourless prisms, from silver nitrate and potassium thiosulphate in the presence of ammonia; the salt, $5K_2S_2O_3 \cdot 3Ag_2S_2O_3$, long, colourless prisms; the compound, $3KAgS_2O_3 \cdot NH_3 \cdot 2H_2O$

(cf. Schwicker, *loc. cit.*, who regards it as $\text{KAgS}_2\text{O}_3 \cdot \text{NH}_3$), colourless plates which are converted by warm dilute ammonia and into a yellow *salt* of the same composition and are transformed by warm water into the *compound*, $\text{KAgS}_2\text{O}_3 \cdot 1.5\text{H}_2\text{O}$, colourless needles, and KAgS_2O_3 , yellow, hexagonal pyramids; the *salt*, $2\text{NaAgS}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, small, irregular plates; the *salt*,



long prisms, and the *compound*, $(\text{NH}_4)_4\text{Ag}_2\text{S}_2\text{O}_3$, prismatic crystals (by the action of ammonium thiosulphate on a solution of silver oxide in ammonia); the *salt*, $5\text{Rb}_2\text{S}_2\text{O}_3 \cdot 3\text{Ag}_2\text{S}_2\text{O}_3$, colourless prisms (cf. Meyer and Eggeling, *loc. cit.*) which is transformed by warm water into the *salt*, $3\text{Rb}_2\text{S}_2\text{O}_3 \cdot 4\text{Ag}_2\text{S}_2\text{O}_3$, yellow prisms; the *salt*, $3\text{RbAgS}_2\text{O}_3 \cdot \text{NH}_3 \cdot 2\text{H}_2\text{O}$ (Meyer and Eggeling record



the unstable yellow *salt*, $\text{Ag}_2\text{S}_2\text{O}_3 \cdot 3\text{NH}_3 \cdot \text{H}_2\text{O}$.

H. W.

Metallic Hydrides. II. Hydrides of the Alkaline-earth Metals and of Lithium. FRITZ EPHRAIM and EDUARD MICHEL (*Helv. Chim. Acta*, 1921, **4**, 900—924; cf. A., 1921, ii, 638).—The preparation of the hydrides and the measurement of their dissociation tensions is recorded.

When attempts are made to compare the tensions of the different hydrides with one another, it becomes apparent that all measurement of dissociation pressure of the alkali and alkaline-earth hydrides are vitiated by the use of impure material containing a greater or less proportion of dissolved metal which tends to depress the tension. Within each group, the effect of the metal increases with its atomic weight, and the influence of sublimation lies in the same direction. In the cases of caesium and barium hydrides, these actions render the measurement of dissociation pressures at high temperatures almost impossible. The influence of the atomic weight of the metal on the stability of the alkali hydride cannot be regarded as elucidated completely, but the authors consider from their own experiments that a slight diminution of stability with increasing atomic weight of the metal is probable. The tension curves of lithium hydride could not be measured, since a material which would withstand the chemical action of the hydride and metal could not be found. It is, however, established that it is the most stable of all the alkali or alkaline-earth hydrides which is in accordance with its great heat of formation. Calcium hydride appears to be more stable than barium hydride, whilst the strontium compound occupies an intermediate position.

The behaviour of the alkali and alkaline-earth metals towards hydrogen is not confined to the formation of hydrides, XH and XH_2 , but extends also to the production of solutions, the phenomenon being more marked with the hydrides of the alkaline earths than with those of the alkalis. The absorption of hydrogen occurs previously to, and, in part, simultaneously with, the formation of the hydrides; this occurs to a greater extent with the alkaline earth than with the alkali metals.

The formation of hydrides occurs slowly with the alkali metals,

rapidly and with incandescence in the cases of the alkaline-earth metals. This appears to be due to the greater solubility of the hydride in the metal. The same explanation applies to the observation that calcium hydride, for example, can be formed at a temperature which is certainly considerably higher than the temperature of dissociation of the pure hydride. The liquid nature of the alkali hydrides at the temperature of their formation contributes also to the slowness of absorption of hydrogen, since the eutectic mass protects the metal from further action.

Investigation of the hydrides of lanthanum and cerium (Mathmann and Baur, A., 1903, ii, 213) and of neodymium and praseodymium (Muthmann and Beck, A., 1904, ii, 409) have given results similar to those now observed with the alkaline-earth metals except that the displacement of the tension due to the presence of an excess of metal is even more considerable. The increase in the action of an excess of metal with increasing atomic weight is therefore apparent not only within a group in the periodic system, but also from left to right with increasing valency of the metal.

H. W.

The Discovery of an Equilibrium between Cement and Lime-water. RICHARD LORENZ and GUSTAV HAEGERMANN (*Z. anorg. Chem.*, 1921, **118**, 193—201).—When finely-ground Portland cement, which has been previously treated with water and dried, is stirred with a fixed quantity of water in absence of air, the quantity of lime taken up by the water eventually reaches a maximum value. This maximum is much less than the solubility of lime in water, and depends on the quantity of cement present in proportion to the water, and also, to some extent, on the fineness of the particles. The existence of this maximum is shown to depend on the partition coefficient of lime between the water and the silica-alumina gel formed by the decomposition of the cement constituents such as monocalcium silicate and tricalcium aluminate. This partition coefficient was determined by repeatedly treating the cement with fresh water until the whole of it had decomposed. The ratio of lime in the solid phase to lime in the water was then found to be about 7.0. The existence of the partition coefficient shows that no definite compound is formed between the lime and the constituents of the gel. [See also *J. Soc. Chem. Ind.*, 1922, 15A.]

E. H. R.

The Solubility of Glucinum Sulphate in Water and Sulphuric Acid at 25°. HUBERT THOMAS STANLEY BRITTON (*T.*, 1921, **119**, 1967—1971).

Ammoniates of Magnesium Haloids. WILHELM BILTZ and GUSTAV F. HÜTTIG (*Z. anorg. Chem.*, 1921, **119**, 115—131).—For the investigation of the ammoniates of magnesium haloids special precautions were taken in the preparation of pure magnesium chloride, bromide, and iodide. Ephraim's results (A., 1912, ii, 546), which were not confirmed, were probably due to the fact that his magnesium chloride contained basic salts. The

hexammoniate of magnesium chloride is formed in about fifteen hours at room temperature, when pure magnesium chloride is saturated with ammonia, and the product is extraordinarily voluminous. Magnesium bromide behaves similarly, but in the case of the iodide the increase in volume when the hexammoniate is formed is relatively slight. Observations were made on the time taken for the vapour pressure to become steady with different proportions of ammonia in the solid phase. From these observations definite rules can be formulated regarding heterogeneous equilibrium in a solid-gas system. When two non-miscible substances are present in the solid phase, equilibrium is reached with gradually diminishing velocity, usually in the course of a few hours, depending on the temperature and the nature of the substances. When one constituent just disappears, for instance from a mixture containing principally a lower ammoniate and a small quantity of a higher ammoniate, equilibrium is attained very rapidly. When unsaturated mixed crystals are present, for example of two ammoniates, equilibrium is reached very slowly, often requiring several days. This case occurs with the magnesium haloids containing 5.5 to 5.8 mols. of ammonia. When the ammonia content is very nearly 6 mols., addition of a very small quantity of ammonia, even a few hundredths of a mol., causes a very rapid rise in vapour pressure, equilibrium being rapidly attained. On account of this, the dissociation pressures of the hexammoniates could not be accurately determined. These ammoniates may be compared with the zeolites, which, unlike normal hydrates, lose water very rapidly. The phenomenon has not been observed with other ammoniates.

Magnesium chloride and bromide both form a diammoniate and a monoammoniate; the iodide forms only a diammoniate. The table gives the heats of formation in Cals. and the absolute temperatures at which the dissociation pressure is 100 mm.

	Saturated mixed crystals.	2NH ₃ .	1NH ₃ .
MgCl ₂	13.3; 367°	17.9; 495°	20.8; 573°
MgBr ₂	15.2; 420°	20.1; 559°	21.7; 606°
MgI ₂	17.2; 475°	22.7; 636°	—

E. H. R.

The Solidification Diagram of the Zinc-Arsenic Alloys.

W. HEIKE (*Z. anorg. Chem.*, 1921, **118**, 264—268).—Thermal examination was made of alloys containing from 6.6 to 92% of arsenic and with the aid of the results the equilibrium diagram was constructed. Two compounds, both melting without decomposition, are formed, Zn₃As₂, m. p. 1015°, and ZnAs₂, m. p. 771°; the former has a transition point at 671°. With excess of zinc, pure zinc appears with Zn₃As₂, no solid solutions being formed. Arsenic dissolves little zinc, but on the other hand is soluble to a considerable extent in the compound ZnAs₂. Two eutectics are formed, at 62% and 81.5% As respectively, the corresponding temperatures being 730° and 723°. Both compounds are very brittle,

and ZnAs_2 shows a well-marked cleavage. This compound always shows super-cooling during crystallisation of the alloys.

E. H. R.

The Fusion Diagram of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at Pressures of 1 to 3000 kilo./cm.². MEINHARD HASSELBLATT (*Z. anorg. Chem.*, 1921, **119**, 313—324).—The fusion diagram of the system $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ at the normal pressure has been previously determined (A., 1913, ii, 484). It was shown that the stable form of calcium nitrate forms a eutectic with cadmium nitrate at 91% $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and 40.6°, whilst the unstable form of the calcium salt forms a continuous series of mixed crystals with the cadmium salt. The effect of increased pressure up to 3000 kilos. per sq. cm. on the diagram has now been investigated. The general form of the diagram is unchanged. The p - t curve for mixed crystals containing a high proportion of the calcium salt could not be followed at higher pressures on account of the rapid change of the calcium salt into the stable form. Excess of the cadmium salt inhibits this change, but as the pressure increases, more cadmium salt is needed to produce this effect. With increasing pressure, the m. p. of the stable calcium salt rises much more rapidly than that of the unstable. The latter does not form mixed crystals with cadmium nitrate. The lowering of the m. p. of the stable calcium salt by the cadmium salt is independent of the pressure. With increasing pressure, the eutectic point moves towards the cadmium side; at 1000 kilo./cm.² it is at 79% calcium nitrate, 47.8°; at 2000 kilo./cm.², 74% and 55°, and at 3000 kilo./cm.², 71% calcium nitrate and 61.5°.

E. H. R.

Light Reactions of the Oxides of Titanium, Cerium, and the Earth Acids. CARL RENZ (*Helv. Chim. Acta*, 1921, **4**, 961—968; cf. A., 1921, ii, 316).—Titanium dioxide, cerium dioxide, niobium pentoxide, and tantalum pentoxide are in themselves stable towards light, but become markedly photosensitive in the presence of suitable media. Reaction is due to reduction; this is the more remarkable since the oxides are reducible by purely chemical means with considerable difficulty.

Titanium dioxide, niobium pentoxide, and, to a less degree, cerium dioxide undergo reduction when exposed to light in the presence of certain organic liquids and reducing solutions, particularly glycerol. A lower oxide appears to be formed (zirconium dioxide is not photosensitive and does not form a lower oxide) which on exposure to air or on being heated regenerates the original material. In the case of niobium pentoxide, the process depends to some extent on the presence of impurities, notably stannic and tungstic acids, zirconium compounds, and titanous acid or its anhydrides. Brown vanadium pentoxide becomes black with greater or less rapidity when exposed to light beneath glycerol, benzaldehyde, cinnamaldehyde, cuminol, or aqueous mannitol solution; a lower oxide, initially vanadium tetroxide, is produced. Solutions of citric or tartaric acid in absolute alcohol become green

and ultimately blue when illuminated in the presence of vanadium pentoxide; carbon dioxide is evolved freely. Similar decomposition is observed with mandelic acid, but, in this instance, the vanadium pentoxide is blackened. Brown neodymium oxide containing praseodymium does not alter in appearance when illuminated under glycerol or phenylhydrazine; it becomes bluish-grey when warmed with the latter, owing to conversion of the brown to the yellow oxide of praseodymium. When exposed to sunlight in the presence of glycerol, benzaldehyde or tartaric acid dissolved in alcohol, bismuth oxide becomes grey and ultimately dark black. Reduction to the lower oxide and, possibly, to the metal takes place. In similar circumstances, antimony trioxide is also photosensitive. H. W.

Concentration of the Erbium Earths. PAUL H. M.-P. BRINTON and C. JAMES (*J. Amer. Chem. Soc.*, 1921, **43**, 1397—1401).—Four methods for the concentration of the less basic of the rare earths have been investigated; the methods examined are: (1) formation of basic nitrates, (2) crystallisation of chlorides from 1:1-hydrochloric acid, (3) formation of basic chlorides, and (4) formation of basic thiosulphates. The authors highly recommend the first method for the separation of erbium, holmium, dysprosium, and the less basic earths from yttrium, and the second method for the separation of holmium and dysprosium from yttrium. The basic nitrate formation was carried out with (a) a solution of yttrium nitrate containing a little erbium, and (b) a yttrium-erbium-holmium mixture. In the former case, the solution was boiled and treated with a fairly concentrated solution of sodium hydroxide and thoroughly boiled. The yttrium hydroxide which first precipitated soon dissolved. The addition of sodium hydroxide was continued until minute crystals of the basic nitrate were observed swirling through the liquid. The whole was then set aside to cool, when a mass of needle-like crystals of the basic nitrate was obtained. These were collected, dissolved in the least amount of nitric acid, and treated with sodium hydroxide solution as before. The basic nitrate crystals from this when dissolved in nitric acid gave a rose-red solution which exhibited intense absorption bands of erbium, thus showing that the erbium was rapidly collecting in this fraction. The original filtrate was treated several times with sodium hydroxide, and although the concentration of nitrates was kept high the erbium absorption bands soon began to fade. The results obtained with the second mixture were equally good. The crystallisation of the chlorides was effected with a solution containing yttrium, holmium, and dysprosium. The solution in hydrochloric acid was boiled down until acid of constant boiling point was obtained. The solution was then evaporated until a scum appeared on the surface, when it was set aside for fifteen to twenty hours. The crystals were separated by decantation and the crystallisation proceeded with; by the time the tail fraction had become No. 9 and the head fraction No. 4 owing to the combination of small

head fractions, it was found that the atomic weights had become 92.5 and 124.0 respectively. After four further fractionations the atomic weight of the tail fraction No. 12 was 91.5 whilst that of the head fraction No. 4 was 133.70. The order of separation in order of decreasing solubility of the chlorides is erbium, yttrium, holmium, dysprosium. J. F. S.

Disglomeration and Formation of the Autogenous Lead Tree. A. THIEL (*Ber.*, 1921, **54**, [B], 2755—2758; cf. A., 1920, ii, 622).—Disglomeration, which has been observed previously in the cases of lead and copper, is also exhibited by tin when the latter is preserved for some time under stannous chloride solution in a loosely stoppered bottle.

Large uniform crystals of lead become strongly corroded when preserved for some weeks beneath Heller's solution; a considerable quantity of lead powder is formed but, as expected, there is no evidence of disglomeration, that is, formation of deep fissures at the boundaries of the crystallites. Unexpectedly in the light of the previous theory, the large crystallites readily exhibit the formation of the lead tree when preserved beneath a solution of lead nitrate acidified with nitric acid. The phenomenon is observed only after the formation of a white skin of basic salt on the metal and is explained in the following manner. The presence of the skin inhibits the contact of dissolved lead salt and metal by convection and greatly impedes the diffusion of the lead ion. Beneath the skin, therefore, the solution soon contains practically only lead nitrate and is poor in lead ions, whereas the external solution still contains lead nitrate and therefore has a much higher lead ion concentration. The possibility of the formation of a short-circuited concentration cell is thus provided. H. W.

The Chemical Behaviour of Crystallised Binary Compounds with one Component Nobler than Hydrogen. G. TAMMANN (*Z. anorg. Chem.*, 1921, **118**, 93—104).—The author draws a comparison between metallic mixed crystal series and binary compounds. In the former case, the members of a mixed crystal series behave chemically and electrically in a similar manner to one or other component, according to the proportion of each present, with sharply defined limits at molecular fractions which are generally a simple multiple of 1/8. This behaviour is correlated with the lattice structure of the mixed crystals, and may be expected also in crystallised binary compounds which have a similar lattice structure, the difference being that in the latter case the proportions of the two kinds of atom are fixed. It is to be expected that binary compounds will show similarity chemically or electrically to one or other component, and when two or more compounds of the two elements are formed, some will resemble one component and some the other. As an example confirming this view, the compounds of lead and palladium are cited. In this series the compounds Pb_2Pd , PbPd , PbPd_2 , and PbPd_3 have been identified. In a solution of lead nitrate against

lead these all give a potential equal to that of palladium, but as soon as any free lead is present the potential drops to zero. Chemically, all the palladium-lead compounds are as resistant as palladium. Binary compounds can be conveniently classed as resistant or non-resistant, the former showing the properties of the nobler, the latter those of the baser component.

The above principles are applied to the discussion of a large number of binary compounds, principally metallic, such as those present in alloys of gold, silver, copper, and platinum, besides sulphides, silicides, and carbides, and it is shown that the compounds can be classified as resistant or non-resistant. The more base the inactive component is, the greater is the number of atoms of the nobler component necessary to protect it. In general, a smaller number of gold than of silver atoms are needed to protect a given atom of a baser metal. These considerations apply to compounds in which one component is nobler than hydrogen. When both are less noble than hydrogen, the classification into resistant and non-resistant does not apply, since both constituents and their compounds decompose water. Apart from compounds of this type, it is possible, in a series of binary crystallised conglomerates, to determine from a few measurements of their galvanic potential which of the components they will resemble in their chemical character.

E. H. R.

The Chemical and Electrical Behaviour of some Series of Alloys. WILHELM JENGE (*Z. anorg. Chem.*, 1921, **118**, 105—122).—With a view to test the theory put forward by Tammann (preceding abstract) that crystallised binary compounds, when no diffusion of the atoms is possible, may be expected to behave chemically and electrically as one or other of the constituent elements a number of series of alloys, in which binary compounds are formed, were examined. The alloys were used as anodes and subjected to the action of halogen, sulphate, or nitrate ions, and were tested against acids and alkalis. In the cobalt-silicon series, in which the compounds formed are Co_2Si , Co_3Si_2 , CoSi , CoSi_2 , CoSi_3 , those having less than 32% of silicon were readily attacked by acidic ions, but those with higher silicon content were resistant. That is to say, CoSi and the higher silicides behave as silicon, the other compounds as cobalt. Towards cold acids, the same compounds were respectively resistant and non-resistant and towards cold alkalis all were resistant except CoSi_3 , the behaviour of which resembled that of silicon. No sharp demarcation of properties was found in the behaviour of the alloys towards hot acids and alkalis because the cobalt loses its passivity and decomposes water. In the series of nickel-silicon alloys somewhat similar results were obtained, but the compound NiSi , unlike CoSi , was not resistant to halogen ions. In the manganese-silicon series only Mn_2Si was non-resistant to acids and all, that is, Mn_2Si , Mn_2Si_3 , and MnSi were resistant to sodium hydroxide.

Alloys of antimony with cadmium and tin and of bismuth with thallium were also examined. The compounds Cd_3Sb_2 and Zn_3Sb_2

have the potentials of cadmium and tin respectively, whilst CdSb and ZnSb soon approximate to the hydrogen potential. The cadmium alloys precipitate antimony and lead from solution, and Zn_3Sb_2 precipitates not only lead, but also cadmium. A bismuth-thallium alloy with the composition Bi_5Tl_3 gives the hydrogen potential, but after etching with hydrochloric acid, the bismuth potential, indicating that the surface thallium atoms have been removed, leaving only bismuth exposed.

Of the lead-thallium alloys, those with over 0.49 mol. of lead show the lead potential, those with 0 to 0.475 mol. of lead show the thallium potential.

Great difficulty was experienced in measuring the potentials of the alloys of magnesium with copper, lead, cadmium, and tin, but it appears that at the moment of contact with the electrolyte they have the magnesium potential, which, however, rapidly falls.

E. H. R.

Physical Chemistry of the Oxides of Lead. II. The Supposed Enantiotropy of Lead Monoxide. SAMUEL GLASTONE (T., 1921, **119**, 1914—1927).

Binary Systems of the Sulphates, Chromates, Molybdates, and Tungstates of Lead. F. M. JAEGER and H. C. GERMS (*Z. anorg. Chem.*, 1921, **119**, 145—173).—The paper comprises an account of thermal investigations of the binary systems of PbO with SO_3 , CrO_3 , MoO_3 , and WO_3 respectively, and of the different systems formed by pairs of the compounds PbSO_4 , PbCrO_4 , PbMoO_4 , and PbWO_4 . By an optical method the transition temperature of PbO from the red, tetragonal, low temperature form to the yellow, rhombic, high temperature modification was found to be 587° . The melting point of pure lead oxide is 879° . The following melting points were also freshly determined, and differ slightly from accepted values: chromium trioxide, 198° ; molybdenum trioxide, 795° ; tungsten trioxide, 1473° . The examination of the binary systems formed by lead monoxide with the acid anhydrides was limited in each case to the partial system $\text{PbO-PbM}'''\text{O}_4$. In the system PbO-PbSO_4 , the existence of the following compounds was recognised: Pb_4SO_7 , Pb_3SO_6 , Pb_2SO_5 , PbSO_4 . The first has no real melting point, but decomposes at 897° , forming Pb_3SO_6 , m. p. 961° , which has a transition point at 450° . Pb_3SO_5 (lanarkite) has m. p. 977° . PbSO_4 decomposes markedly at 1135° and its m. p. is estimated by extrapolation to be 1170° . The transition point of PbSO_4 from the β to the low temperature α form is $864 \pm 1^\circ$. Three eutectics are formed at 89 mols. % PbO and 835° , 60 mols. % PbO and 950° , and 34 mols. % PbO and 960° .

In the system PbO-PbCrO_4 , the compounds Pb_5CrO_8 , $\text{Pb}_7\text{Cr}_2\text{O}_{13}$, Pb_2CrO_5 , and PbCrO_4 were recognised. The first has no real melting point and exists only below 815° . $\text{Pb}_7\text{Cr}_2\text{O}_{13}$, m. p. 854° , has a reversible transition point at 744° , and forms with Pb_2CrO_5 , m. p. 920° , a eutectic at 68 mols. % PbO and 841° . Lead chromate, PbCrO_4 , is found to be trimorphous; the α -form

is stable below 707° ; the β -form between 707° and 783° , and the γ -form above 783° , melting at about 844° with evolution of oxygen. The heat effect of the change $\alpha \rightleftharpoons \beta$ is small and is sharper in binary mixtures with lead oxide than in the pure substance. The eutectic between PbCrO_4 and Pb_2CrO_5 occurs at 820° , but this part of the equilibrium diagram could not be determined accurately on account of decomposition.

The system PbO-PbMoO_4 shows only two compounds, Pb_3MoO_5 , m. p. 951° , and PbMoO_4 , m. p. 1065° . There are two eutectics, at 87.5 mols. % PbO , 762° , and at 40 mols. % PbO , 933° . The tungstates correspond with the molybdates, Pb_2WO_5 , m. p. 899° , and PbWO_4 , m. p. 1123° , with a transition point at 877° .

The equilibrium diagram for the system $\text{PbCrO}_4\text{-PbSO}_4$ is largely conjectural owing to the considerable amount of decomposition occurring at higher temperatures. There is a gap in the mixed crystal series between about 40% and 30% PbCrO_4 . The mixed crystals have transition points at 934° , 874° , and 748° . In the $\text{PbSO}_4\text{-PbMoO}_4$ system mixed crystals are formed containing up to 6 mols. % sulphate or 2 mols. % molybdate. There is a eutectic at 57 mols. % molybdate and 962° . At 879° , the mixed crystals have a transition point. In the $\text{PbSO}_4\text{-PbWO}_4$ system the mixed crystals of the β -type separating at the eutectic temperature contain respectively 37 mols. % sulphate and 7 mols. % tungstate. The eutectic is at 51 mols. % tungstate and 995° . At 875° occurs the $\beta \rightleftharpoons \alpha$ -sulphate transformation and at 859° the corresponding tungstate change. The $\text{PbCrO}_4\text{-PbMoO}_4$ diagram is largely hypothetical. The composition of the limiting mixed crystals on the molybdate side is 48 mols. % PbCrO_4 at 838° , the eutectic temperature. Transitions occur at 799° of $\gamma \rightarrow \beta$ -chromate mixed crystals, and at 697° $\beta \rightarrow \alpha$. In the $\text{PbCrO}_4\text{-PbWO}_4$ system the eutectic temperature is 837° and the limiting mixed crystals on the tungstate side contain 41 mols. % PbCrO_4 . Lead molybdate and lead tungstate form an isodimorphous mixed crystal series with a transition temperature at 1082° . A mixture containing 75 mols. % PbMoO_4 is in equilibrium at this temperature with both kinds of mixed crystal. E. H. R.

Photochemistry of Thallous Chloride. II. CARL RENZ (*Helv. Chim. Acta*, 1921, 4, 950—960).—A continuation of previous work (A., 1920, ii, 71). Thoroughly illuminated, blackish-brown, thallous chloride, in consequence of photolysis, contains as primary product more or less grey to slate-grey photothallous chlorides in addition to yellow intermediate thallous-thallic chlorides formed in accordance with the scheme: $6\text{TlCl} + \text{Light} = \text{photochloride} + \text{TlCl}_3, 3\text{TlCl}$. Thallic hydroxide, formed by subsidiary actions, is also present. These phases characterise the photo-processes in those cases in which the change of colour extends over the scale, greyish-brown, dark greyish-brown, blackish-brown, and hence occur when thallous chloride is illuminated in the dry condition, under water, and in the presence of solutions of many neutral salts. In the presence of reducing agents or of organic hydroxy-

acids, the action of light on thallous chloride only leads to the production of the photochloride. The formation of thallous-thallic chlorides is not observed in the presence of alkalis or alkali carbonates, which decompose these compounds immediately. The production of photothallous chlorides and of thallic hydroxide does not occur in the presence of hydrochloric acid, even without the addition of organic substances.

Photothallous chloride can be prepared by purely chemical methods if ferrous sulphate is added to a boiling, saturated aqueous solution of thallous chloride and the mixture is treated with an excess of ammonia. The black precipitate of photothallous chloride and iron hydroxides is allowed to settle, and is subsequently washed with hydrochloric acid until the iron compounds are dissolved; the slate-grey photothallous chloride so obtained behaves in exactly the same manner as the photosynthetic product.
H. W.

Ammoniates of Cupro- and Thallo-haloids. WILHELM BILTZ and WILHELM STOLLENWERK (*Z. anorg. Chem.*, 1921, **119**, 97—114).—The formation and vapour pressures at different temperatures of ammoniates of cuprous and thallous chloride, bromide, and iodide were investigated, using apparatus similar to that employed in experiments on the ammoniates of silver haloids (A., 1921, ii, 201). When saturated with ammonia gas, cuprous chloride first shrinks to a yellow mass, then swells and becomes greyish-white. Saturation at -70° to -30° requires at least a day. When the excess of ammonia is allowed to evaporate at room temperature and atmospheric pressure, cuprous chloride triammoniate remains. In damp air, it quickly turns green. The pressure isotherms also indicate the existence of a sesquiammoniate and a monammoniate. Cuprous bromide behaves similarly, forming a white triammoniate, a sesquiammoniate, and a monammoniate. Cuprous iodide absorbs ammonia quickly at room temperature. It forms four compounds, containing respectively 3, 2, 1, and $\frac{1}{2}$ mol. of ammonia. In the following table are given the heats of formation Q in Cals. and the temperatures in absolute degrees at which the dissociation pressures of all these compounds are equal to 100 mm.

	3NH_3 .	2NH_3 .	$1\frac{1}{2}\text{NH}_3$.	1NH_3 .	$\frac{1}{2}\text{NH}_3$.
CuCl	9.48; 283°	—	12.61; 326°	16.73; 417.5°	—
CuBr	9.50; 283°	—	13.15; 339°	14.64; 369.0°	—
CuI	10.37; 286.5°	11.30; 298°	—	14.70; 371.0°	15.22; 390°

Thallous haloids do not absorb ammonia at the ordinary temperature, but in liquid ammonia they all form triammoniates. The vapour pressures are all very close to those of ammonia itself. The triammoniates are soluble to a certain extent in liquid ammonia, the solubility increasing with rising temperature and with the atomic weight of the halogen. The heat of formation is about 7.1 Cal. for the ammonia compound of each of the three haloids. No lower ammoniates are formed.

E. H. R.

The Action of Molten Alkali Chlorides on Copper Oxide. J. ARVID HEDVALL and GUNNAR BOOBERG (*Z. anorg. Chem.*, 1921, **119**, 213—216).—It was shown in a former paper (Hedvall and Heuberger, A., 1921, ii, 508) that potassium chloride could not be used as a flux in the fusion of cupric oxide with aluminium oxide on account of a reaction taking place between the potassium chloride and copper aluminate. It is now shown that when copper oxide is heated with potassium chloride, cuprous oxide is formed and oxygen evolved. This is best demonstrated by adding cupric oxide in small quantities to a mixture of potassium and sodium chlorides at 1000° and continuing the heating for one and a half hours. At the same time, a basic cupric chloride is formed which, by prolonged heating with sodium or potassium chloride solution, is obtained as the compound $3\text{CuO}, \text{CuCl}_2, 4\text{H}_2\text{O}$. E. H. R.

Phenomena of Diffusion in Metals in the Solid State and Cementation of Non-ferrous Metals. I. Cementation of Copper by means of Ferro-manganese. G. SIROVICH and A. CARTOCETI (*Gazzetta*, 1921, **51**, ii, 245—261).—A bar of copper was arranged centrally in a porcelain tube glazed internally and the tube then packed with ferro-manganese containing 5% of wood charcoal, both these materials being capable of passing through a sieve with 64 meshes per sq. cm. and of being retained by one of 324 meshes per sq. cm. The tube was closed by means of rubber stoppers luted with sodium silicate, one of the stoppers having two holes to admit a thermo-couple for measuring the temperature and a glass tube bent at right angles and with its end dipping into mercury. After the tube had been heated for some hours at 900° in a Heraeus furnace, considerable proportions of the manganese were found to have penetrated the copper (cf. *J. Soc. Chem. Ind.*, 1922, 17A). T. H. P.

Tervalent Copper. G. SCAGLIARINI and G. TORELLI (*Gazzetta*, 1921, **51**, ii, 225—228).—Contrary to Moser's statement (A., 1907, ii, 549), the action of potassium persulphate on cupric hydroxide in presence of barium hydroxide at temperatures obtained by cooling with ice and salt results in various changes in the colour of the solution and in the deposition of a tenuous amaranth-red precipitate, which may be purified by repeated washing with ice-water by decantation. The compound thus obtained yields oxygen when treated with sulphuric acid, oxidises hydrochloric acid with liberation of chlorine, oxidises ammonia in the cold with production of nitrogen, nitrous acid, and traces of nitric acid, decolorises permanganate, and decomposes potassium iodide with liberation of iodine in quantity greater than that corresponding with the proportion of copper present. Since it does not yield hydrogen peroxide when treated with dilute acid, the compound lacks the grouping characteristic of peroxides and is thus different from the orange-yellow copper peroxide obtained by means of hydrogen peroxide. The ratio between the percentages of copper and active oxygen present is in agreement with the formula Cu_2O_3 . T. H. P.

Production of Single Crystals of Aluminium and their Tensile Properties. H. C. H. CARPENTER and CONSTANCE F. ELAM (*Proc. Roy. Soc.*, 1921, [A], **100**, 329—353; cf. A., 1921, ii, 641).—A continuation of work previously published (*loc. cit.*) on the production of large crystals of aluminium. The metal used in the present work had a purity of 99·6%, the impurity being 0·19% silicon and 0·14% iron. The test-pieces used were 70 mm. with a parallel portion 103 mm. long, 26 mm. broad, and 3 mm. thick, and were estimated to contain 1,687,000 small crystals in the parallel portion ($103 \times 26 \times 3$ mm.). The authors first describe the treatment necessary to convert the whole of the crystals into a single crystal. Three separate processes are shown to be necessary: (i) the aluminium strip is heated at 550° for six hours, (ii) the strip after cooling is subjected to a stress which is equivalent to 378 kilos. per sq. cm., and gives an average elongation of 1·6% on 76 mm., (iii) the test-piece is finally placed in a furnace at 450° and the temperature raised 15—20° per day up to 550° and then for 1 hour at 600°. Applying this treatment to thirty-eight test pieces showed that nine pieces consisted of a single crystal, fourteen of two crystals, nine of three crystals, four of four crystals, and two of six crystals. The tensile strength of aluminium strips consisting of known numbers of crystals has been determined. It is shown that for strips consisting of 150 crystals per 25 mm. it is 708—740 kilos. per sq. cm., and these give an elongation of 36—38% on 76 mm. The tensile strength of strips consisting of a single crystal varies between 598 and 642 kilos. per sq. cm. and these strips suffer an elongation of 34—86% on 76 mm. The varying tensile strength and elongation was accompanied by differences in the type of stretching and fracture. Strips consisting of two crystals have a tensile strength of 441—550 kilos. per sq. cm. and suffer an elongation of 29—70% on 76 mm., whilst strips consisting of three crystals have a tensile strength of 456—567 kilos. per sq. cm. and suffer an elongation of 36—55% on 76 mm. A further series of experiments on the production of single crystals in bars is described. J. F. S.

The Thermal Treatment of certain Complex Aluminium Alloys. LÉON GUILLET (*Compt. rend.*, 1921, **173**, 979—982).—In order to determine the effect of each constituent on the behaviour of duralumin under thermal treatment (cf. *ibid.*, 1919, **169**, 508), the author has studied alloys of aluminium and copper, aluminium and silicon, aluminium, silicon, and copper, aluminium, magnesium, and silicon, and quaternary alloys containing all four elements. Measurements of hardness have been made on annealed samples, and on samples tempered at different temperatures, the measurements being made in the latter case immediately after tempering and also after the alloy had been kept for forty-eight hours at 20°. From the results of these measurements and from micrographic examinations of the alloys it is shown that the simultaneous presence of silicon, magnesium, and copper is indispensable to obtain the interesting results given by tempering high resistance aluminium alloys. W. G.

Solubility Limits of Carbon in Ternary Steels. I. The System Chromium-Iron-Carbon. KARL DAEVES (*Z. anorg. Chem.*, 1921, **118**, 55—66).—Experiments were made to determine the influence of chromium on the solubility of carbon in iron and to determine the position of the corresponding solubility line in the ternary chromium-iron-carbon diagram. The solubility falls off rapidly at first as the chromium content increases, then more slowly, the general form of the curve being hyperbolic. Points on the curve were determined by observing what chromium content was necessary, with a given carbon content, to cause the appearance of a eutectic in the structure of the metal. To make the hard alloys workable, for the preparation of polished surfaces, it was necessary to heat for several hours at 800°, just below the Ac_1 point, by which treatment the solid solution was broken up and the metal softened. Etching was accomplished by electrolysis in ammonium persulphate solution. In eutectoid alloys, the cementite is practically unattacked by hot sodium picrate solution. Cold alkaline potassium ferricyanide turns the hard constituent of the eutectic brown to yellow, leaving the mixed crystals untouched. The solubility curve explains many of the known properties of chromium steels. The melting point of steel and the arrest points are little affected by chromium up to 10%. [Cf. *J. Soc. Chem. Ind.*, 1922, 16A.]
E. H. R.

Solubility Limits of Carbon in Ternary Steels. II. The System Tungsten-Iron-Carbon. KARL DAEVES (*Z. anorg. Chem.*, 1921, **118**, 67—74).—The effect of tungsten on the solubility of carbon in iron was studied in the same way as that of chromium (preceding abstract), and a solubility curve of similar form was obtained, separating eutectic from non-eutectic steels in the ternary diagram. Sudden changes in the physical properties of tungsten steels are correlated with changes of composition involving the passage from one side to the other of this limiting curve. The appearance of so-called double carbides of iron and chromium or of iron and tungsten, observed by different workers, is attributed to the same cause. Small amounts of tungsten in steel raise the melting point, but larger amounts depress it.

E. H. R.

The Colour of Iron Alum. JANE BONNELL and EDGAR PHILIP PERMAN (*T.*, 1921, **119**, 1994—1997).

Complex Selenates. JULIUS MEYER (*Z. anorg. Chem.*, 1921, **118**, 1—47).—A large number of new complex selenates and incidentally some simpler compounds which have not hitherto been described, were prepared for comparison with the corresponding sulphates. The new selenates described belong to the chromi- and cobalti-series, and show the closest resemblance to the sulphates, differing from these occasionally only in their water of crystallisation. On account of the ease with which selenic acid is reduced, difficulties were at times encountered in the preparation of certain of the compounds.

[With LEONHARD SPEICH.]—Chromiselenates. Violet chromic selenate, $[\text{Cr}(\text{H}_2\text{O})_6]_2(\text{SeO}_4)_3 \cdot 3(\text{or } 4)\text{H}_2\text{O}$, forms a crystalline powder, readily soluble in water, from which it is precipitated by alcohol or acetic acid. Its aqueous solution dissolves chromic hydroxide with formation of green basic salts. When the violet salt is heated in solution or in the solid state at 90° it changes irreversibly into a green chromiselenate. The green salt prepared in the solid state has the composition $\text{Cr}_2(\text{SeO}_4)_3 \cdot 10\text{H}_2\text{O}$ and dissolves very slowly in water, probably only after addition of water. The green salt may have a constitution of the type $[\text{Cr}(\text{SeO}_4)(\text{H}_2\text{O})_5]_2\text{SeO}_4$. When a solution of the violet salt is boiled for some time, a green compound is formed which is precipitated by alcohol as a green oil and dries to an amorphous, green solid. It is very soluble in water and gives no precipitate with barium salts or with ammonia. It is probably a triselenatochromic acid, $[\text{Cr}(\text{SeO}_4)_3]\text{H}_3$.

Chloropentaquochromiselenate, $[\text{CrCl}(\text{H}_2\text{O})_5]\text{SeO}_4 \cdot 3\text{H}_2\text{O}$, was prepared from chloropentaquochromichloride and sodium selenate; it forms a bright green powder very soluble in water and alcohol. Attempts to obtain other chloro-selenates, corresponding with known chloro-sulphates, were not successful.

Dichlorotetraquochromihexaquoichromiselenate,
 $[\text{CrCl}_2(\text{H}_2\text{O})_4]_2(\text{SeO}_4)_2[\text{Cr}(\text{H}_2\text{O})_6]$,
 forms a green, crystalline powder, readily soluble in water, slightly so in alcohol. An attempt to prepare a corresponding double chromi-aluminium selenate failed, although sulphates of the type $[\text{CrCl}_2(\text{H}_2\text{O})_4](\text{SO}_4)_2[\text{M}(\text{H}_2\text{O})_6]$, where $\text{M} = \text{Cr}, \text{Fe}, \text{Al}, \text{or V}$, were prepared by Werner and Huber (A., 1906, ii, 170).

Hexamminechromiselenate, $[\text{Cr}(\text{NH}_3)_6]_2(\text{SeO}_4)_3$, was prepared from the corresponding nitrate and selenic acid. It is precipitated from aqueous solution by alcohol as a heavy, yellow, finely crystalline powder. The salt is amorphous whilst the corresponding sulphate has $5\text{H}_2\text{O}$.

Chloropentamminechromiselenate, $[\text{CrCl}(\text{NH}_3)_5]\text{SeO}_4$, was prepared from purpureochromichloride and silver selenate. It forms a heavy, red, amorphous powder sparingly soluble in water. The corresponding sulphate is much more soluble, and crystallises with $2\text{H}_2\text{O}$.

Hexacarbamidechromiselenate, $[\text{Cr}(\text{NH}_2 \cdot \text{CO} \cdot \text{NH}_2)_6]_2(\text{SeO}_4)_3$, prepared from hexacarbamidechromichloride and silver selenate, was obtained as a bright green, finely crystalline powder, moderately soluble in water, from which alcohol precipitates it.

Triethylenediaminechromiselenate, $[\text{Cr}(\text{en})_3]_2(\text{SeO}_4)_3$, from the corresponding chloride and silver selenate, is a reddish-yellow, heavy, crystalline powder, soluble in water and precipitated by alcohol. When the dry salt is heated at 100° , the colour changes to reddish-violet.

Aluminium selenate, which has not before been described, forms a white, crystalline powder, easily soluble in water and precipitated by alcohol. It appears to contain less than $18\text{H}_2\text{O}$, but the analysis did not distinguish between 15 and $17\text{H}_2\text{O}$.

[With HANNS MOLDENHAUER.]—Complex cobaltiselenates. The

complex cobaltiselenates prepared were confined to those containing only one cobalt complex and to those with 6, 5, or 4 molecules of ammonia or 4 molecules of pyridine.

Hexammine(luteo)cobaltiselenate, $[\text{Co}(\text{NH}_3)_6]_2(\text{SeO}_4)_3 \cdot 5\text{H}_2\text{O}$, corresponds in every respect with luteocobaltisulphate.

Aquopentamminecobaltiselenate, $[\text{Co}(\text{H}_2\text{O})(\text{NH}_3)_5]_2(\text{SeO}_4)_3 \cdot 3\text{H}_2\text{O}$, was prepared both from the corresponding cobaltichloride and from selenatopentamminecobaltiselenate. The salt is similar in physical and chemical properties to roseocobaltisulphate.

Diaquotetramminecobaltiselenate, $[\text{Co}(\text{H}_2\text{O})_2(\text{NH}_3)_4]_2(\text{SeO}_4)_3 \cdot 3\text{H}_2\text{O}$, was prepared from carbonatotetramminecobaltiselenate and selenic acid. It dissolves in water to a deep red solution from which alcohol precipitates it as a bright red, crystalline powder. It loses its water of crystallisation on exposure to air.

Chloropentamminecobaltiselenate, $[\text{CoCl}(\text{NH}_3)_5]\text{SeO}_4$, was prepared from purpureocobaltichloride and silver selenate; it corresponds in its properties with purpureocobaltisulphate.

Chloro-aquotetramminecobaltichloride selenate, $\{\text{CoCl}(\text{H}_2\text{O})(\text{NH}_3)_4\}\text{Cl}_2\text{SeO}_4$, was obtained when dichlorotetramminecobaltichloride was treated with silver selenate, through hydration of one of the nuclear chlorine atoms. It forms a violet, crystalline powder, giving a violet aqueous solution.

Nitropentamminecobaltiselenate, $[\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{SeO}_4$, from the corresponding chloride and silver selenate, forms bright yellow, microscopic crystals, giving a yellowish-brown, aqueous solution. It forms a periodide, as does the corresponding sulphate.

Sulphatopentamminecobaltiselenate, $[\text{Co}(\text{SO}_4)(\text{NH}_3)_5]_2\text{SeO}_4 \cdot 2\text{H}_2\text{O}$, was prepared from the corresponding sulphato-bromide and silver selenate. It is precipitated from aqueous solution by alcohol in rose-coloured leaflets consisting of microscopic, rhombic tablets. The corresponding sulphatosulphate contains only $1\text{H}_2\text{O}$.

Acid selenatopentamminecobaltiselenate, $[\text{Co}(\text{SeO}_4)(\text{NH}_3)_5]\text{SeO}_4 \cdot \text{H}_2\text{O}$, was prepared by treating chloropentamminecobaltichloride with concentrated selenic acid. From the diluted solution the acid salt crystallised in reddish-violet crystal aggregates. It closely resembles the sulphato-sulphate and forms the starting material for the preparation of a series of selenatopentamminecobalti-salts including several of the following.

Normal selenatopentamminecobaltiselenate, $[\text{Co}(\text{SeO}_4)(\text{NH}_3)_5]_2(\text{SeO}_4) \cdot \text{H}_2\text{O}$, was obtained by treating the above acid selenate with alcohol; it has a brighter red colour than the acid salt.

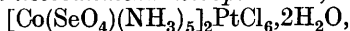
Selenatopentamminecobaltisulphate, $[\text{Co}(\text{SeO}_4)(\text{NH}_3)_5]_2\text{SO}_4 \cdot \text{H}_2\text{O}$, was obtained from the selenato-bromide and silver selenate. It is precipitated by alcohol from aqueous solution in bright red, lustrous tablets. This salt is metameric with the above sulphatopentamminecobaltiselenate, but the two are not isomorphous, as the latter crystallises with $2\text{H}_2\text{O}$.

Selenatopentamminecobaltinitrate, $[\text{Co}(\text{SeO}_4)(\text{NH}_3)_5]\text{NO}_3$, was pre-

pared from the above acid selenate and ammonium nitrate. It separates in well-formed, bright red, sparingly soluble crystals.

Selenatopentamminecobaltibromide, $[\text{Co}(\text{SeO}_4)(\text{NH}_3)_5]\text{Br}$, was prepared from the above acid selenate and hydrobromic acid. It is thrown down by alcohol from aqueous solution as a bluish-red precipitate.

Selenatopentamminecobaltihexachloroplatinate,



forms lustrous, orange-red tablets, sparingly soluble in water.

In the tetramminecobalt-series only carbonic acid of the bivalent acids could be introduced into the complex. With two univalent acid radicles, stereoisomerism becomes possible, and it was found possible to prepare the 1 : 2- and 1 : 6-dinitrotetramminecobaltiselenates.

Carbonatotetramminecobaltiselenates, $[\text{Co}(\text{CO}_3)(\text{NH}_3)_4]_2\text{SeO}_4 \cdot 3\text{H}_2\text{O}$, is similar to the corresponding sulphate, crystallising in dark red leaflets which lose their water of crystallisation on exposure to air.

Acid dichlorotetramminecobaltiselenate, $[\text{CoCl}_2(\text{NH}_3)_4]\text{SeO}_4\text{H}$, crystallises in dark green, well-formed needles but is unstable and readily changes to the chloroaquotetrammine salt described above.

Acid dichlorotetrapyridinecobaltiselenate, $[\text{CoCl}_2\text{Py}_4]\text{SeO}_4\text{H} \cdot 2\text{H}_2\text{O}$, is more stable than the dichlorotetrammine salt; it crystallises in lustrous green leaflets. The salt corresponds with the sulphate described by Werner and Feenstra (A., 1906, i, 450).

1 : 2-Dinitrotetramminecobaltiselenate, $[\text{Co}(\text{NO}_2)_2(\text{NH}_3)_4]_2\text{SeO}_4$, was prepared from flavocobaltinitrate (Jørgensen, A., 1898, ii, 592) and ammonium selenate; it forms dark brown crystals.

1 : 6-Dinitrotetramminecobaltiselenate, stereoisomeric with the last, was prepared from croceocobaltichloride (Jørgensen, *loc. cit.*) and silver selenate; it is precipitated from aqueous solution by alcohol in the form of minute, bright yellow crystals.

The electrical conductivities of many of the above salts in aqueous solution were measured at 25° and their magnitudes were found to agree with the constitutions ascribed to the different salts.

E. H. R.

The Green Colour of Tungsten Trioxide. J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1921, **119**, 310—312).—Tungsten trioxide generally has a yellow colour, but is sometimes green. A number of explanations of this phenomenon have been offered, but it is now shown experimentally that the green colour is due to reduction at ordinary temperatures by traces of organic matter to lower oxides. Provided the green oxide has not been ignited, the yellow colour may be restored by heating it in a current of oxygen.

E. H. R.

Chlorination by Mixed Carbon Monoxide and Chlorine. F. P. VENABLE and D. H. JACKSON (*J. Elisha Mitchell Sci. Soc.*, 1920, **35**, 87—89).—Chlorination is successfully accomplished with a mixture of carbon monoxide and chlorine, containing the former in excess, in the following cases : zirconium dioxide at 480°, stannic

oxide at 400°, magnesium oxide at 475°, aluminium oxide at 450°, ferric oxide at 460°, chromic oxide at 625°, manganese dioxide at 460°, uranoso-uranic oxide at 500°. With chlorine in excess, the requisite temperature for zirconium dioxide is 425° and for ferric oxide 370°.

CHEMICAL ABSTRACTS.

Antimonic Acid and the Use of Sodium Antimonate in Analysis. E. S. TOMULA (*Z. anorg. Chem.*, 1921, **118**, 81—92).—The constitution of antimonic acid and of the salts derived from it has never been satisfactorily settled, and an attempt has now been made to solve the problem by the application of physico-chemical methods. The conductivity of the potassium salt was measured at 25° at dilutions from $V=32$ to 1024, and the basicity of the acid, by the Oswald-Walden rule, was found to be 1. This rules out the possibility that the salt is a pyroantimonate, $K_2H_2Sb_2O_7$, and since it gives a solution having an acid reaction, it cannot be the metantimonate, $KSbO_3$. It must therefore be the orthoantimonate, KH_2SbO_4 . Hydrogen-ion determinations in a 1/1024*N*-solution by the calorimetric method confirmed this view. The dissociation constant at this dilution was found to be $\alpha=0.957$ and the hydrogen-ion concentration $C_H=10^{-6.3}$. The equivalent conductivity of the sodium salt was, on account of its low solubility, determined only at dilutions $V=512$ and 1024, and was found to be of the same order as, although slightly lower than, that of the potassium salt. The hydrogen-ion concentration at $V=1024$ was $C_H=10^{-6.4}$, and it is concluded that the two salts have the same constitution. Delacroix (A., 1898, ii, 340; 1900, ii, 145) and Senderens (A., 1899, ii, 557) both isolated a soluble and an insoluble form of antimonic acid, which they called ortho- and pyro-acids, but they differed as to which was which. Conductivity experiments on the potassium salts show that the soluble acid is the ortho-acid, whether prepared by Senderens's or Delacroix's method. It is concluded, however, that a concentrated solution of antimonic acid is not a true solution but a supersaturated colloidal pseudo-solution, from which the acid soon separates in the insoluble form.

Determinations were made at 18°, 25°, and 33.5° of the solubility of sodium antimonate in water, in aqueous sodium acetate, and in aqueous methyl and ethyl alcohols. Expressed in mg. of $Na_2O, Sb_2O_5, 6H_2O$ per 100 c.c. of solution, the solubility at 18° is, in water 56.4, in equal volumes of water and ethyl alcohol 0.1, and in 2.5% sodium acetate 3.1.

The following method is recommended for the estimation of antimony as sodium antimonate. The antimony must be in alkaline solution as sodium sulphantimonate, Na_3SbS_4 , and must be free from potassium, since in presence of potassium salts precipitation is incomplete. The solution is warmed at 80° and stirred while a solution of 30% hydrogen peroxide is run in drop by drop until vigorous evolution of oxygen commences, and it is then boiled until all oxygen evolution ceases. The alkaline solution is neutralised with acetic acid until it is acid to phenolphthalein, but still weakly alkaline to litmus. It is stirred a further quarter

of an hour and then one-half its volume of 96% alcohol is added, after which stirring is continued for ten minutes. After twelve hours, the crystalline sodium antimonate is filtered, washed on the filter with a solution containing 3 grams of sodium acetate, 3 grams of acetic acid, and 400 c.c. of ethyl alcohol per litre, and finally with 50% alcohol. The dried precipitate is separated from the filter-paper, which is burnt separately, is ignited for fifteen minutes in a porcelain crucible, and weighed as sodium metantimonate, NaSbO_3 . Special directions are given for procedure when tin is present, as it is then necessary to redissolve and reprecipitate the sodium antimonate. [See also *J. Soc. Chem. Ind.*, 1922, 12A.] E. H. R.

The Reaction Limit of Chemical Agents on Copper-Gold Alloys and their Galvanic Tension. G. TAMMANN (*Z. anorg. Chem.*, 1921, 118, 48—54).—The reaction limit in different copper-gold alloys is reached when the molecular fraction of gold present is $1/8$, $2/8$, or $4/8$, according to the chemical reagent used. The reactivity of the mixed crystals may be regarded as due to the loosening of the copper atoms from their lattice combination by the chemical agent or, from another point of view, to the action of the chemical agent on copper atoms which have become detached from the lattice on account of their solution tension. From the latter point of view it was important to determine how the solution tension of the alloys varied with the composition. Measurements were made against a gold electrode in a number of electrolytes, and against silver with silver sulphate as electrolyte. The results showed that the limiting composition beyond which no copper ions appear in the solution and the alloy behaves electrically as pure gold, is at $2/8$ mol. fraction of gold. This method does not give such sharp limiting values as the chemical method, however, owing to the sensitiveness of the galvanic tension to impurities on the surface of the metal. The case of the cell silver | saturated silver sulphate | copper-gold is specially interesting, since, when the proportion of gold in the alloy does not exceed 0.145 mol., silver is visibly precipitated and the metal becomes negatively charged, whilst the alloys richer in gold do not precipitate silver and assume a weak positive charge. This weak positive charge indicates a superficial deposit of silver, so that the surface acts as a silver-gold alloy of corresponding composition. It is shown, from consideration of the mixed crystal lattice, that when $1/8$ mol. of gold or less is present in the copper alloy, conditions are favourable for the formation of silver crystals. It is suggested that those agents which find their active limit at $2/8$ mol. of gold, corresponding with the solution tension limit for copper ions, act first on the copper ions in solution, but as soon as the osmotic pressure of the copper ions exceeds the solution tension, the agent attacks the mixed crystal surface. E. H. R.

Ruthenium Tetroxide. F. KRAUSS (*Z. anorg. Chem.*, 1921, 119, 217—220).—An aqueous solution of ruthenium tetroxide has 3*—2

apparently a weak acid reaction, although this is difficult to demonstrate on account of the rapid decomposition of dyes by the solution. The solution behaves as an electrolyte, and is decomposed by the current with formation of a green colour. With alkali hydroxides it forms salts, but only the ammonium salt could be obtained in the pure state. It was prepared by adding concentrated ammonia to a concentrated solution of ruthenium tetroxide in water until the colour changed from yellow to greyish-brown. By evaporating, a salt of the composition $(\text{NH}_4)_2\text{RuO}_5$ was obtained. Under certain conditions, which could not be accurately determined, a mono- and a di-hydrate of this salt were obtained. In the preparation of ruthenium tetroxide, besides the yellow compound, a brownish-red substance was observed, less soluble in water than the tetroxide. This has not been identified. Ruthenium tetroxide can be estimated by distilling it in a current of dry air at 15° into a specially constructed weighed flask, dissolving in a little water, reducing with alcohol, evaporating with dilute hydrochloric acid, igniting in a stream of hydrogen, and weighing the ruthenium. E. H. R.

Mineralogical Chemistry.

Native Antimony from Kern County, California. C. H. BEHRE, JUN. (*Amer. J. Sci.*, 1921, [v], 2, 330—333).—A statement of the results of an examination of nodular masses of antimony with a crust of oxidation products. L. J. S.

Identity of Flagstaffite with Terpin Hydrate. F. N. GUILD (*Amer. Min.*, 1921, 6, 133—135).—A comparison of the crystal constants of flagstaffite (A., 1921, ii, 51) with those of terpin hydrate suggests the identity of these; and this is confirmed by comparative tests made on the natural and artificial materials. Variable results for the m. p. are obtained, owing to loss of water before melting. When heated very slowly the crystals soften at about 100°, and finally melt near 116°. Anhydrous terpin from flagstaffite has m. p. 105°. The terpin hydrate formula, $C_{10}H_{20}O_2 \cdot H_2O$, is adopted, since the material analysed had been partly dehydrated by remaining over sulphuric acid. L. J. S.

The Natural Iron Hydroxides. KARL WILLMANN (*Centr. Min.*, 1921, 673—678).—A review is given of the colloidal and crystalline forms of iron hydroxides. The scaly (Rubinglimmer) and acicular (Samtblende or needle-iron-ore) forms of goethite differ in optical characters and are regarded as dimorphous forms of $Fe_2O_3 \cdot H_2O$. New analyses of Rubinglimmer from the Eleonore mine near Giessen gave Fe_2O_3 89.90, H_2O 10.77 = 100.67, and Fe_2O_3 88.11, H_2O 11.97 = 100.08, agreeing with this formula. L. J. S.

Curite, a New Radioactive Mineral. ALFRED SCHÖEP (*Compt. rend.*, 1921, **173**, 1186—1187).—The new mineral is found at Kasolo, Katanga, Belgian Congo, as translucent, reddish-brown, acicular crystals on torbernite or as compact or earthy masses, and consists of minute needles with straight optical extinction. It is readily soluble in cold nitric acid and in hot hydrochloric acid; when heated, it turns dark brown. Analysis gives the formula $\text{PbO}, 5\text{UO}_3, 4\text{H}_2\text{O}$.

PbO.	UO ₃ .	H ₂ O.	Fe ₂ O ₃ .	Total.	<i>d</i> ¹⁷
21.32	74.22	4.00	0.17	99.71	7.192

L. J. S.

Analytical Chemistry.

The Conditions for the Maximum Precipitation of an Amphoteric Electrolyte. ADA PRINS (*Chem. Weekblad*, 1921, 18, 657—658).—The minimum solubility occurs at a definite hydroxyl-ion concentration depending for each amphoteric electrolyte on its solubility product as base and as acid. The concentrations of the positive and negative ions are inversely proportional to their charges. S. I. L.

Use of Cæsium Chloride in Microchemistry. ENRIQUE HERRERO DUCLOUX (*Anal. Asoc. Quím. Argentina*, 1921, 9, 215—227).—Cæsium chloride may be used as a reagent in microchemistry by reason of the well-defined double chlorides which it forms with different metals. Crystallographic descriptions, with photomicrographs, are given of the double salts thus formed with silver, mercury, lead, platinum, gold, palladium, arsenic, antimony, cadmium, tin, copper, aluminium, iron, zinc, nickel, cobalt, manganese, calcium, magnesium, thallium, cerium, and indium.

G. W. R.

Use of the Zeiss Water Interferometer (Rayleigh-Löwe) for the Analysis of Non-aqueous Solutions. ERNST COHEN and H. R. BRUINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1921, 24, 114—122).—A description of the Rayleigh-Löwe water interferometer and the method of use for estimating the concentration of aqueous solutions are given. The accuracy obtainable with this instrument is about 99·9998% for aqueous solutions. To use this instrument for non-aqueous solutions greater precautions in the fixing of the temperature are required. The thermostat liquid should also be chosen so as to have a refractive index of the same order as that of the solvent used. When these precautions are taken an accuracy equal to that obtained for water solutions may be obtained with solutions in organic solvents. J. F. S.

A Buffer Solution for Colorimetric Comparison. T. C. McILVAINE (*J. Biol. Chem.*, 1921, **49**, 183—186).—The author covers the whole range from P_H 2.2 to P_H 8.0 by mixing two solutions only, viz. a 0.2*M*-disodium phosphate solution with 0.1*M*-citric acid. A table to obtain any desired P_H is given and also a graph.
G. B.

A Simplified Form of Apparatus for Air Analysis. CHARLES CLAUDE GUTHRIE (*J. Biol. Chem.*, 1921, **48**, 365—371).—The apparatus, which is illustrated in the original, “differs from the well known forms in dimensions rather than in principles or in design.”
E. S.

Estimation of the Gases of the Blood. DONALD D. VAN SLYKE and WILLIAM C. STADIE (*J. Biol. Chem.*, 1921, **49**, 1—42).—Improvements in the technique of using the apparatus previously described for the extraction from the blood and measuring of the carbon dioxide (A., 1917, ii, 422—423), oxygen (A., 1918, ii, 82), and carbon monoxide (A., 1920, ii, 53). All the gases can now be estimated in 1 c.c. of blood by a modified form of the original apparatus with narrow measuring tube enclosed in a water-jacket. In the oxygen estimation, the blood is now laked with water, and the amount of ferricyanide has been greatly reduced; the results are about 5% higher than those obtained by Haldane's method. Particularly in the case of the carbon dioxide estimation, the errors are fully analysed, and examples of calculations are given.
G. B.

Mechanical Shaker and other Devices for Use with the Van Slyke Blood Gas Apparatus. WILLIAM C. STADIE (*J. Biol. Chem.*, 1921, **49**, 43—46; cf. preceding abstract).—A motor-driven shaker, a levelling scale, and tonometer rotator are described with the help of figures.
G. B.

Estimation of Chlorine in Benzaldehyde. SCHIMMEL & Co. (*Ber. Schimmel & Co.*, 1921, 56—61; from *Chem. Zentr.*, 1921, iv, 771).—Benzaldehyde is burnt in a small lamp so constructed that the amount of liquid burnt may be found by weighing at the beginning and end of the experiment. The products of combustion are passed through two U-tubes containing glass beads moistened with 0.02*N*-potassium hydroxide solution, foaming being prevented by the use of a few drops of petroleum. The washings from the absorption apparatus are united and, after addition of an equivalent amount of 0.02*N*-sulphuric acid, concentrated in a closed flask. The solution is then made alkaline to phenolphthalein and the colour discharged by one or two drops of 0.02*N*-sulphuric acid. Five drops of 10% potassium chromate solution are added and the chlorine is estimated in the usual way with 0.02*N*-silver nitrate solution.
G. W. R.

Action of Potassium Ferrocyanide on Silver Haloids. G. B. BONINO (*Gazzetta*, 1921, **51**, ii, 261—265).—Potassium ferrocyanide does not appear to interact with silver bromide or iodide,

but with the chloride it reacts according to the equation : $3\text{AgCl} + \text{K}_4\text{Fe}(\text{CN})_6 = \text{Ag}_3\text{KFe}(\text{CN})_6 + 3\text{KCl}$. The chlorine ion may therefore be estimated in presence of the iodine ion by precipitating and washing the mixed silver haloids, treating the latter with a known volume of 0.1N-potassium ferrocyanide solution, removing the insoluble silver potassium ferrocyanide by filtration, and determining the amount of the residual potassium ferrocyanide by titration with standard permanganate solution. The reaction has not yet been studied quantitatively in presence of bromides.

T. H. P.

Estimation of Small Quantities of Bromides and Chlorides in Iodides. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, 58, 1568—1569).—The iodide in solution is treated with excess of sodium nitrite in presence of sulphuric acid. After filtering and boiling, to remove iodine and excess of nitrous acid, chlorides and bromides are estimated by Volhard's method. The method is quantitative, but does not distinguish between chlorides and bromides.

S. I. L.

Bromine Normally Present in Animal Tissues. A. DAMIENS (*Bull. Sci. Pharmacol.*, 1921, 28, 85—93; from *Chem. Zentr.*, 1921, iv, 847).—Thirty grams of finely-divided tissue are extracted by heating with dilute potassium hydroxide solution. The dried residue is incinerated with a mixture of potassium nitrate and sodium carbonate, and the ash dissolved in water. Iodine is estimated in a portion of the solution as follows: the silver haloid precipitate, obtained by addition of silver nitrate solution in the presence of nitric acid, is suspended in water and a stream of chlorine is passed, first in the cold and then in the presence of 1 c.c. of sulphuric acid with warming. Air is passed through and the precipitate removed by centrifuging. The iodine is then estimated by a colorimetric method. Another portion of the solution is precipitated with silver nitrate and nitric acid. The precipitate is removed and the filtrate is treated with zinc and sulphuric acid. When less than a milligram of iodine is present, bromine may be estimated colorimetrically in the filtrate. In the presence of larger amounts of iodine, the filtrate, after the reduction of the silver haloid precipitate, is neutralised with ammonia, diluted to 40 c.c. and after addition of 1 gram of iron ammonium sulphate, concentrated to 10 c.c. Bromine may then be estimated as before (cf. A., 1921, i, 476).

G. W. R.

Estimation of Sulphur in Pyrites. L. GADAI (Ann. Chim. Analyt., 1921, 3, 330—335).—A critical review of Lunge's method and certain suggested modifications. For accurate work, the original method without alteration is to be preferred, care being taken to adhere strictly to all details of the operations. A variation of this method, in which the insoluble gangue is not filtered off before the precipitation of the iron with ammonia, is not recommended, as this gangue contains substances such as the sulphates of barium, strontium, calcium, and lead which may be partly

dissolved by ammonia and reprecipitated on subsequent acidification and addition of barium chloride. A second modification of Lunge's procedure, which obviates the washing of the gangue, consists in making up the solution in aqua regia to 100 c.c., filtering off 50 c.c., and proceeding with this aliquot portion as in the original method. This is free from serious objection provided the insoluble residue is comparatively small in amount. Finally, a rapid control method, not suitable for accurate work, consists in diluting the original solution to about 800 c.c., adding ammonia directly to this, digesting for two hours at a moderate temperature, cooling, making up the volume to 1000 c.c., and filtering off 500 c.c. in which sulphate is estimated in the usual way. G. F. M.

Volumetric Estimation of Sulphide by Oxidation to Sulphate. H. H. WILLARD and W. E. CAKE (*J. Amer. Chem. Soc.*, 1921, **43**, 1610—1614).—Sulphide is rapidly and quantitatively oxidised to sulphate by an excess of hypobromite in 2.5*N*-sodium hydroxide or by hypochlorite in 4*N*-sodium hydroxide. The excess of oxidising agent is determined iodometrically. The method gives accurate results for the estimation of sulphur in steels and in sulphides if care is taken to exclude all other reducing agents. In the case of steels, the method is used as follows: 5 grams of steel are placed in a flask, through which hydrogen may be passed, which is connected with a 10-bulb tube for absorbing the hydrogen sulphide. Air is removed from the apparatus by hydrogen and 100 c.c. of hydrochloric acid (*d* 1.1) are added. After the reaction has moderated, the solution is heated just to boiling for five minutes after the steel has dissolved. The solution in the absorption tube should contain 6—7 grams of sodium hydroxide in 50 c.c. of solution. The contents of the bulbs are washed with as little water as possible into a flask containing 10 c.c. of 0.3*N*-hypobromite solution and kept for three or four minutes, then 2 or 3 grams of potassium iodide are added, and the solution is diluted to 150 c.c. It is then exactly neutralised with concentrated hydrochloric acid and 5 c.c. excess added and titrated with 0.1*N*-sodium thiosulphate. If hypochlorite has been used instead of hypobromite, more sodium hydroxide must be used. Sulphides which are soluble in hydrochloric acid are estimated in the same way as steels. Insoluble sulphides are ignited with powdered iron in an atmosphere of hydrogen or carbon dioxide, thus producing ferrous sulphide. The estimation is then carried to completion as above. The error of the method is about 0.1%. J. F. S.

Estimation of Sulphurous Acid. VICTOR COPPETTI (*Ann. Chim. Analyt.*, 1921, **3**, 327—330).—The gravimetric method of Haas for the estimation of sulphurous acid, which consists in expelling the sulphur dioxide from the solution under examination by distillation in an atmosphere of carbon dioxide, absorbing the gas in a solution of iodine, and weighing the resulting sulphuric acid as barium sulphate, gives accurate results volumetrically if means are taken to prevent loss of iodine by volatilisation in the

current of carbon dioxide. For this purpose, an apparatus is described consisting essentially of a 300 c.c. flask to contain the iodine solution, to the bottom of which extends the gas delivery tube from the distillation flask. Surmounting the flask is a spherical absorption vessel containing $N/10$ -thiosulphate solution, through which the carbon dioxide and iodine vapours leaving the flask must pass. When distillation is complete, the thiosulphate solution containing all the volatilised iodine is allowed to run back into the flask and the excess of iodine in the latter is titrated back with standard thiosulphate solution. G. F. M.

The Estimation of Sulphates by means of a Suspension of Barium Chromate. I. M. KOLTHOFF (*Rec. trav. chim.*, 1921, **40**, 686—699; cf. Andrews, A., 1890, 414).—Although it would appear on theoretical grounds that an estimation of sulphate by means of barium chromate was not practicable, the method is valid, since the reaction $\text{BaSO}_4 + \text{CrO}_4'' \rightleftharpoons \text{BaCrO}_4 + \text{SO}_4''$ proceeds very slowly from left to right. The solution, acidified with hydrochloric acid, should be heated during neutralisation with ammonia to avoid the loss of chromic acid which accompanies the precipitation of barium chromate at ordinary temperatures, and, having regard to the hydrolysis of ammonium chromate, a slight excess of ammonia should be added. Barium chromate is adsorbed by ferric, aluminium, and zinc hydroxides, so that when these metals are present the method gives results which are too low, but trustworthy results can be obtained when ions which affect the reacting substances are absent. In presence of calcium, the results are too low, the error becoming smaller with increasing acidity of the solution and decreasing concentration of calcium. Practical details are given. H. J. E.

Catalytic Action of Copper in the Oxidation of Ammonia by means of Persulphate. G. SCAGLIARINI and G. TORELLI (*Gazzetta*, 1921, **51**, ii, 277—280).—Quantitative investigation of the oxidation of ammonia by means of either potassium or ammonium persulphate in presence of copper sulphate shows that the oxygen of the persulphate first oxidises the ammonia to nitrous acid, which is converted into ammonium nitrite, this being decomposed, with liberation of nitrogen, by the heat developed: $2\text{NH}_3 + 3\text{O}_2 = 2\text{HNO}_2 + 2\text{H}_2\text{O}$, $2\text{NH}_3 + 2\text{HNO}_2 = 2\text{NH}_4\cdot\text{NO}_2$, and $2\text{NH}_4\cdot\text{NO}_2 = 4\text{H}_2\text{O} + 2\text{N}_2$. The catalytic effect of copper salts appears to be due to oxidation of the copper to a more highly oxidised compound, which passes on its surplus oxygen to the ammonia.

The estimation of persulphate by means of ferrous salts may be replaced advantageously by the following method, in which use is made of a Schultze and Tiemann's apparatus furnished with a mercury valve (*Z. anal. Chem.*, 1870, **9**, 401; *Ber.*, 1873, **6**, 1041): 40 c.c. of water and 0.4—0.6 gram of copper sulphate are boiled in the flask for about ten minutes, the caoutchouc tube being then clipped and the boiling continued for five minutes to expel the air. The apparatus is allowed to cool, the mercury rising in

the barometer tube and a vacuum becoming established in the flask. A known volume of the persulphate solution and afterwards about 100 c.c. of ammonia solution are drawn into the cold flask through the clipped tube, the flask being then heated and the evolved gas collected over water and measured. The results obtained in this way agree exactly with those yielded by the ferrous sulphate method.

T. H. P.

[Method for the Estimation of Tri-, Tetra-, and Pentathionates present together in Solution with Sulphite, Thio-sulphate, and Sulphate.] E. H. RIESENFELD and G. W. FELD (*Z. anorg. Chem.*, **119**, 225—270). See this vol., ii, 45.

The Accuracy of Dumas's Method for the Estimation of Nitrogen in the Cases of Substances rich in Nitrogen. ERNST MOHR (*Ber.*, 1921, **54**, [B], 2758—2767).—A mathematical treatment of the influence of the errors in measuring weight of substance, volume of nitrogen, temperature and pressure on the accuracy of the process.

The usual procedure of estimating the volume accurately to within 0.05 or 0.1 c.c., and the temperature and pressure to degrees Centigrade and millimetres of mercury is sufficient for substances containing 20—25% of nitrogen, but involves considerable error when more than this amount is present. The errors due to inaccurate reading of pressure and temperature cannot be minimised by increasing the weight of substance taken. On the other hand, the errors due to volume and weight of substance become considerable when a small quantity of substance is taken and can be diminished by increasing the amount. The practice of using small weights of material when dealing with substances rich in nitrogen by Dumas's method is to be deprecated; Pregl's method should be used in preference. The error involved in the measurement of pressure does not depend to an appreciable extent on whether the gas is moist or dry (above 50% potassium hydroxide solution), but the error involved in measurement of temperature is lower in the latter case. In spite of this fact, the measurement is generally made in preference over water by reason of the customary large diameter of the Schiff's nitrometer and the formation of foam over the potassium hydroxide solution.

A simple and accurate method of calculation is as follows. The temperature is first brought to whole degrees by addition or subtraction of x° in the direction of smallest change and the pressure is then changed by $3x$ mm. in the same sense as the alteration of temperature.

A plea is entered for the more uniform recording of analytical data in the literature and more precise statement of the exact condition of the nitrogen with respect to moisture as also for the reduction of pressures to 0° .

H. W.

The Kjeldahl Nitrogen Method and its Modifications. A. E. PAUL and E. H. BERRY (*J. Assoc. Off. Agric. Chem.*, 1921, **5**, 108—132).—Investigations are described into the most suitable

apparatus and method for the nitrogen estimation, with particular reference to the case of cotton-seed meal as presenting special difficulty. The most suitable type of bulb-trap for use in the distillation is the one in which both inlet and outlet tubes enter the bulb and are bent in opposite directions. It is advisable, although not absolutely necessary, to have enough acid in the receiver to neutralise all the ammonia distilled. Practically all the ammonia appears in the first 75 c.c. of the distillate, and all is in the first 100 c.c. During the initial digestion of the material with acid, the flame should never touch the flask above the surface of the liquid; the flask should be protected by a ring of asbestos. The volume of the digesting liquid should at no time be less than 10 c.c. If mercury is used to aid the digestion there is a loss of from 2 to 15% of ammonia unless enough potassium sulphide is added to precipitate all the mercury before distillation. The use of copper sulphate during digestion does not necessitate the subsequent addition of potassium sulphide. The use of permanganate is unnecessary. Digestion with sulphuric acid alone never gives maximum results. Mercury gives a much more rapid digestion than copper salts, and potassium sulphate is more efficient than sodium sulphate. The most rapid and efficient digestion is given by the use of 0.7 gram of mercuric oxide and 10 grams of potassium sulphate. In this way, the liquid becomes clear in one to one and a half hours and further heating for three hours completes the digestion. The amount of copper used in the digestion has little effect on the result. A 2 gram sample of cotton-seed meal and similar substances is preferable. Digestion should not be carried out in an atmosphere containing nitrous fumes. Nitrates in the digestion mixture are not only entirely lost, but they also bring about a considerable reduction in the amount of ammonia recovered.

A. G. P.

Modification in the Kossel-Neumann Method for the Estimation of Phosphorus in Organic Substances. MARIO A. MANCINI (*Biochem. ter. sper.*, 1921, **8**, 4—7; cf. Falk and Sugiura, A., 1915, ii, 577).—0.5 Gram of the substance is heated in a 200 c.c. Kjeldahl flask with 6—8 c.c. of sulphuric acid (*d* 1.184), the boiling being continued for one hour. Nitric acid (*d* 1.4) having been carefully added drop by drop, boiling is continued until the evolution of oxides of nitrogen ceases. The operation is repeated four or five times. The clear, light yellow liquid is washed into a beaker with hot water, and ammonium hydroxide solution is added in slight excess, followed by 30—40 c.c. of 40% ammonium nitrate solution and 20 c.c. of 25% nitric acid. The liquid is mixed, at 100°, with 120—140 c.c. of a boiling 3% solution of ammonium molybdate. After being kept for at least two hours, it is filtered and the precipitate washed with a hot solution containing 50 c.c. of nitric acid and 50 grams of ammonium nitrate per litre. Hot 25% ammonium hydroxide solution is poured over the filter, which is washed with hot water until the washings give no reaction with Nessler's reagent. To the filtrate is added

50 c.c. of ammoniacal "magnesia mixture," and, after being kept for twenty-four hours, the precipitate is filtered, washed, and ignited in the usual manner.

CHEMICAL ABSTRACTS.

The Composition and Preparation of a Neutral Solution of Ammonium Citrate. C. S. ROBINSON (*J. Assoc. Off. Agric. Chem.*, 1921, 5, 93—97).—To overcome the confusion attached to the term "neutral ammonium citrate solution," it is recommended that such a solution should be one showing a p_H value of 7.0. The solution contains 45.33 grams of ammonia and 172.00 grams of anhydrous citric acid per litre at 20° and has d 1.09. To prepare a litre of solution 172.00 grams of anhydrous citric acid are dissolved in 700 c.c. of water, nearly neutralised, cooled, and made up to a convenient volume, maintaining the density above 1.09. Of this, 5 c.c. are diluted to about 20 c.c., and standard ammonia solution is added until the colour produced with phenol-red indicator matches that produced with the same quantity of indicator by an equal volume of neutral standard phosphate solution (50 c.c. of $M/5$ -dihydrogen potassium phosphate + 29.63 c.c. of $M/5$ sodium hydroxide in 200 c.c.). The calculated amount of ammonia is then added to the bulk of the solution.

A. G. P.

A Modified Method for the Estimation of Phosphoric Acid. A. W. CLARK and R. F. KEELER (*J. Assoc. Off. Agric. Chem.*, 1921, 5, 103—105).—Two grams of the sample are dissolved in 30 c.c. of concentrated nitric acid and 10 c.c. of hydrochloric acid. The solution is diluted to 200 c.c. and filtered through a dry filter. A portion equivalent to about 0.25 gram is neutralised with ammonia and acidified with nitric acid. Fifty c.c. of 20% ammonium nitrate solution are added and then sufficient ammonium molybdate solution. After remaining over-night, the precipitate is collected on a Gooch crucible, washed eight times with 2% nitric acid (12—13 c.c. each time), then twice with cold water, and dried for two hours at 120°. Precipitation in the cold and drying at 120° give a less variable precipitate than the usual method. The conversion factor of ammonium phosphomolybdate to phosphoric acid is 0.03723.

A. G. P.

Nephelometric Method for the Estimation of Phosphoric Acid and its Compounds in Small Quantities of Blood. W. R. BLOOR (*Bull. Soc. Chim. Biol.*, 1921, 3, 451—475).—A detailed description of the author's adaptation (A., 1918, ii, 452) of Kober and Egerer's method (A., 1915, ii, 794).

E. S.

Toxicology of Arsenic. N. TARUGI (*Boll. Chim. Farm.*, 1921, 60, 569—576).—The results of experiments with rabbits and guinea-pigs show that arsenic, either organically combined or mixed mechanically with organic matter, always yields gases containing arsenic when putrefaction occurs. Such evolution of gas may occur quickly and must be borne in mind in cases of suspected arsenical poisoning. In the putrefaction of animal matter, the mechanism by which gaseous arsenic compounds are formed

is more complicated than the action of the "arsenic moulds," since such gases are not formed in the initial stages of the putrefaction where aerobiosis appears to predominate, and since also the gases contain not only alkylarsines but hydrogen arsenide as well.

T. H. P.

The Use of Silica Crucibles for the Estimation of Potassium in Soils. J. S. JONES and J. C. REEDER (*Soil Sci.*, 1921, **12**, 419—432).—For the estimation of potassium in soils by the fusion method, silica crucibles may be used instead of platinum, provided that certain limits of temperature are observed. To ensure perfect fusion, the muffle must reach a temperature of 812°, and to avoid loss of potassium by volatilisation the temperature must not exceed 855°. For this purpose an electrically heated muffle is preferable. An electrical arrangement for heating a silica crucible of the J. L. Smith type, 10 cm. long, 2 cm. in diameter at the top, and 1.8 cm. at the bottom is described and is very satisfactory for this type of work.

W. G.

Detection of Magnesium in Presence of Manganese and Phosphoric Acid. A. PURGOTT (*Gazzetta*, 1921, **51**, ii, 265—266).—In presence of phosphoric acid, manganese is precipitated almost completely as tertiary manganous phosphate, even from solutions containing large proportions of ammonium chloride; the precipitate undergoes gradual or, in the hot, rapid transformation into pale pink crystals of manganous ammonium phosphate, analogous in composition and properties to magnesium ammonium phosphate. The formation of this manganese precipitate and hence the danger of mistaking it for the magnesium precipitate may be avoided by treating the hydrochloric acid solution, not only with ammonia solution to remove the kations accompanying magnesium, but also at the same time with ammonium sulphide, which eliminates the whole of the manganese as sulphide; the filtrate is then tested for magnesium.

If the metals of the third group are precipitated in the usual way with ammonia solution, manganese phosphate is precipitated in considerable quantity in addition to certain amounts of calcium, barium, and strontium phosphates, a little manganese and much calcium, barium, and strontium passing into solution. Similar behaviour is shown by a mixture of magnesium phosphate with a manganese salt, but less magnesium goes into solution and still less manganese is precipitated as phosphate. If the quantity of manganese salt is very considerably greater than that of the calcium, barium, and strontium phosphates, the equilibrium, $\text{Ca}_3(\text{PO}_4)_2 + 3\text{Mn}(\text{OH})_2 \rightleftharpoons \text{Mn}_3(\text{PO}_4)_2 + 3\text{Ca}(\text{OH})_2$, is displaced towards the right hand side and the calcium, barium, and strontium pass into solution almost completely.

T. H. P.

Apparatus for the Gasometric Estimation of Zinc in Zinc Powder. EDGAR BEYNE (*Ann. Chim. Analyt.*, 1921, **3**, 360).—The apparatus consists of a gas burette, the upper part of which below the glass stop-cock is expanded into a bulb of 300 c.c.

capacity, and the lower part is graduated in 0.5 c.c. from 300 c.c. to 375 c.c. The lower end of the burette is connected with a rubber tube to a bulb for adjusting the liquid level and gas pressure in the burette, and the upper end is connected through a small refrigerating spiral to a Koninck apparatus which is charged with the zinc dust under examination, and a mineral acid. In a simpler form of apparatus the latter is replaced by an ordinary flask connected by means of a glass tube with the stop-cock of the burette.

G. F. M.

The Direct Iodometric Estimation of Lead Peroxide. SAMUEL GLASSTONE (T., 1921, 119, 1997—2001).

A Very Sensitive Reagent for Copper : the Kastle-Meyer Reagent. PIERRE THOMAS and GEORGES CARPENTIER (*Compt. rend.*, 1921, 173, 1082—1085).—The Kastle-Meyer reagent, which is a 2% solution of phenolphthalein in 20% potassium hydroxide solution decolorised by boiling with zinc powder, gives a pink coloration with copper salts and is capable of detecting 1 part of copper in 100,000,000 parts of water. Four drops of the reagent are added to 10 c.c. of the solution to be tested and then one drop of hydrogen peroxide (5—6 vols.).

W. G.

The Iodometric Estimation of Copper and Arsenic present together, especially in Paris and Schweinfürth Green. I. M. KOLTHOFF and C. J. CREMER (*Pharm. Weekblad*, 1921, 58, 1620—1624).—Arsenic trioxide can be estimated by means of iodine if the cupric-ion concentration is very much reduced, which can be effected by addition of excess of pyrophosphate or tartrate, with which the copper forms complex salts. 0.6—0.8 Gram of the pigment is boiled with 25 c.c. of water and 5 grams of sodium pyrophosphate to a clear solution. After cooling, *N*/10-iodine solution is added until the deep blue solution becomes green; the end-point is very sharp. The iodine required is equivalent to the arsenious oxide present. Ten c.c. of 4*N*-sulphuric acid and 2 grams of potassium iodide are then added, and after ten minutes the iodine liberated by reduction of the cupric compound is titrated with *N*/10-thiosulphate, starch being added towards the end.

The results were checked by analysis of the pigments by the standard Lunge-Berl method. This method was found unsatisfactory for copper, the results being always high. Addition of hydrazine sulphate before the sodium hydroxide reduces the copper compound, the element being precipitated and weighed as metal; this modification is much more accurate than the accepted method.

The iodine titration is rapid and simple, and gives accurate results for both elements.

S. I. L.

Separation and Estimation of Copper, Lead, Antimony, and Tin. Analysis of White Metals. A. KLING and A. LASSIEUR (*Compt. rend.*, 1921, 173, 1081—1082).—0.5—1.0 Gram of the alloy is dissolved in 10 c.c. of hydrochloric acid in the presence of potassium chlorate. The solution is diluted to 100 c.c.,

and neutralised with sodium hydroxide. Any precipitate formed is redissolved by the addition of 4—5 grams of tartaric acid. The liquid is transferred to a conical flask coated inside with wax, and to it are added 10 c.c. of concentrated hydrofluoric acid and then, after half an hour, 10 grams of sodium acetate, 1 c.c. of glacial acetic acid and water to bring the volume to 300 c.c. A white precipitate of lead fluoride is formed, but to the liquid 20 c.c. of a 10% solution of sodium sulphide are added and after a time the precipitate of the sulphides of copper, lead, and antimony is filtered off. In the filtrate the tin may be estimated either by precipitation with cupferron (cf. A., 1920, ii, 452), or electrolytically after decomposition of the complex fluoro-compound by the addition of boric acid and redissolving the tin sulphide by boiling with hydrogen peroxide. The precipitate of the mixed sulphides is extracted with 80 c.c. of sodium sulphide solution (d 1.14) and the antimony estimated electrolytically in the extract after the addition of potassium cyanide. The copper and lead sulphides are dissolved in nitric acid and the two metals estimated simultaneously by electrolysis. W. G.

Estimation of Mercury in the Mercurial Pills of the [French] Codex. MAURICE FRANÇOIS (*J. Pharm. Chim.*, 1921, 24, 369—379; *Ann. Falsif.*, 1921, 14, 340—347).—The pills are heated with concentrated nitric acid for two hours on a water-bath, and after a further two hours the solution is filtered, and the destruction of the organic matter is completed by adding a small quantity of a 10% solution of bromine. After ten minutes the liquid is rendered strongly alkaline with sodium hydroxide and after adding potassium iodide the mercury is precipitated in the form of a grey powder by means of formaldehyde solution. After two hours the supernatant liquid is decanted through a filter, the mercury is washed with dilute sodium hydroxide solution, and is then treated, together with the filter-paper and its contents, with diluted acetic acid and $N/10$ -iodine solution. After ten minutes' agitation, the mercury is completely transformed into mercuric iodide, which dissolves in the potassium iodide present, and the excess of iodine is titrated back with thiosulphate. The method is of general application to all the mercurial pills of the French Codex without modification except in the case of opiated mercurous iodide pills, with which, after treatment with nitric acid, a crystalline precipitate of mercuric iodonitrate, $\text{HgI}_2 \cdot \text{Hg}(\text{NO}_3)_2$, is formed. All that is necessary in this case, however, is to dissolve the crystals in the liquor by addition of potassium iodide, and omitting the bromine treatment, to proceed with the precipitation of the mercury as above. In pills containing soap, although the fat acids are not destroyed by the nitric acid treatment, they do not retain any mercury in combination, and form a layer on the surface of the liquor, which solidifies on cooling, and is therefore easily separated. G. F. M.

Volumetric Estimation of Aluminium. ERNST JOSEF KRAUS (*Chem. Zeit.*, 1921, 45, 1173).—The neutral or faintly acid solution containing the aluminium in the form of sulphate, and free from

other interfering metals, is titrated with standard disodium hydrogen phosphate solution, a few drops of silver nitrate solution being used as indicator, as yellow silver phosphate only commences to form after all the aluminium has been precipitated as phosphate according to the equation: $\text{Al}_2(\text{SO}_4)_3 + 2\text{Na}_2\text{HPO}_4 = 2\text{AlPO}_4 + 2\text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$. The titration is preferably carried out in a boiling solution as the silver phosphate is more pronouncedly yellow in colour and therefore more easily noticeable under these conditions. In presence of other metals, such as iron, etc., the aluminium should first be separated, by addition of excess of sodium hydroxide, for example, and finally precipitated as hydroxide with ammonia. The precipitate after washing is dissolved in a slight excess of dilute sulphuric acid to form a solution suitable for the titration. The method gives good results even when only very small quantities of the metal are to be estimated. G. F. M.

Improved Method for the Separation of Iron and Manganese. M. CARUS (*Chem. Zeit.*, 1921, **45**, 1194).—In the usual method for the separation of manganese from the metals of the iron group by precipitating the latter as basic acetates, the contamination of the precipitate with manganese is not due to the coprecipitation of the basic acetate of this metal, but to the formation of insoluble higher oxidation products owing to the action of dissolved oxygen. A perfect separation of the manganese in one operation, even when a large excess is present, is obtained by causing the precipitation with sodium acetate to occur in presence of a small quantity of hydrogen peroxide, in which case no oxidation of the manganese salts can occur. The precipitate obtained, after washing with dilute acetic acid containing a small quantity of sodium acetate and hydrogen peroxide, and finally with hot water, is then completely free from manganese. G. F. M.

The Acidimetric Estimation of Dichromate. I. M. KOLTHOFF and E. H. VOGELZANG (*Rec. trav. chim.*, 1921, **40**, 681—685).—By reason of the hydrolysis of potassium chromate solution, neither chromic acid nor dichromate can be neutralised using phenolphthalein as indicator. A study of the neutralisation of dichromate with sodium hydroxide leads to the following conclusions:—Thymolphthalein should be used as indicator; if phenolphthalein is used the solution must have been saturated previously with sodium chloride, or barium chloride must be used to precipitate the chromate formed. The barium chloride may only be added when the solution is already yellow, otherwise the precipitate of barium chromate contains chromic acid. It is claimed that the results are correct to within 0.2%, but the method is not recommended owing to difficulties with the indicator.

H. J. E.

Modified Method for the Estimation of Iron and Vanadium after Reduction by Hydrogen Sulphide. G. E. F. LUNDELL and H. B. KNOWLES (*J. Amer. Chem. Soc.*, 1921, **43**, 1560—1568).—The estimation of iron or of vanadium by reduction with

hydrogen sulphide followed by titration with potassium permanganate or dichromate ordinarily leads to high values. These high values are not due to the presence of sulphur, and persist in spite of the complete expulsion of hydrogen sulphide and the avoidance of organic matter extracted from filter-paper. They may be ascribed to polythionic acids which are not destroyed by boiling in moderately concentrated sulphuric acid solution and are volatilised slowly from dilute and more rapidly from concentrated solutions. Reasonably accurate estimations may be made by restricting the volume of the original solution to 100 c.c. and proceeding by the following modified process. The solution is acidified with sulphuric acid until it contains 2.5% sulphuric acid by volume, reduced by hydrogen sulphide for thirty minutes in cold solution, and for a further fifteen minutes, during which the solution is raised to the boiling point. The hot solution is treated with 15 c.c. of 1 : 1-sulphuric acid and boiled for thirty to sixty minutes, during which a stream of carbon dioxide is passed through, until the total volume of liquid is about 50 c.c. The solution is cooled, the current of carbon dioxide being maintained, diluted to 200 c.c., and titrated with standard permanganate solution. In some cases it is advisable to filter off the separated sulphur after the hydrogen sulphide treatment. The filtrate is treated for a further ten minutes with hydrogen sulphide and the process completed as above. The average errors found by this method are for iron 0.5% and for vanadium 0.1%. For accurate estimations of iron and vanadium in solutions containing platinum (as in rock analysis), a preliminary separation of the hydrogen sulphide group, followed by expulsion of the gas, complete oxidation with permanganate, and reduction with sulphur dioxide is recommended. J. F. S.

Estimation of Vanadium and Chromium in Ferrovandium by Electrometric Titration. G. L. KELLEY, J. A. WILEY, R. T. BOHN, and W. C. WRIGHT (*J. Ind. Eng. Chem.*, 1921, **13**, 939—941).—Three grams of the ferrovandium are dissolved in a mixture of nitric acid and hydrochloric acid, sulphuric acid is then added, the mixture evaporated to expel all nitric acid and hydrochloric acid, cooled, and the solution diluted to 1000 c.c. One hundred c.c. of this solution are treated with 25 c.c. of sulphuric acid (d 1.58), diluted to 300 c.c., boiled, and 20 c.c. of 10% ammonium persulphate solution and 10 c.c. of 0.25% silver nitrate solution are added; the mixture is boiled for ten minutes, 5 c.c. of hydrochloric acid (1 : 3), are then added, the boiling is continued for a further ten minutes, the mixture treated with 26 c.c. of sulphuric acid, cooled at 5°, and titrated with ferrous ammonium sulphate solution, the end-point of the titration being determined electrometrically. This titration is a measure of the vanadium and chromium together. The vanadium is estimated by boiling 100 c.c. of the original solution with a few c.c. of ferrous sulphate solution, adding 20 c.c. of sulphuric acid, d 1.58, and 40 c.c. of nitric acid (d 1.40), diluting the mixture to 200 c.c., and boiling it at such a rate that the volume is reduced to 100 c.c. in one hour.

The solution is then cooled and titrated as before. The difference between the two titrations is a measure of the amount of chromium present.

W. P. S.

[**Estimation of Antimony as Sodium Antimonate.**] E. S. TOMULA (*Z. anorg. Chem.*, 1921, **118**, 81—92).—See this vol., ii, 74.

Estimation of Bismuth. O. A. CRITCHETT (*Eng. and Min. J.*, 1921, **112**, 58).—A solution of the ore in a mixture of nitric and hydrochloric acids, having been evaporated with sulphuric acid until fumes appear, is diluted, treated with a drop of hydrochloric acid, filtered, and the filtrate boiled with sodium thiosulphate and aluminium foil. The precipitate is collected, returned to the beaker with hot water, potassium hydroxide added, and the liquid, after having been boiled, is filtered through the original paper. The latter, with the precipitate, is repeatedly evaporated with nitric and sulphuric acids until the paper is completely destroyed. After dilution, boiling, filtering, addition of a slight excess of ammonium hydroxide, and again boiling, the precipitate is collected, washed, and dissolved in hot dilute nitric acid. The bismuth may then be estimated (a) as oxide after treatment with ammonium carbonate, (b) as oxychloride after neutralising with ammonium hydroxide, adding a little hydrochloric acid, diluting, and boiling, or (c) by titration with permanganate after dilution, treatment with ammonium oxalate, boiling, and separation, with subsequent washing by decantation with hot water, of the precipitate of bismuth oxalate.

CHEMICAL ABSTRACTS.

Analytical Chemistry of Tantalum, Columbium, and their Mineral Associates. I. The Use of Tartaric Acid in the Analysis of Natural Tantalocolumbates. II. The Separation of Zirconium from Tantalum and from Columbium. WALTER RAYMOND SCHOELLER and ALAN RICHARD POWELL (*T.*, 1921, **119**, 1927—1935).

Evaluation of the Degree of Unsaturation of Mineral Oils in the Bergius Process. H. I. WATERMAN and J. N. J. PERQUIN (*Rec. trav. chim.*, 1921, **40**, 677—680; cf. Dean and Hill, Technical Paper 181, *Bureau of Mines*, 1917).—Determination of the iodine number of an unrefined mineral oil, before and after treatment by the Bergius process, shows that it is a little greater after treatment.

H. J. E.

Estimation of Phenanthrene. ARTHUR G. WILLIAMS (*J. Amer. Chem. Soc.*, 1921, **43**, 1911—1919).—The phenanthrene is oxidised by iodic acid to phenanthraquinone, which is precipitated as toluphenanthrazine by means of 3:4-tolylenediamine and weighed as such, the procedure being as follows:

For materials containing 30% or more of phenanthrene, 0.25 gram is weighed into a 50 c.c. conical flask, 0.75 gram of iodic acid and 20 c.c. of glacial acetic acid are added and the mixture is boiled for two and a half hours under an air condenser. After cooling for

several hours, any anthraquinone formed from anthracene present in the original material is filtered off on a Gooch crucible and washed with the minimum amount of glacial acetic acid. The filtrate and washings are evaporated to slightly less than 25 c.c. and then the volume is made exactly to 25 c.c., the mixture is cooled and 1 gram of 3:4-tolylenediamine is added and the flask left in running water at 20° over-night. The toluphenanthrazine is collected in a Gooch crucible and washed first with 25 c.c. of 50% acetic acid saturated with the phenanthrazine and then with 200 c.c. of cold water. The precipitate is dried and weighed and to the weight is added 0.053 gram to allow for the toluphenanthrazine remaining in solution in the 25 c.c. of glacial acetic acid. The factor for conversion into phenanthrene is 0.6052. Carbazole, if present in amounts exceeding 10%, interferes in the determination of phenanthrene, and some of the high-boiling coal tar constituents interfere; a crude anthracene cannot be directly analysed.

For the detection of phenanthrene, the material is oxidised as described above, the mixture being cooled and filtered. The filtrate is poured into water and the precipitate collected and washed with water. The precipitate is warmed with concentrated sodium hydrogen sulphite solution and any residue is filtered off. The filtrate is washed in a separating funnel with one or two portions of carbon tetrachloride and then, after the addition of a fresh portion of carbon tetrachloride, is acidified with hydrochloric acid containing ferric chloride. The carbon tetrachloride layer, which contains the phenanthraquinone, is separated and tested by Hilpert and Wolf's reaction (cf. A., 1913, ii, 733), using a solution of antimony pentachloride in carbon tetrachloride, a purplish-red precipitate being obtained on boiling if phenanthrene was originally present.

W. G.

Chemical Analysis of Caoutchouc Articles. ANDRÉ DUBOSC (*Ann. Chim. Analyt.*, 1921, 3, 335—344).—A résumé of the methods employed and the estimations necessary for a complete chemical analysis of caoutchouc and ebonite articles. (1) The acetone extract contains the natural resins, added resins, free sulphur, oils, and waxes, and is evaporated to dryness and quantitatively examined for these substances by the usual methods. (2) The chloroform extract should be almost colourless. Brown coloration indicates the presence of tar or asphaltic adulterants. (3) The extract in alcoholic potash of the insoluble residue of the chloroform extraction should not exceed 15% from a material containing about 50% of caoutchouc, a larger proportion indicating added oils or fats. (4) The aqueous extract reveals the presence of starch or dextrans. (5) The estimation of total sulphur is best carried out by Henriquez's method as modified by the Bureau of Standards. (6) The ash is determined on the residue from the acetone extraction, and a rough estimate of the caoutchouc content can be obtained by subtracting ash and total sulphur from 100. (7) None of the various methods which have been proposed for the estimation of caoutchouc itself give entire satisfaction. The

total foreign matter may be obtained, however, by solution in boiling nitrobenzene, diluting with chloroform, filtering through a tared filter, washing with acetone, drying, and weighing. G. F. M.

Estimation of Oxalic Acid in Urine. E. SALKOWSKI (*Biochem. Z.*, 1921, **118**, 259—266).—A reply to Bau's criticism of the author's method (*A.*, 1921, ii, 356). H. K.

Estimation of the Amino-acids of Feeding Stuffs. T. S. HAMILTON, W. B. NEVENS, and H. S. GRINDLEY (*J. Biol. Chem.*, 1921, **48**, 249—272).—Further improvements are made in the application of Van Slyke's method to the estimation of amino-acids in feeding stuffs (cf. Eckstein and Grindley, *A.*, 1919, ii, 204). Non-protein nitrogen is first removed from the material by successive extractions with anhydrous ether, cold absolute alcohol, and cold 1% trichloroacetic acid, any protein removed by the latter being recovered by precipitation with colloidal ferric hydroxide. The main portion of the protein is then extracted with dilute (0.2%) sodium hydroxide. Starch is removed from the residue by treatment with hot 2% trichloroacetic acid and the remaining protein extracted by treatment first with boiling 20% hydrochloric acid and then with cold 5% sodium hydroxide. A small quantity of protein extracted with the starch is recovered by precipitation of the latter by addition of alcohol. The various fractions of protein thus obtained are hydrolysed with concentrated hydrochloric acid, united, and submitted to the Van Slyke analysis. The method is applied to oats, corn, cotton-seed meal, and lucerne. E. S.

Estimation of Hippuric Acid in Urine. J. SNAPPER and E. LAQUEUR (*Arch. Néerl. Physiol.*, 1921, **6**, 48—57).—To 100 c.c. of urine 25 grams of sodium chloride are added, and a little concentrated hydrochloric acid. An aliquot portion is extracted six times with ethyl acetate, and the total extract is washed once with one-quarter of its volume of water. The wash water is washed with an equal volume of ethyl acetate, which is added to the original extract. After evaporation of the ethyl acetate, the urea is decomposed by sodium hypobromite, and the residual hippuric acid estimated by Kjeldahl's method. G. B.

The Rotation of Dextrose in Solutions of Trisodium Phosphate. Mutarotation as an Analytical Method. HANS MURSCHHAUSER (*Biochem. Z.*, 1921, **117**, 215—225).—The mutarotation of dextrose is accelerated by trisodium phosphate. It follows a unimolecular law, the velocity constants being also linear functions of the concentration of sodium phosphate. As the mutarotation is a function of the hydroxyl ion, its use is indicated for distinguishing salts of different alkalinity. H. K.

Conditions Affecting the Quantitative Estimation of Reducing Sugars by Fehling's Solution. Elimination of certain Errors Involved in Current Methods. F. A. QUISUMBING and A. W. THOMAS (*J. Amer. Chem. Soc.*, 1921, **43**, 1503—1526).—The various sources of error in the current methods of

using Fehling's solution are discussed. The inter-relationship of temperature, 60—110°, and time of heating, ten minutes to two hours, to determine the best time and optimum temperature for reduction has been investigated. Fehling's solution has been studied from the point of view of the nature and concentration of the alkali, concentration of copper sulphate and potassium sodium tartrate, to find the maximum and minimum concentrations of these constituents necessary to give the greatest yield of cuprous oxide and to ensure the formation of the complex cupric tartrate ion. Auto-reduction of Fehling's solution at different times and temperatures of heating has been measured, showing those conditions under which absolutely no "blank" reduction is obtained. Conditions affecting the physical properties of the precipitated cuprous oxide, the photosensitiveness, and the keeping quality of Fehling's solution are recorded. A study of surface oxidation involving different methods of heating and vessels of various sizes has been carried out in order to determine the loss of copper due to surface oxidation and how to avoid it. The catalytic effect of the walls of the container has been demonstrated. A modified method of procedure for the estimation of sugars by means of Fehling's solution is described. In this method the solutions required are, (1) copper sulphate solution containing 82.4 grams of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ per litre, (2) alkaline tartrate solution; 376 grams of crystallised potassium sodium tartrate dissolved in water in a litre flask, and the calculated amount of sodium hydroxide solution added to make 1 litre of this solution containing 130 grams of sodium hydroxide. The sodium hydroxide is made from material purified by alcohol which is kept in concentrated solution for several days to allow carbonates and other insoluble impurities to separate. To make an estimation, 25 c.c. of the copper sulphate solution, 25 c.c. of the alkaline tartrate solution, and 50 c.c. of the sugar solution are placed in a beaker and warmed on a water-bath at 80°. After exactly thirty minutes, the cuprous oxide is filtered on a Gooch crucible and washed. This may either be dried and weighed as cuprous oxide, or dissolved in nitric acid and estimated electrolytically. From the weight of copper, the amount of sugar may be obtained from tables which are given in the paper or by means of the following equations, in which x is the amount in milligrams of copper obtained from y mg. of sugar: dextrose, $y = 0.474x + 0.000115x^2$; lævulose, $y = 0.526x + 0.000078x^2$; lactose, $y = 0.813x + 0.000003x^2$; maltose, $y = 0.990x + 0.0000005x^2$; and invert-sugar, $y = 0.504x + 0.0000870x^2$. This method is designed for use in the analysis of saccharine materials containing sucrose, dextrose, lævulose, invert-sugar, lactose, and maltose. It is not claimed that the method can be used for the accurate quantitative estimation of 0.1% or less of invert-sugar in approximately pure sucrose.

J. F. S.

Errors in the Estimation of Sugar by Fermentation with Yeast. CARL LANGE (*Berlin Klin. Woch.*, 1921, 58, 957—959; from *Chem. Zentr.*, 1921, iv, 848).—The estimation of sugar in

urine by fermentation with yeast is subject to certain errors. The evolved gas is not entirely carbon dioxide, but contains also nitrogen from the reaction of carbamide, ammonia, or amino-acids with nitrites. The latter may be formed by reduction of nitrates in the urine, or may occur in the yeast. There may also be an evolution of carbon dioxide from carbonates present in the urine. Errors may be diminished to some extent by sterilisation, and precipitation of carbonates with calcium chloride. The estimation of sugar in urine, however, gives only an approximate value.

G. W. R.

Limitations of the Modified Lewis-Benedict Method of Blood Sugar Estimation. RUTH A. GUY (*Biochem. J.*, 1921, **15**, 575—576).—0.0001 Gram of acetone added to 2 c.c. of blood produces an observable colour change in Lewis and Benedict's picric acid method of sugar estimation (A., 1915, ii, 111), but no change is noted with similar quantities of acetoacetic acid. G. B.

The Catalytic Power of Flour. O. FERNÁNDEZ and A. PIZARROSO (*Anal. Fis. Quím.*, 1921, **19**, 265—268).—The catalytic activity of flour, measured by its decomposition of hydrogen peroxide, has been proposed as a measure of its grade of extraction. The results obtained by the authors, using samples of flour of different origin, showed no correlation between catalytic activity and total- or phytin-phosphorus. The test is held to be of little value.

G. W. R.

Identification of Oxycellulose by means of the Barium Compound. ERNST BECKER (*Zellstoff u. Papier*, 1921, **1**, 5—7).—When 2 grams of oxycellulose are shaken with 50—60 c.c. of barium hydroxide solution for four hours, and the insoluble portion is washed with water until the filtrate is free from barium compounds, a barium compound of oxycellulose remains, of which the content of barium varies according to the origin of the oxycellulose.

CHEMICAL ABSTRACTS.

Benzidine Hydrochloride as a Reagent for Wood Cells. C. VAN ZIJP (*Pharm. Weekblad*, 1921, **58**, 1539—1542).—A solution of 0.2 gram of benzidine in 19 c.c. of water, to which 1 c.c. of 25% hydrochloric acid has been added, gives an orange stain to ligneous matter in microscope sections. Sections of material containing tannins or acids which act on iron should be washed free from iron with a 1% solution of hydrochloric acid in alcohol after cutting. Starch can be stained with iodine in the same section without interfering. The reagent also detects diseased tissues in Hevea bark, and for this reason, as well as because of its cheapness as compared with phloroglucinol, is of great use for control on rubber plantations.

S. I. L.

Detection of Formaldehyde with Phenols. B. PFYL, G. REIF, and A. HANNER (*Chem. Zeit.*, 1921, **45**, 1220—1221).—Phenol reactions for the detection of formaldehyde as previously carried out (cf. A., 1921, ii, 663) are not sufficiently trustworthy

when the test is to be adapted to the detection of methyl alcohol in potable spirits and tinctures after distillation with permanganate, as colour reactions are often simultaneously given by the traces of other aldehydes, alcohols, etc., which pass over into the distillate, and the mixed colours produced allow of no certain conclusions being drawn. A solution of guaiacol, or of *apomorphine* hydrochloride in concentrated sulphuric acid (0.02 gram in 10 c.c.) gives, however, a reagent with which a sharp distinction can always be observed if methyl alcohol is present in the original tincture. The reaction is best carried out by adding a few drops of the distillate to 0.5 c.c. of the reagent in a watch glass. With the guaiacol reagent a clear dark red colour is produced when formaldehyde is present which is readily distinguished from the pale yellow coloration produced in its absence, whilst with the *apomorphine* reagent a characteristic precipitate is formed in presence of formaldehyde. As little as 0.25% of methyl alcohol in tinctures, etc., can be detected with certainty by the new method. G. F. M.

Orcinol Reaction of Furfuraldehyde. ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1921, [vii], **24**, 334—336).—As little as 1 part of furfuraldehyde in 600,000 parts of solution may be detected by the blue coloration which is obtained when 5 c.c. of the solution, 5 c.c. of hydrochloric acid, and 0.02 gram of orcinol are heated together, cooled, and shaken with a few drops of amyl alcohol.

W. P. S.

Source of Error in Tests for Acetone. E. PITTARELLI (*Polìclinico*, 1921, **28**, 621; *J. Am. Med. Assoc.*, **76**, 1803).—Caoutchouc under the influence of steam or boiling water yields a volatile substance which responds to all the tests most characteristic of acetone; therefore conclusions based on technique involving distillation in the presence of caoutchouc may be misleading.

CHEMICAL ABSTRACTS.

Microchemical Reactions of "Dulcin" [*p*-Ethoxyphenylcarbamide]. G. DENIGÈS and R. TOURROU (*Compt. rend.*, 1921, **173**, 1184—1186).—When a few particles of "dulcin" on a microscope slide are moistened with one drop of nitric acid (*d* 1.39) they dissolve and on the addition of a drop of water microscopic orange or brick-red crystals of *p*-ethoxynitrophenylcarbamide are obtained. These crystals are soluble in chloroform and, on evaporation after the addition of a drop of acetic acid, characteristic crystals are obtained. If dilute nitric acid is used in place of the concentrated acid the "dulcin" does not dissolve, but the mass gradually becomes permeated with crystals of the nitro-compound and under the microscope there is the appearance of a marked effervescence. "Dulcin" is soluble in concentrated sulphuric acid or glacial acetic acid and is deposited as a microcrystalline precipitate from such solutions on the addition of water or alkali.

W. G.

The Vitali Reaction for Cocaine. PAUL HARDY (*J. Pharm. Chim.*, 1921, [vii], **24**, 325—330).—Pure cocaine, and most sub-

stituted cocaines, yield a yellow coloration with the Vitali test in the cold; isoatropylcocaine, however, yields a violet coloration, and the presence of a small quantity of this substance in certain specimens of cocaine causes these to give a violet coloration with the test. When the reaction mixture is heated, pure cocaine produces at most a slight yellow coloration. W. P. S.

Morphine, Codeine, and Narcotine in Indian Opium. JITENDRA NATH RAKSHIT (*Analyst*, 1921, **46**, 481—488).—The morphine content of the bulk of Indian opium is between 8.5 and 10.5%. The B.P. process for estimating morphine is inefficient in India owing to the high temperature which prevails. The U.S.P. process is better and compares favourably with the author's polarimetric process (*Analyst*, 1918, **43**, 321). The solubility of codeine and narcotine has been determined in various solvents at temperatures between 20° and 100°. Methods have also been worked out for the estimation of codeine and narcotine, for which the original should be consulted. H. K.

Estimation of Tannin and Colouring Matters in Wines. W. FRESENIUS and L. GRUNHÜT (*Z. anal. Chem.*, 1921, **60**, 406—417).—One hundred c.c. of the wine is evaporated to expel alcohol, cooled, diluted to 100 c.c. and 50 c.c. of this solution are treated with a few grams of pure animal charcoal; after some hours, the mixture (a further quantity of charcoal must be added if all the colour has not been removed) is diluted to 1 litre, filtered, and 400 c.c. are diluted to 1 litre, treated with 10 c.c. of sulphuric acid, (*d* 1.11), and 30 c.c. of indigo solution (3 grams of indigo dissolved in 20 c.c. of sulphuric acid and diluted to 1 litre) and the mixture is titrated with permanganate solution. Twenty c.c. of the de-alcoholised wine not treated with charcoal are titrated in a similar manner. The difference between the two titrations is a measure of the tannin and colouring substances in the wine. The permanganate solution should contain 1.33 grams of potassium permanganate per litre and be standardised against 10 c.c. of *N*/10-oxalic acid solution; the volume of permanganate solution used is divided into 0.0416 to obtain the tannin value of 1 c.c. of permanganate solution. W. P. S.

Determination of the Size of Particles. Attempts to Explain the Formation of Layers in Clay Turbidities and their Use in Soil Analysis. ERNST UNGERER (*Kolloid Chem. Beihefte*, 1921, **14**, 63—95).—The layers in clay suspensions are brought about solely by the size and weight of the suspended particles, so that each layer corresponds with particles of a definite size. The turbidity between two layers contains particles uniformly dispersed. Layers are formed both in solutions containing electrolytes and in solutions which do not contain electrolytes, but a high concentration of a coagulating electrolyte will probably prevent the formation of layers. The individual layers either rise or fall with a uniform velocity, and from the rate of falling or rising the size of the particles in a given layer may be calculated by means of Stokes's law. J. F. S.

General and Physical Chemistry.

Refraction of Light at Corresponding Temperatures. W. HERZ (*Z. physikal. Chem.*, 1921, **98**, 175—180).—A theoretical paper in which from the examination of the data for a large number of substances it is shown that the refractive index of all substances has the same value 1.126 at the critical temperature. The formulæ of Gladstone and Dale, and of Lorentz and Lorenz yield approximately the same specific refraction values for this temperature. It is also shown that at other comparable temperatures the refractive indices approximate to the same value, although in these cases considerable differences do occur. Thus at the boiling point, ten liquid substances give a mean value of 1.335 for the refractive index, the extreme values being 1.348 and 1.320. J. F. S.

The Spectrochemistry of Aliphatic Dienes with Conjugated Double Bonds. K. VON AUWERS and H. WESTERMANN (*Ber.*, 1921, **54**, [B], 2993—2999).—The physical constants of a number of carbinols and the corresponding dienes are recorded. The specific exaltations in the cases of the latter substances with “undisturbed, doubly disturbed, and singly disturbed” conjugation are $E\Sigma_{\text{Refr.}} +2.0$, $+1.4$, and $+0.9$ and $E\Sigma_{\text{Disp.}} +50\%$, $+43\%$, and $+35\%$, respectively. The boiling points of the dienes are depressed by branching of the chain, but raised by the approximation of the methyl group to the double bond; this regularity is not always very definitely marked. The density of isomeric compounds increases relatively greatly when the methyl group is attached to a doubly-bound carbon atom. Similarly, the index of refraction increases with similar alteration in structure; these changes are consonant with those observed with cyclic compounds.

The following constants are recorded: Δ^{β} -pentene- δ -ol, b. p. $64^{\circ}/62$ mm., $d_4^{17.95}$ 0.8382, $n_a^{17.95}$ 1.42558, $n_D^{17.95}$ 1.42821, $n_B^{17.95}$ 1.43502, $n_{\gamma}^{17.95}$ 1.44065. Δ^{β} -Hexen- δ -ol, b. p. $59^{\circ}/27$ mm., $d_4^{23.3}$ 0.8370, $n_a^{23.3}$ 1.43025, $n_B^{23.3}$ 1.43286, $n_{\beta}^{23.3}$ 1.43962, $n_{\gamma}^{23.3}$ 1.44510. Δ^{β} -Heptene- δ -ol, b. p. $63^{\circ}/11$ mm., $d_4^{14.4}$ 0.8422, $n_a^{14.4}$ 1.43698, $n_D^{14.4}$ 1.43965, $n_B^{14.4}$ 1.44620, $n_{\gamma}^{14.4}$ 1.45176. ϵ -Methyl- Δ^{β} -hexen- δ -ol, b. p. $75^{\circ}/45$ mm., d_4^{19} 0.8411, n_a^{19} 1.43539, n_D^{19} 1.43788, n_B^{19} 1.44478, n_{γ}^{19} 1.45045. ζ -Methyl- Δ^{β} -hepten- δ -ol, b. p. $67^{\circ}/11$ mm., $d_4^{15.2}$ 0.8354, $n_a^{15.2}$ 1.43679, $n_D^{15.2}$ 1.43926, $n_B^{15.2}$ 1.44585, $n_{\gamma}^{15.2}$ 1.45127. η -Methyl- Δ^{β} -octen- δ -ol, b. p. $85^{\circ}/12$ mm., $d_4^{14.5}$ 0.8402, $n_a^{14.5}$ 1.44202, $n_D^{14.5}$ 1.44448, $n_B^{14.5}$ 1.45114, $n_{\gamma}^{14.5}$ 1.45651. δ -Methyl- Δ^{γ} -heptene- ϵ -ol, b. p. $66^{\circ}/17$ mm., $d_4^{17.9}$ 0.8525, $n_a^{17.9}$ 1.44525, $n_D^{17.9}$ 1.44792, $n_B^{17.9}$ 1.45454, $n_{\gamma}^{17.9}$ 1.46018. δ -Methyl- Δ^{γ} -octen- ϵ -ol, b. p. $89^{\circ}/16$ mm., $d_4^{19.5}$ 0.8495, $n_a^{19.5}$ 1.44576, $n_D^{19.5}$ 1.44838, $n_B^{19.5}$ 1.45490, $n_{\gamma}^{19.5}$ 1.46059.

$\Delta^{\beta\delta}$ -Pentadiene, b. p. 43° , $d_4^{13.6}$ 0.6887, $d_{20}^{13.6}$ 0.685, $n_a^{13.6}$ 1.42991, $n_D^{13.6}$ 1.43443, $n_B^{13.6}$ 1.44655, $n_{\gamma}^{13.6}$ 1.45694, n_D^{20} 1.4309. $\Delta^{\beta\delta}$ -Hexadiene, b. p.

80° , $d_4^{15.05}$ 0.7237, $d_{20}^{15.05}$ 0.720, $n_a^{15.05}$ 1.44962, $n_D^{15.05}$ 1.45420, $n_\beta^{15.05}$ 1.46651, $n_\gamma^{15.05}$ 1.47764, n_D^{20} 1.4514. Δ^{88} -Heptadiene, b. p. 107° , $d_4^{16.3}$ 0.7341, $d_{20}^{16.3}$ 0.731, $n_a^{16.3}$ 1.45101, $n_D^{16.3}$ 1.45543, $n_\beta^{16.3}$ 1.46695, $n_\gamma^{16.3}$ 1.47735, n_D^{20} 1.4534. ζ -Methyl- Δ^{88} -heptadiene, b. p. 117° , $d_4^{15.5}$ 0.7361, $d_{20}^{15.5}$ 0.733, $n_a^{11.5}$ 1.44887, $n_D^{15.5}$ 1.45302, $n_\beta^{15.5}$ 1.46397, $n_\gamma^{15.5}$ 1.47379, n_D^{20} 1.4505. η -Methyl- Δ^{88} -octadiene, b. p. 149° , $d_4^{11.6}$ 0.7515, $d_{20}^{11.6}$ 0.751, $n_a^{11.6}$ 1.45427, $n_D^{11.6}$ 1.45831, $n_\beta^{11.6}$ 1.46903, $n_\gamma^{11.6}$ 1.47812, n_D^{20} 1.4553. ϵ -Methyl- Δ^{88} -hexadiene, b. p. 104° , $d_{20}^{19.7}$ 0.745, n_D^{20} 1.4606, (i) $d_4^{19.7}$ 0.7439, $n_a^{19.7}$ 1.45659, $n_D^{19.7}$ 1.46117, $n_\beta^{19.7}$ 1.47340, $n_\gamma^{19.7}$ 1.48433, (ii) $d_4^{19.65}$ 0.7473, $n_a^{19.65}$ 1.45589, $n_D^{19.65}$ 1.46037, $n_\beta^{19.65}$ 1.47262, $n_\gamma^{19.65}$ 1.48316. β -Methyl- $\Delta^{\alpha\gamma}$ -butadiene, b. p. 34° , $d_4^{18.8}$ 0.6826, $d_{20}^{18.8}$ 0.682, $n_a^{18.8}$ 1.41902, $n_D^{18.8}$ 1.42309, $n_\beta^{18.8}$ 1.43422, $n_\gamma^{18.8}$ 1.44405, n_D^{20} 1.4224. δ -Methyl- $\Delta^{\gamma\epsilon}$ -heptadiene, b. p. 131° , $d_4^{24.4}$ 0.7598, $d_{20}^{24.4}$ 0.763, $n_a^{24.4}$ 1.45610, $n_D^{24.4}$ 1.46003, $n_\beta^{24.4}$ 1.47125, $n_\gamma^{24.4}$ 1.48103, n_D^{20} 1.4625. δ -Methyl- $\Delta^{\gamma\epsilon}$ -octadiene, b. p. 150° , $d_4^{20.3}$ 0.7708, $d_{20}^{20.3}$ 0.771, $n_a^{20.3}$ 1.46206, $n_D^{20.3}$ 1.46617, $d_\beta^{20.3}$ 1.47724, $n_\gamma^{20.3}$ 1.48708, n_D^{20} 1.4663. $\beta\gamma$ -Dimethyl- $\Delta^{\alpha\gamma}$ -butadiene, b. p. 70° , $d_4^{22.1}$ 0.7239, $d_{20}^{22.1}$ 0.725, $n_a^{22.1}$ 1.43307, $n_D^{22.1}$ 1.43703, $n_\beta^{22.1}$ 1.44758, $n_\gamma^{22.1}$ 1.45704, n_D^{20} 1.4382. H. W.

[Substitution Processes]. K. VON AUWERS (*Ber.*, 1921, **54**, [B], 3000—3003).—A reply to K. H. Meyer (*A.*, 1921, i, 853). The view that the methyl group causes optical exaltation cannot be maintained. In certain of the examples quoted by Meyer the differences lie within the limits of experimental error, whereas in other examples readily polymerised substances, for instance, acrylic acid and its esters, have been chosen and the data obtained are not due to the unimolecular forms. H. W.

The Molecular Refraction of Aromatic Hydrocarbons and "Aromatic" Carbon. K. VON AUWERS (*Ber.*, 1921, **54**, [B], 3188—3194).—In a recent communication (*A.*, 1921, ii, 473), von Steiger has endeavoured to show that the molecular refraction of hydrocarbons can be calculated more accurately from linking refractions than from atomic refractions and he has postulated that all C—C bonds and all C—H bonds in aromatic hydrocarbons are equivalent among themselves but different from the corresponding values in the aliphatic series. This mode of calculation appears to the author to be unsound theoretically, since the atomic refraction of aromatic hydrogen as deduced from the molecular refraction of benzene, diphenyl, and naphthalene, in these circumstances is negative, whilst also the "linking refraction" for (C—H)_{ar} falls with decreasing wave-lengths. Von Steiger has illustrated his arguments by citing the cases of benzene, diphenyl, and naphthalene, and the agreement between the observed and calculated values is excellent. Unfortunately, the data quoted for naphthalene are incorrect, and the amended figures show that the presumption of additivity is not fulfilled. Further, the data for the three hydrocarbons are not directly comparable, since they are obtained under widely-differing conditions; when due allowance is made for this factor, it is found to be impossible to deduce constant atomic or linking refractions. The molecular refractions

of homologues of benzene, and other aromatic hydrocarbons cannot be calculated from von Steiger's aromatic and aliphatic linking refractions, since the differences between the observed and calculated values increase more and more with increase in the number of side-chains.

The fundamental idea in von Steiger's refractometric hypothesis and thermochemical theories (A., 1920, ii, 355) is the existence of a practically tervalent "aromatic" carbon atom of the graphite type which differs from the quadrivalent "diamond" carbon atom of the paraffins (cf. Debye and Scherrer, A., 1917, ii, 437). To the author, this view of the varying valency appears to be misleading. The supposed ter- and quadri-valency of the carbon atom does not, as in the case of other elements, correspond with different stages of oxidation or different electric charges; the atom is invariably quadrivalent and the apparent variation is caused by alteration in the distribution or compensation of its affinity.

H. W.

The Mechanism of Continuous Luminous Radiation. J. DUCLAUX (*Compt. rend.*, 1921, **173**, 1355—1357).—The author has previously put forward the hypothesis (cf. *ibid.*, 1914, **158**, 1879) that the emission and absorption of the continuous spectrum depend on the establishment or rupture of chemical valencies. Evidence in support of this hypothesis is now given. W. G.

The Spectrum of Fluorine. WILLIAM R. SMYTHE (*Astrophys. J.*, 1921, **54**, 133—139).—With a discharge passing between gold electrodes, the ultra-violet region of the fluorine spectrum was photographed through a fluorite window, the gas having been prepared by the electrolysis of potassium hydrogen fluoride and purified by being passed through sodium fluoride and a freezing trap. Ten fluorine lines, all in the red, were observed and tabulated with an accuracy of $\pm 0.1 \text{ \AA}$. An impurity which was supposed to have the composition CF_4 was observed following a flare back from the charcoal chamber. The approximate positions of nine heads of bands between $\lambda 4829$ and $\lambda 6525$ were observed in this spectrum.

CHEMICAL ABSTRACTS.

Arc-cathode Spectra. ARTHUR ST. C. DUNSTAN and BENJAMIN A. WOOTEN (*Astrophys. J.*, 1921, **54**, 65—75).—The spectra of strontium, barium, lithium, copper, and lead were observed when the vapours of the metals were introduced into a direct current arc by means of an alternating current arc placed below it in the same enclosure. It was shown that by cooling the electrodes alternately, the intensity of the metallic lines remained, as before, greater at the cathode than at the anode when the metal was introduced into the arc symmetrically; neither was the effect due to electrolytic or electrostatic separation. Since the phenomenon is fully developed in $1/120$ second, the transference of vapour from one electrode to the other must be of little importance. The light appears to be due chiefly to bombardment of the metallic vapour by electrons from the cathode. Whilst the lines of all

metals are stronger at the cathode, the difference decreases with increasing atomic weight.

CHEMICAL ABSTRACTS.

The Electric Furnace Spectrum of Scandium. ARTHUR S. KING (*Astrophys. J.*, 1921, 54, 28—44).—The spectrum of a pure sample of scandium oxide was observed in the carbon arc and in the electric furnace through the range λ 3015—6559 Å. The furnace was operated at the usual low gas pressure, and temperatures of 2200°, 2250°, and 2600° were used. A table gives the classification of 257 lines with respect to their behaviour in the arc and at various furnace temperatures. Some 25 lines are indicated as being enhanced in the arc; 150 are enhanced in the furnace. The 29 arc-flame lines belong to the latter class, some of them showing moderate strength at all temperatures, whilst others increase in intensity more or less rapidly with increasing temperature. These lines are not due to oxidation, but the bands, on the other hand, are quite probably due to the oxide. Lines which appear at a low temperature and those enhanced in the furnace are weak or lacking in the general solar spectrum but prominent in that of sun-spots. The Zeeman effect for scandium lines is large and apparently uniform in sunspot spectra, although laboratory observations have not as yet been made. Scandium oxide fused in the furnace seemed to form a carbide with the graphite of the boat. The glossy black residue became a greyish-brown powder on exposure to the air, presumably reabsorbing oxygen.

CHEMICAL ABSTRACTS.

Wave-length Measurements in Arc Spectra Photographed in the Yellow, Red, and Infra-red. F. M. WALTERS, jun., (*Bureau of Standards, Sci. Papers*, 1921, 17, No. 411, 161—177).—Observations were made with a grating spectrograph of 640 cm. radius and 299 lines per mm. The photographic plates were sensitised to yellow, red, or infra-red light with pinacyanol and dicyanin. The wave-lengths of silver, aluminium, gold, bismuth, cadmium, mercury, lead, antimony, tin, and zinc are given in international units and to 0.01 Å. The longest wave-length measured is that at 10395 Å. in the spectrum of cadmium. The work is compared with previous results of others and discrepancies are accounted for as arising from impurities, ghosts, or overlapping spectra of higher orders.

CHEMICAL ABSTRACTS.

Extension of the Ultra-violet Spectrum and the Progression with Atomic Number of the Spectra of Light Elements. R. A. MILLIKAN (*Proc. Nat. Acad. Sci.*, 1921, 7, 289—294).—The results of an investigation of the extreme ultra-violet radiations emitted by the second ring or shell of electrons in the atoms of atomic number 2 to 13 (helium to aluminium) are recorded. The ultra-violet spectrum has been photographed down to $\lambda=136.6$ Å. in the case of aluminium and to $\lambda=149.5$ Å. in the case of copper. The L_a lines of aluminium, magnesium, and sodium are found at 144.3 Å., 232.2 Å., and 372.2 Å., respectively. Aluminium emits no radiations when excited by condensed sparks in a vacuum between

144.3 Å. and 1200 Å., where the M spectrum due to the three outer electrons begins. The chief lines below 2000 Å. due to the three outer electrons of aluminium are 1379.7, 1384.5, 1605.9, 1612.0, 1671.0, 1854.7, and 1862.7 Å. Magnesium is like aluminium, there is a blank between its L_α line at 232.2 Å. and the lines due to the two outer electrons which begin at 1700 Å. The lines measured below 2000 Å. are 1735.2, 1737.9, 1751.0, and 1753.7 Å. Sodium emits no lines between the L line 376.5 Å. and the lines due to the single M electron which have their convergence wave-length at 2412.63 Å. The spectrum due to the six L ring electrons of oxygen begins at 230 Å. and extends with much complexity and strength up to 834.0 Å., where the strongest line is found; above this point the lines are few in number and relatively faint. The ratio of the K/L frequency for oxygen is about 35. The strongest oxygen lines are 321.2, 374.3, 507.8, 525.7, 554.2, 599.5, 610.1, 616.7, 625.2, 629.6, 644.0, 703.1, 718.5, and 834.0 Å. The spectrum of the four L -ring electrons of carbon begins at 360.5 Å. and extends with much complexity and strength up to 1335.0 Å., where the strongest line lies; above this point the lines are widely scattered and relatively weak. The ratio of the K/L frequency in carbon is about 30. The spectrum due to the five L -ring electrons of nitrogen is simple; it begins at 685.6 Å. and reaches a maximum at 1085.3 Å. The only other strong lines of nitrogen are 685.6 Å., 916.2 Å., and 991.1 Å. The ratio of the K/L frequency is 34.8. In the case of fluorine, a strong line appears at 657.2 Å. and a second at 607.2 Å.; these are the only lines thus far identified as coming from the seven L -ring electrons of fluorine. The spectrum from the three L -ring electrons of boron is very simple. It consists of 676.8, 760.0, 1624.4, two doublets, 2164.2, 2166.2, and 2496.9, 2497.8, and a single spark line, 3451.5 Å. The ratio of the frequency K/L is 37. The spectrum of the two L -ring electrons of glucinum begins at 2175 Å. and finishes in its L_α doublet at 3130.6 and 3131.2 Å. Similar experiments with lithium reveal no lines between the shortest wave-lengths measurable by the present method and the familiar series due to its single L -ring electron the L_α line of which is at 6708 Å., and its convergence wave-length at 2299 Å. The progression shown in these optical spectra is simple and very like that exhibited by X -ray spectra.

J. F. S.

The Structure of the Elements of Mean Atomic Number.

A. DAUVILLIER (*Compt. rend.*, 1921, **173**, 1458—1461).—An extension of previous work (cf. A., 1921, ii, 669), further results being given for gold and new measurements of the L series for cerium and antimony.

W. G.

The Structure of the Bismuth Lines.

H. NAGAOKA and Y. SUGIURA (*Astrophys. J.*, 1921, **53**, 339—348).—The light resulting from the bombarding of bismuth by an electronic current was observed by means of a glass Lummer-Gehrcke plate crossed with one of quartz or crossed with an echelon grating. For the line λ 4722 the five known positive components were confirmed and

seven weak negative satellites were discovered, showing the line to have the general structure common to lines of heavy metals. The principal component is probably multiple, its constituents varying in relative intensity. The line λ 4122 has four strong components. The line λ 4308 consists of two principal lines separated by 0.350 Å., each being a narrow doublet; there are also two faint satellites. The authors point out some constant frequency differences and suggest that these may be interpreted in terms of the quantum theory.

CHEMICAL ABSTRACTS.

The Zeeman Effect. H. R. WOLTJER (*Chem. Weekblad*, 1921, **18**, 677—682).—A paper written in connexion with the twenty-fifth anniversary (October 31st, 1921) of the first announcement of Zeeman's discovery. The importance and subsequent developments of his work are discussed at some length. S. I. L.

Anisotropy of Molecules. C. V. RAMAN (*Nature*, 1922, **109**, 75—76).—An extension to direct visual observations is described of the method whereby it has been shown photographically (Lord Rayleigh, A., 1920, ii, 574) that the light scattered by molecules is, in general, not completely polarised when observed in a direction transverse to the pencil of light traversing the gas. With carbon dioxide, the effect is conspicuous, and visual determinations of its magnitude have been made. Similar evidence that the molecules of gases are not spherically symmetrical and are anisotropic in their properties is furnished by observations on the polarisation of light of the sky; liquids also show an imperfect polarisation attributable to anisotropy.

A. A. E.

Sols with Non-spherical Particles. H. ZOCHER (*Z. physikal. Chem.*, 1921, **98**, 293—337).—The double refraction discovered by Diesselhorst, Freundlich, and Leonhardt (A., 1916, ii, 65) with flowing vanadium pentoxide sols has been found in the following sols: Soap solution, clay suspensions, sols of silver cyanate, benzo-purpurin, "benzo-brown," primulin, sodium alizarinsulphonate, alizarin, *p*-azoxyphenetole, *p*-azoxyanisole, anthracene, cerasin-orange, and aniline-blue. Some observations on the spacial partition of the double refraction in agitated sols showed that in the eddies phenomena were observed which exhibited many analogies to the behaviour of uniaxial crystals in convergent light. These observations serve as methods for determining the flowing-double refraction and pleochroism and for determining the character of the sols. The rotation of the dark cross in eddies in opposition to the polarisation direction shows the direction of flow does not always need to correspond with the main vibration direction of the light. The coincidence of the dark cross with the direction of polarisation in old vanadium pentoxide sols and soap solutions is attributed to the bending of the doubly refracting particles. The sign of the double refraction of soap solutions varies with the age and concentration of the sol. The change in the sign of the double refraction is explained as follows: Colloidal particles in the form of short rods must arrange themselves with their symmetry axis

in the direction of flow, particles in the form of leaflets must arrange themselves with the axis of symmetry at right angles to this direction. If now, in the process of ageing, the rods pass into leaflets, then the optical character of the direction of flow must at first be the same as that of the colloidal particles and afterwards of the opposite sign. Aniline-blue sols, prepared by pouring an alcoholic solution of the dye into water, show on flowing a strong negative double refraction in the red, negative pleochroism in the region orange to green, and a positive double refraction in the blue. Anomalous interference bands are produced by this anomalous behaviour. The optical anisotropy produced by a magnetic field has the opposite sign, that is, the colloidal particles arrange themselves at right angles to the lines of force. On the other hand, they arrange themselves parallel to the electrical lines of force. The negative double refraction of benzopurpurin can be made to disappear by heating. The addition of electrolytes causes the double refraction to reappear on cooling. The coagulum obtained by the addition of an excess of electrolyte gives a doubly refracting sol on peptisation if the addition of the electrolyte was slow or if the original sol was doubly refracting, but if the coagulation took place rapidly or if the original sol was isotropic, there will be no double refraction. When acidified, double refracting red sols may be changed into double refracting blue sols. The strong pleochroism has always a negative sign, and the particles of the sols are diamagnetic. The double refraction of vanadium pentoxide sols disappears more slowly the older and more concentrated the sol. Very concentrated old vanadium pentoxide sols and concentrated, electrolyte-poor benzopurpurin solutions show a persistent double refraction similar to that of the crystalline liquids. The view of Diesselhorst and Freundlich (*loc. cit.*), that the growth of non-spherical particles in parallel layers, is confirmed, with the addition that the primary particles may be crystalline and that eventually they may undergo crystalline processes.

J. F. S.

Recent Advances in Stereochemistry. B. K. SINGH (*J. Proc. Asiatic Soc. Bengal*, 1921, **17**, 213—230).—A general account of the historical development of stereochemistry and a discussion of the relation between optical activity and chemical constitution. Particular consideration is given to optical activity in homologous series, the effect of conjugated unsaturation, and of position isomerism on optical activity. The Walden inversion is also discussed.

H. W.

Investigations on the Fundamental Law of Photochemistry. P. LASAREV (*Z. physikal. Chem.*, 1921, **98**, 94—97).—A theoretical discussion of work previously published on the bleaching of dyes by light (*A.*, 1912, ii, 219; *Ann. Physik*, 1907, [iv], **24**, 661). The experiments on the bleaching in the presence of oxygen under increased pressures (up to 150 atm.) are particularly considered. The fundamental law for the bleaching of dyes has the form

$-dC/dt = \alpha_0(1 - e^{-K_1 C})(1 - e^{-K_2 C_1})$, in which C is the concentration of the dye, K a constant proportional to the absorption constant, C_1 and K_1 similar values for the substance non-sensitive to light, and α the photochemical constant. It is assumed that in the reaction, during the absorption of light, an electron from the first Bohr orbit springs over to the furthest orbit. It is shown that the total absorption of light is proportional to the absorption of the largest (ionised) atoms. The increase in volume during photochemical reactions is explained by the assumption that the light, inasmuch as it occasions an increase in the volume of the atoms by effecting the electron spring, brings about an increase in the gaseous volume.

J. F. S.

New Measurements of Precision in the X-Ray Spectrum. M. SIEGBAHN (*Compt. rend.*, 1921, **173**, 1350—1352).—By the use of three spectrographs, each adapted to a particular spectral region, it was possible to measure a wave-length with an accuracy of 0.01—0.005%, and by this means the wave-length of the copper line $K\alpha_1$ was found to be 1537.36×10^{-11} cm. in a vacuum. A more precise instrument is described the readings of which are accurate to within 0.002%, and with this the value of λ for $K\alpha_1$ was found to be 1537.302×10^{-11} cm.

W. G.

Spectrographic Study of the De-intensifying of Barium Platinocyanide in the Villard Effect. A. ZIMMERN and E. SALLES (*Compt. rend.*, 1922, **174**, 80).—Fluorescent screens which have undergone the Villard effect can be regenerated by exposure to diffused light. It is shown that the radiations capable of destroying the Villard effect are found in four principal bands of almost equal breadth. The first is entirely in the infra-red, the second in the greenish-yellow, the third in the blue, and the fourth in the ultra-violet.

W. G.

The Theory of Absorption of X-Rays by Matter and the Principle of Correspondence. LOUIS DE BROGLIE (*Compt. rend.*, 1921, **173**, 1456—1458).—An expression for the atomic coefficient of absorption of a substance for a radiation of wave-length λ has previously been given (cf. A., 1920, ii, 208) in which the constant, α , was defined by the hypothesis that, for the possible changes of internal configuration of an atom placed in a system in thermodynamic equilibrium at the temperature T , the probability A_{12} of the return of the atom from a configuration of energy ϵ_1 to a configuration of less energy, ϵ_2 , is proportional to $\epsilon_1 - \epsilon_2$ and also to the absolute temperature in such a way that $A_{12} = \alpha(\epsilon_1 - \epsilon_2)T$. A mathematical proof of the truth of this hypothesis and a means of calculating the constant α are given, and it is shown that the coefficient of the Bragg-Pierce law is a universal constant capable of being expressed as a function of the constants of the electron and of the radiation.

W. G.

Calculation of the X-Ray Absorption Frequencies of the Chemical Elements. I and II. WILLIAM DUANE (*Proc. Nat. Acad. Sci.*, 1921, **7**, 260—267; 267—273).—In the first paper,

the author has calculated the K critical absorption frequencies of the elements magnesium, sulphur, calcium, iron, selenium, molybdenum, tin, cerium, dysprosium, tungsten, lead, and uranium on the basis of the Rutherford-Bohr theory of the structure of atoms and the mechanism of radiation. The assumption is made that the electrons are distributed in circular orbits, which do not lie in planes passing through the nucleus of the atom. In order to estimate the forces exerted on an electron in one orbit, A , due to the electrons in the parallel orbit, B , it is assumed that they are the same as if the charges are concentrated, half at the nearest point to the orbit A and half at the point furthest from A . A series of values is obtained which are in fair agreement with those observed. In the second paper, it is assumed that the forces are the same as if the electricity of the electrons in the orbit B is uniformly distributed along the orbit. The values calculated on the second assumption are somewhat smaller than those of the first calculations.

J. F. S.

The Laws of Absorption of X-rays. F. K. RICHTMYER (*Physical Rev.*, 1921, **18**, 13—30).—An experimental study of the absorption of X-rays by water (oxygen), aluminium, copper, molybdenum, silver, and lead, each over a great part of the range of wave-lengths 0.093 Å. to 0.95 Å. The longest of these waves is shorter than the critical K absorption wave-length of oxygen, aluminium, or copper, and falls between K and L for molybdenum, silver, and lead. Rays from a Coolidge tube were analysed by a spectrometer with a sodium chloride crystal, and the intensity was measured by ionisation of methyl bromide. Scattered and fluorescent radiation from the absorbing screen were suppressed by placing the screen in front of the spectrometer slit nearest the tube. Detailed tables and curves of the results are given. The mass-absorption coefficients, μ/ρ , of these substances is given by $\mu/\rho = F\lambda^3 + (\sigma/\rho)$ where λ is wave-length and σ/ρ is the mass-scattering coefficient, except in the region close to λ_K on the short-wave-length side, where the equation gives values which are somewhat too large, the error being greater as the difference between λ and λ_K is smaller. For each substance F has a constant value for $\lambda < \lambda_K$ and another much smaller constant value for $\lambda > \lambda_K$. The mass-scattering coefficient is independent of wave-length, and is, to a first approximation, the same for all elements. The atomic-absorption coefficient is given by $\mu_a = 2.29 \times 10^{-27} N \lambda^3 + \sigma_a$, where N is the atomic number and σ_a the atomic-scattering coefficient, for $\lambda < \lambda_K$. No trace of the suggested “ J ” absorption discontinuity was found. At 0.093 Å., μ/ρ for water is still much greater than for the hard rays of radium- C .

CHEMICAL ABSTRACTS.

The Luminescence of certain Oxides Sublimed in the Electric Arc. E. L. NICHOLS and D. T. WILBER (*Physical Rev.*, 1921, **17**, 707—717).—Thin films of metallic oxides were obtained by subliming the metal or one of its salts from the crater of a direct-current carbon arc on to a metal disk. Oxides prepared by sublimation are found to respond to excitation by cathode rays.

The shift in colour with increasing temperature in luminescence is in general to the violet. The effect of pressure on luminescence is discussed. The most active oxides were those of calcium, magnesium, zinc, zirconium, silicon, and aluminium.

CHEMICAL ABSTRACTS.

Anode Rays of Glucinum. G. P. THOMSON (*Nature*, 1921, 107, 395).—The method of positive ray analysis applied to lithium (Aston, A., 1920, ii, 344) has been extended to glucinum and found to yield a well-marked parabola corresponding with a single charge and an atomic weight 9.0 ± 0.1 ($\text{Na} = 23$). No second parabola was observed which could be ascribed with certainty to glucinum, but it is doubtful if a line of intensity one-tenth that of the first could have been detected. No indication was found which would suggest that the atom of glucinum can lose two electrons under the prevailing experimental conditions. A. A. E.

Reactions in Penetrating Radium Radiation and in Ultra-violet Radiation Filtered by Quartz Glass. II. The Hydrogen Peroxide Equilibrium set up in Radium Radiation. ANTON KAILAN (*Z. physikal. Chem.*, 1921, 98, 474—497; cf. A., 1912, ii, 10, 522; 1920, ii, 576).—Radiation from 0.1 gram of radium metal after passing through 1 mm. of glass into 100 c.c. of water in contact with air produces a solution containing 6×10^{-6} gram-equivalent of hydrogen peroxide; in the presence of 0.01N-sulphuric acid the amount of hydrogen peroxide becomes 10^{-4} , and in 1.0N-acid the amount is 5×10^{-4} gram-equivalent. In the last-named solution 6×10^{12} and in the first 3×10^{12} molecules of hydrogen peroxide are formed per second. These values are considerably less than those obtained nine or ten years ago, and reasons for the discrepancy are advanced. A comparison of the values obtained for the velocity of formation of hydrogen peroxide then and now with the rate of formation by other reactions which have been obtained in a similar manner to the present shows that both in aqueous and in non-aqueous solutions, when the decomposition of hydrogen peroxide is neglected, the number of molecules of hydrogen peroxide formed is of the same order as that of the ion pairs absorbed from the radiation by the medium. In ultra-violet light from a quartz glass lamp under similar conditions, the reduction of the peroxide concentration by increase in the hydrogen-ion concentration is less than in the radium rays, whilst the decomposition of hydrogen peroxide is more than one hundred times greater than in the radium rays. J. F. S.

Stationary Electron Vibrations without Radiation Resistance. A. D. FOKKER (*Physica*, 1921, 1, 107—109).—It is theoretically shown that a Bohr atom with electrons revolving in closed paths may be free from radiation resistance without violating the principles of the classical theory. CHEMICAL ABSTRACTS.

The Radioactivity of the Oxides of Uranium. CHARLES STAEHLING (*Compt. rend.*, 1921, 173, 1468—1471; cf. A., 1920, ii, 5).—In continuation of previous work (*loc. cit.*), it is shown that

the radioactivity of the green oxide, which has been restored to its original value, commences to diminish as before. The restoration of activity may be brought about by simple calcination without passage through ammonium uranate. During this process of restoration, the oxide undergoes loss in weight, due, for the most part, to the removal of moisture. The black oxide which shows little loss in activity also shows little loss in weight or alteration in activity on calcination. The author considers that the green oxide exposed to the air in thin layers undergoes hydration as well as loss in activity, the hydration diminishing the superficial density of the uranium atoms. The black oxides obtained by calcination at high temperatures do not hydrate and show little or no decrease in radioactivity. These facts tend to confirm the existence of a definite black oxide, which is probably an allotropic modification of the green oxide.

W. G.

Isotopy of the Radio-elements and Meitner's Nucleus Model. MAXIMILIAN CAMILLO NEUBURGER (*Z. physikal. Chem.*, 1921, **99**, 161—167).—A theoretical paper in which, on the basis of Meitner's nuclear hypothesis (A., 1921, ii, 293), the author has subdivided isotopes into four groups. These are termed isotopes of the first, second, third, and fourth order. Isotopes of the first order have the same nuclear charge and arrangement of the outside electrons, but different nuclear mass, total number of nuclear constituents, arrangement of the nuclear constituents, number of each kind of nuclear constituent, and probability of disintegration; radium and meso-thorium-I illustrate this group. Isotopes of the second order have the same nuclear charge, arrangement of the outside electrons, nuclear mass, and total number of nuclear constituents, but different numbers of each kind of nuclear constituent, arrangement of the nuclear constituents, and probability of disintegration. An example of this class is furnished by ionium and uranium-Y. Isotopes of the third order differ only in the arrangement of the nuclear constituents and the probability of disintegration, all other properties being identical; this is the case with radium-D and actinium-B. Isotopes of the fourth order are identical in all the properties mentioned; no examples of this class are known.

J. F. S.

Calculation of the Branching Relationships for Dual α -Disintegration and the Meitner Nucleus Model. MAXIMILIAN CAMILLO NEUBURGER (*Z. physikal. Chem.*, 1921, **99**, 168—171; cf. Meitner, A., 1921, ii, 293).—A theoretical paper in which it is shown that the method of calculation adopted by Smekal (A., 1921, ii, 149) for determining the branching relationship is so closely dependent on the assumptions made as to the structure of the radioactive nucleus, that it cannot possibly be of general use. The branching relationship cannot be calculated by this method, since it leads to inaccurate values which lead to results opposed to the experimental data. The agreement found for the branching relationship by this method for the uranium, radium, thorium,

and actinium families with the experimentally determined values for this relationship is accidental. J. F. S.

Emissivity of Iron and Copper. K. LUBOWSKY (*Elektro-techn. Z.*, 1921, **42**, 79—81).—The emissivity of both bright and blackened iron and copper was determined. Curves are given showing the effect of convection currents obtained from a flat plate of the material, first perpendicular to, and second in the direction of the air stream. Expressed in watts per sq. cm. per 1° of temperature excess, the emissivity varies from 0.75×10^{-3} to 1.5×10^{-3} under the various conditions. CHEMICAL ABSTRACTS.

The Effects of Impurities on the Ionisation Potentials Measured in Thermionic Valves. L. S. PALMER (*Radio Rev.*, 1921, **2**, 113—125).—The method of investigation used is based on a study of the current-voltage curves measured in hard and soft 3-electrode tubes. The details of the method have been given in a previous paper. Certain bends in these curves are interpreted as being due to the bombardment of the filament by positive ions. The ionisation potentials of helium, mercury, and argon have thus been determined. There are variations in the values for the ionisation potentials obtained in helium. These are ascribed to impurities, and the amount of impurity active accords with the values found by Horton in helium (A., 1919, ii, 210; 1920, ii, 660; 1921, ii, 672). This effect of the impurity also explains the low values of the potentials obtained by Stead and Gossling (A., 1920, ii, 659). The characteristic of the soft 3-electrode tube can be used to determine the resonance and ionising potentials of the contained gas. The nature of the gas and presence of the impurities can be determined from the critical points of the characteristics. Methods of measuring ionisation potentials are liable to error if impurities are present. Horton's previous work is confirmed and the result has been extended to argon with traces of mercury. The value of the ionisation potential decreases slightly with increase of gas pressure, causing changes in the characteristics similar to those for impurities. A number of critical potentials obtained for helium and argon are given. CHEMICAL ABSTRACTS.

Estimation of the Radium Content of Radioactive Luminous Compounds. E. A. OWEN and WINIFRED E. PAGE (*Proc. Physical Soc.*, 1921, **34**, 27—32).—The absorption of γ -radiation in zinc sulphide has been measured by different methods, and its value found to be approximately the same by all. No indication was observed of the occurrence of an abnormal absorption when the radioactive salt was mixed with the sulphide. A table has been drawn up which gives the values of the ratio of the true to the apparent radium content for tubes of different diameters filled with a radioactive luminous compound. This table applies to a compound the apparent density of which is 2.03 grams per c.c. The value of the absorption of γ -radiation from radium has been measured for zinc sulphide (0.101), barium sulphate (0.079), barium chloride (0.100), barium carbonate (0.046), lead monoxide (0.294),

bismuth sesquioxide (0.206), and uranium pentoxide (0.315). The absorption coefficients are given in brackets in cm^{-1} . The mass absorption coefficient has been calculated in each case, and it is shown that the barium salts have nearly the same value, the mean value being 0.053.

J. F. S.

Electrical Conductivity of Salts and Mixtures of Salts.

A. BENRATH and K. DREKOFF (*Z. physikal. Chem.*, 1921, 99, 57—70).—The specific conductivity of molten mixtures of potassium sulphate with sodium sulphate, magnesium sulphate, potassium fluoride, and lithium sulphate respectively has been determined over the whole range of compositions and from the results relationships to the diagram of condition are drawn. It is shown that the conductivity isotherm can be deduced only to a small extent from the diagram of condition. It is also shown that the point at which the eutectic appears is a well defined conductivity point. Pure salts as well as salt compounds change their conductivity with temperature according to the formula $\log k = a + bT$. This formula is not generally applicable to mixtures of salts and mixed crystals; attempts to obtain a theoretical basis for the formula gave the relationship: $\log k'' + bT'' = \text{const.}$ The formula of Tubandt, $\log K = c - d/T$, is not generally applicable. For the complete explanation of the phenomena, other factors, particularly the viscosity, must be known and taken account of in the calculation.

J. F. S.

The Electrical Conductivity of Anhydrides of the Higher Fatty Acids. D. HOLDE and IDA TACKE (*Chem. Ztg.*, 1921, 45, 1246—1247; cf. A., 1921, i, 842).—The values previously given for the molecular conductivity of oleic anhydride and oleic acid in acetone, on being adjusted to a dilution of 50 and 8 respectively gave 2.015×10^{-4} and 0.53×10^{-4} . If it is assumed that these two compounds are only slightly dissociated, that is, that the molecular conductivity increases proportionally to the square root of the dilution, the calculated figure for λ_{50} for oleic acid becomes 1.33×10^{-4} , a figure not differing very greatly from that of the anhydride; the difference may be due to impurities in the acetone used.

A. R. P.

Measurement of Dielectric Constants. J. F. KING and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1921, 43, 1835—1843).—A bridge method for the measurement of dielectric constants is described in which an arrangement consisting of an electron tube, a condenser, and an induction coil connected in a circuit serve as the source of alternating current of symmetrical wave form. Preliminary measurements of the dielectric constant of mixtures of ethyl alcohol with benzene, ethyl ether, and carbon tetrachloride respectively up to 100% by weight of alcohol, are recorded. The dielectric constant increases with each addition of alcohol to the other constituent in a fairly regular manner.

J. F. S.

Electrical Moments of Carbon Monoxide and Dioxide Molecules. HANS WEIGT (*Physikal. Z.*, 1921, 22, 643).—The

dielectric constants of carbon monoxide and carbon dioxide and their dependence on temperature have been determined with the object of ascertaining by means of the Debye theory the electrical moment of the two gases. The values obtained are $\mu_{\text{CO}} = (0.1420 \pm 0.0017) \times 10^{-18}$, $\mu_{\text{CO}_2} = (0.1180 \pm 0.0016) \times 10^{-18}$, both of which are in good agreement with that calculated from the Lorentz-Lorenz formula. J. F. S.

Application of the Theory of Allotropy to Electromotive Equilibria. IV. A. SMITS (*Z. physikal. Chem.*, 1921, **98**, 455—459; cf. A., 1915, ii, 217; 1916, ii, 77; 1917, ii, 232).—The author offers a corrected interpretation of that published ("Theorie der Allotropie," Leipzig, 1921, 403—405) for the electromotive behaviour of metals as soon as they are attacked by acids. The *E.M.F.* of *M*/2-zinc sulphate dissolved in water, 0.05*N*-sulphuric acid, 0.1*N*-, 0.5*N*- and 1.0*N*-sulphuric acid, and *N*-potassium sulphate has been determined at 18° in an atmosphere of nitrogen. The results show that the potential of zinc is not effected by the presence of acid below 0.5*N*, and from this point upwards the potential is only changed by 2 millivolts. Similar experiments are described with zinc chloride in hydrochloric acid solutions; here it is shown that a concentration of hydrochloric acid of 0.1*N* is without influence on the potential, but that 0.5*N* and 1.0*N* cause a change in the *E.M.F.* of 0.021 and 0.038 volt, respectively. J. F. S.

Electromotive Behaviour of Aluminium. A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1921, **27**, 579—582).—A reply to Smits, in which the author maintains his previous assertions (cf. this vol., ii, 20). J. F. S.

Electromotive Behaviour of Metallic Compounds with Electron Conductivity. G. TRUMPLER (*Z. physikal. Chem.*, 1921, **99**, 9—56).—Metallic or mixed conducting binary compounds combined with the metallic component as conductor and immersed in a solution of a salt of the metal which is saturated with the compound, have a zero potential when measured against the metallic component in the same solution. The formula put forward previously by Haber for such cases has been confirmed in the case of cuprous iodide, and cuprous, lead, and silver sulphides. It is also shown that metallic and mixed conducting compounds combined with the metallic component as conductor possess the same potential as an indifferent electrode (platinum) when immersed in a solution saturated with these substances and containing the negative component both as ion and in the free condition. A necessary condition in this case is the stability of the compound towards the metallic conductor and the solution. This has been investigated in the case of lead, cupric, cuprous, silver, and ferrous sulphide against sodium sulphide and polysulphide solutions. If in the last case pure electrolytes are used, the free negative component has no influence on the potential against the solution; this is much more dependent on the concentration of the components in the solution. This has been shown in the cells $\text{Ag}|\text{AgBr}|\text{KBr}, \text{Br}_2(\text{sat.})$; $\text{Ag}|\text{AgI}|\text{KI}, \text{I}_2(\text{sat.})$. In the case of the

mixed conducting silver sulphide in the presence of free sulphur the potential lies between that of the pure components. This potential is a characteristic of the mixed conductor. The three forms of conductors, metallic, mixed, and electrolytic, are characterised by the potential relationship obtained by the above-named measurements. From the different behaviour of the metallic and electrolytic conductors (compounds) with respect to the influence of the negative component on the potential relations as obtained by the above method, a fundamental difference of the internal structure is deduced, according to which in the pure metallic conducting compounds the space lattice points are occupied by atoms or molecules and not by ions. They appear, in opposition to electrolytes, to be non-polar. It is shown that pure cuprous sulphide is an electrolyte, or a mixed conductor in which the metallic component of the conductivity is very small. The passivity of lead sulphide in solutions of lead salt has been investigated and a process for activating the substance is put forward. The data in the literature on the solubility of lead sulphide and cupric sulphide are corrected. The electro-metric determination of the solubility of lead sulphide is not possible on account of the complete passivity of the lead electrode in sulphide solutions. The solubility product of lead sulphide has been determined approximately from the solubility in hydrochloric acid and the value $[Pb^{2+}][S^{2-}] = 5 \times 10^{-29}$ obtained. It is shown that cupric sulphide is not stable in sodium sulphide and that in the presence of copper only cuprous sulphide can exist in sodium sulphide solution, and consequently the measurement of the copper potential in sodium sulphide solution does not give the solubility product of cupric sulphide (cf. Knox, A., 1908, ii, 830). The solubility product of cuprous sulphide is found to be $[Cu^+][S^{2-}] = 2 \times 10^{-47}$.

J. F. S.

The "Salt Error" of the Quinhydrone Electrode. S. P. L. SØRENSEN, M. SØRENSEN, and K. LINDERSTRØM-LANG (*Compt. rend. Trav. Lab. Carlsberg*, 1921, **14**, No. 14, pp. 31).—Bilimann's quinhydrone electrode (A., 1921, ii, 372) gives, in the presence of sodium chloride, too small a potential (with 3.99*N*-sodium chloride + 0.01*N*-hydrochloric acid 0.6931 volt instead of 0.7044 volt at 18°). This is due to a lowering of the solubility of quinhydrone and can be overcome by saturating the salt solution with quinhydrone and with one of its constituents, for example, with quinol. This and various other questions are discussed theoretically in detail, and the theory is verified by experiments. G. B.

The Quinhydrone Electrode. EINAR BILIMANN and HAKON LUND (*Ann. Chim.*, 1921, [ix], **16**, 321–340).—It has previously been shown (A., 1921, ii, 372) that aqueous solutions of quinhydrone may be used for the preparation of reversible electrodes with very constant potential, which may serve to determine hydrogen-ion concentrations in solutions which are one-tenth molar. Concordant results are not obtained with stronger solutions. It is possible to construct electrodes, however, in which the electromotive

reaction is a transformation of one solid body into another solid body. The preparation of such electrodes with benzoquinone-quinhydrone and with quinol-quinhydrone is described. Such electrodes have hydrogenation potentials $\pi_{18}=0.7562$ and 0.6179 , respectively. They may be used for measurements over a wide range of hydrogen-ion concentration. W. G.

Electromotive Force produced by the Relative Displacement of an Electrode and an Electrolyte. STÉFAN PROCOPIU (*J. Chim. Physique*, 1921, **19**, 121—134).—It is found that the movement of an electrode in a liquid gives rise to an *E.M.F.* of movement which is general for all metallic electrodes. The dimensions of this *E.M.F.* are determined only by the solution pressure of the metal and the osmotic pressure of the metallic ion in the solution. The effects produced when a series of metals is moved in water, nitric acid, sulphuric acid, salts of the metals, and potassium hydroxide have been measured. The phenomenon is explained by the existence of a layer of solution round the electrode of composition different from that of the rest of the solution. This leads to a relationship between the photoelectric *E.M.F.* and that of movement, and makes it possible to find the effect of movement on the electrical resistance of liquids. J. F. S.

The Overvoltage of the Mercury Cathode. EDGAR NEWBERRY (*T.*, 1922, **121**, 7—17).

Theory of the Electrolytic Ionic Condition and the Calculation of the Electrolytic Solution Constants, and of the Related Quantities from the Chemical Relationships. KARL FREDENHAGEN (*Z. physikal. Chem.*, 1921, **98**, 38—69).—A theoretical paper in which it is shown that neither Arrhenius's electrolytic dissociation theory nor Nernst's theory of solution tension furnishes any information on the nature of the ionic condition or the nature of ionic dissociation. Neither of these theories can be directly deduced from the facts of inorganic chemistry, and they do not bring these facts into relationship with one another. The author has put forward an hypothesis of the ionic condition and the electrolytic solution constants which removes the above-named defects and shows how ordinary thermal dissociation passes into electrolytic dissociation. The hypothesis also shows how the solution constants of the elements, and the partition and dissociation constants of chemical compounds may be calculated from the chemical relationships of the compounds and elements and from a factor which expresses the condition of the solvent. The hypothesis permits a qualitative deduction of the electrical and dielectrical behaviour of conductors of the second class.

J. F. S.

An Electrolytic Current Intensification Effect, a New Electrolytic Displacement Effect, and the Connexion between Electrolysis and the Emission of Electrons in a Vacuum. II. D. REICHINSTEIN and F. KLEMENT (*Z. physikal. Chem.*, 1921, **99**, 275—289; cf. *A.*, 1921, ii, 729).—A continuation of work previously

published (*loc. cit.*). It is shown that in a closed circuit by means of superimposed alternating current a stronger direct current can be produced, the work from which can be greater than that of the alternating current used to generate it. The action of a high frequency current on an electrolytic cell is not a specific high frequency action; qualitatively, it is the same as that of a low frequency current. All passivity phenomena, both anodic and cathodic, show on superposing an alternating current on the direct current a decrease of the direct current polarisation, and thereby allow themselves to be used as detectors or current intensifiers. Using the commutator method, an intensification of two hundred times has been obtained and the experiments indicate that this may be still further increased. A new experiment with a highly evacuated electron tube is described, which indicates that after removal of the polarisation it is possible to generate cathode rays with low potentials and cold electrodes.

J. F. S.

Applicability of the Gas Laws to Strong Electrolytes. II. J. N. BRONSTED (*K. Danske Videnskab. Selskab., Math.-fys. Medd.*, 1920, **3**, 1—21; cf. A., 1920, ii, 78).—By a modification of the original electrometric method, consisting in the use of a streaming electrode, *E.M.F.* determinations have been carried out with one electrolyte dissolved in a concentrated solution of another. Cells of the type : $\text{Ag, AgCl} \left| \begin{array}{c} \text{solvent } (n-c_1) \\ \text{chloride } (c_1) \end{array} \right| \begin{array}{c} \text{solvent } (n-c_2) \\ \text{chloride } (c_2) \end{array} \left| \text{AgCl, Ag and} \right.$
 $\text{Ag} \left| \begin{array}{c} \text{solvent } (n-c_1) \\ \text{silver salt } (c_1) \end{array} \right| \begin{array}{c} \text{solvent } (n-c_2) \\ \text{silver salt } (c_2) \end{array} \left| \text{Ag} \right.$ were employed. Support is afforded to the theory that the simple gas laws are valid for ions present in salt solutions the concentrations of which are large in comparison with that of the ions concerned. Conditions under which the law fails to apply are discussed, and the results of Loomis, Essex, and Meacham (A., 1917, ii, 353), that slight changes in the activity coefficient occur with varying concentrations, are confirmed.

CHEMICAL ABSTRACTS.

Newer Investigations on the Anomaly of the Strong Electrolytes. LUDWIG EBERT (*Jahrb. Radioaktiv. Elektronik*, 1921, **18**, 134—196).—An alphabetical bibliography of the work on strong electrolytes is given. The whole subject of the behaviour of strong electrolytes is discussed under the headings (i) chief anomalies, and (ii) the hypothesis of complete dissociation of the strong electrolytes and the activity of electrical forces between the ions.

J. F. S.

Transport Numbers of Sulphuric Acid by the Concentration Cell Method. ALFRED L. FERGUSON and WESLEY G. FRANCE (*J. Amer. Chem. Soc.*, 1921, **43**, 2150—2160).—A method is described for the determination of the transport numbers of a uni-bivalent electrolyte by measurement of the potentials of concentration cells. The transport number of the anion of sulphuric acid for concentrations between 0.1*M* and 0.01*M* has been measured and found to be 0.1868 ± 0.0007 at 25°. This value is compared

with the values obtained by other investigators. It is shown that the dissociation values determined from freezing-point data are more satisfactory for calculating the potentials of concentration cells than those obtained from conductivity data. A correction to the formula for the potential of a concentration cell has been developed which takes into account the undissociated part of the acid. It is shown that the concentration cell method is entirely satisfactory for the determination of the transport numbers of sulphuric acid.

J. F. S.

Influence of Gelatin on the Transport Numbers of Sulphuric Acid. ALFRED L. FERGUSON and WESLEY G. FRANCE (*J. Amer. Chem. Soc.*, 1921, **43**, 2161—2171).—The effect of gelatin on the transport numbers of gelatin has been investigated. It is shown that the addition of sulphuric acid up to 20% increases the transport number of the anion of sulphuric acid (0.1—0.01*M*) from 0.187 in the absence of gelatin to 0.685 in the presence of 20% gelatin. The effective concentration of 0.1*M* and 0.01*M* sulphuric acid solution is reduced by the addition of gelatin. The conductivities of sulphuric acid are reduced by the addition of gelatin. An hypothesis is put forward to account for the action of gelatin in the presence of electrolytes.

J. F. S.

Electro-osmosis. A. H. W. ATEN (*Chem. Weekblad*, 1921, **18**, 690—692).—The theory of electro-osmosis of liquids through porous solids is discussed, and the volume passing in unit time shown to be directly proportional to the current density, the dielectric constant of the liquid and the potential difference between the liquid and the porous material, and inversely proportional to the viscosity and conductivity of the liquid. The various attempted technical applications of the phenomenon, and of kataphoresis (which term is restricted to the motion of solid particles suspended in a liquid under the influence of the electric field) are described.

S. I. L.

Some Electro-osmotic Experiments with de Haen's Membrane Filters. P. H. PRAUSNITZ (*Kolloid Z.*, 1921, **29**, 293—309).—The electro-osmosis of water, solutions of ammonia, sulphuric acid, ammonium sulphate, sodium sulphate, potassium ferricyanide, and aluminium sulphate, through de Haen filters for varying size of pores, has been investigated at 25° and under a pressure of 43 cm. of water. It is shown that the de Haen filters are particularly well adapted to the study of the influence of electrolytes on electro-endosmosis. Filters of medium-sized pores (Nos. 20 and 320) when 5 cm. thick allow 100—500 c.c. of water to pass per hour under the pressure used in the experiments. Distilled water ($\lambda = 6 \times 10^{-6}$) travels toward the cathode through the membrane under a current of 100 volts and about 0.1 ampere at the rate of 1—2 litres per hour. The addition of sulphuric acid to the anode compartment, or any addition of thorium chloride or aluminium sulphate, reduces the electro-endosmosis to values below that of water and in cases may produce even a weak anodic endosmosis. In

other cases, the addition of electrolytes brings about an increased cathodic endosmosis, in which the amount of water transported varies with the time the current is flowing and the nature and concentration of the electrolyte. It is shown that, in general, with an electrical conductivity of $200-400 \times 10^{-6}$ and a consumption of energy of $0.01-0.06$ *KWH*/litre of transported liquid, 8-16 litres/hour of liquid can be made to pass through a diaphragm of 100 cm.². It is not always necessary that the electrolyte should pass through the membrane as such; particularly in the case of ammonia it is shown that the addition of the base to the cathode compartment can bring about a very considerable endosmosis of the water, which is to be attributed to the wandering in the opposite direction of those ions which are responsible for the discharging of the membrane. The transport of the SO_4 -ion through a de Haen membrane from negative to positive compartments brings about a considerable passage of water from the positive to the negative compartment. In every case there is an optimum electrolyte concentration, and if this is exceeded anomalies occur which are found to be connected closely with the electrical conductivity. The discharge of the membrane is held to be due in all probability to the adsorption of hydroxyl ions, for all processes which effect a reduction of the hydroxyl-ion concentration also effect a reduction of the electro-endosmosis (cf. *D.R.-P.* 333575, 1919).

J. F. S.

Attainment of Constant High Temperatures. E. MOSER (*Z. angew. Chem.*, 1921, **34**, 625).—The apparatus or object to be maintained at constant temperature is immersed in paraffin contained in a cylindrical glass vessel surrounded by an outer glass vessel of similar shape but enlarged to a spherical form at the bottom to accommodate a liquid of suitable boiling point, which is kept in ebullition so that its vapour surrounds the inner vessel. The two vessels are sealed together round the top except where a tube serves to connect the vapour jacket with a reflux condenser. The lower end of the condenser tube projects downwards for some distance into the vapour jacket and the vapour enters it through a lateral orifice. The end of the tube is drawn out to a jet and disposed vertically above the boiling liquid. By this arrangement the condensed liquid is warmed again before it falls back into the jacket and is prevented from falling on the hot walls of the vessels. Liquids of high boiling point, such as ethyl benzoate, b. p. 212.5° , have been successfully used in the outer vessel.

J. H. L.

The Expansions of some Refractory Materials at High Temperatures. B. BOGITCH (*Compt. rend.*, 1921, **173**, 1358-1360).—The expansion curves for bauxite, clay, silica, chromite, and magnesia over the temperature range 0° to 1600° are given. The smallest expansion was shown by the bauxite, which is suitable for use in furnaces subject to sudden changes in temperature. Silica showed the most irregular expansion; it expanded rapidly up to 600° and then only very slowly, and above 1000° showed a slight contraction. The curve shows two singular points at 210°

and 570° respectively, which are the transformation points of cristobalite and quartz. Furnaces constructed with such bricks must only be heated up very slowly, the temperature rise being less than 50° per hour. The curve for the clay bricks is intermediate between the curves for bauxite and silica. Magnesia and chromite showed the biggest expansions, and such bricks are only suitable for the construction of furnaces in continuous work. W. G.

Coefficient of Expansion of Molten Salts. W. HERZ (*Z. physikal. Chem.*, 1921, **98**, 98—102).—In previous papers (A., 1914, ii, 25, 245; 1921, ii, 381) it has been shown that Mendeléev's equation is true for the expansion of normal organic liquids. In the present paper, the equation has been applied to the molten inorganic substances, sodium molybdate, lithium nitrate, sodium nitrate, rubidium bromide, caesium nitrate, potassium tungstate, caesium iodide, potassium molybdate, sodium tungstate, rubidium fluoride, caesium sulphate, and thallous nitrate. The data employed are taken from the work of Jaeger (A., 1918, ii, 33). The densities calculated by the Mendeléev formula agree in most cases to about 1 per 1800 with the experimental values. The only cases where divergence is shown are thallous nitrate and sodium tungstate, and here it is not much greater than in the other cases. The density values calculated by the Mendeléev equation are compared with those calculated by Jaeger (*loc. cit.*) by a single constant formula for caesium iodide and rubidium fluoride, and by a two constant formula for caesium sulphate and the value of the single constant Mendeléev formula demonstrated. J. F. S.

General Methods for the Determination of the True Molecular Constitution of Pure Substances and their Mixtures. MARIO BASTO WAGNER (*Z. physikal. Chem.*, 1921, **98**, 81—93).—A theoretical paper in which the author differentiates between the thermodynamics of mixtures treated in connexion with their independent components and the thermodynamics of mixtures treated in connexion with their true components. The advantages and drawbacks of both methods of treatment are explained and the nature of the results obtainable is pointed out in each case. The various properties which may be used in the determination of constitution are enumerated and their application is indicated. These include volume, heat change, vapour pressure, solubility, freezing point, boiling point, specific heat, compressibility, thermal coefficient of expansion, and osmotic pressure. The properties, dielectric constant, viscosity, refraction, and surface tension do not permit conclusions being drawn which may be used in the second method of treatment. J. F. S.

Thermodynamics of Mixtures. IX. MARIO BASTO WAGNER (*Z. physikal. Chem.*, 1921, **98**, 151—156; cf. A., 1921, ii, 375).—A theoretical paper in which the theory of the heat of mixtures is developed on the basis of the thermodynamics of mixtures treated in connexion with the true components (cf. preceding abstract). J. F. S.

Theory of Equations of State. II. MARIO BASTO WAGNER (*Z. physikal. Chem.*, 1921, **98**, 244—251; cf. preceding abstract).—The hypothesis developed previously is extended. The present paper deals with the theory of the heat of vaporisation and the internal pressure.
J. F. S.

Equation of Condition of Nitrogen at Small Pressures and Low Temperatures. R. BARTELS and A. EUCKEN (*Z. physikal. Chem.*, 1921, **98**, 70—79).—The equation of condition of nitrogen has been measured by means of a constant pressure gas thermometer between the temperatures 90° and 76° Abs. and between the pressures 0.5 and 1.0 atm. The results are represented by means of an empirical formula for the correction quantity B' of the form $v=RT'/p-RTB'$. This formula has been used to calculate the molecular heat of nitrogen for the ideal gas conditions, and the value 6.873 obtained for C_p . This value is 0.07 cal., or 1% lower than that (6.944 cal.) demanded by the classical theory, whilst the Berthelot equation of condition leads to a value 0.2 cal. lower than the classical value for the temperature 92° Abs. A comparison of the reduced B' values for a range of temperature shows that the curves for hydrogen and nitrogen cannot be brought into coincidence, but that at low temperatures they diverge.
J. F. S.

Equation of Condition. II. Principal Equation of Condition. III. Principal Equation of Condition and the Equation of Condition for Individual Substances. IV. Compressibility Equations of Liquids. A. WOHL (*Z. physikal. Chem.*, 1921, **99**, 207—225, 226—233, 234—241; cf. A., 1914, ii, 430).—A series of theoretical papers in the first of which the author further develops the equation of condition previously published (*loc. cit.*). The various relationships brought out by this equation are considered and compared with the equations of van der Waals and Kamerlingh Onnes. In the second paper, equations of condition are developed and considered for helium, hydrogen, water, and ethyl alcohol. The third paper deals with compressibility equations for liquids, particularly highly compressed substances. The substances ethyl ether, carbon dioxide, and hydrogen are considered.
J. F. S.

Extension of Ebullioscopy and its Application to Binary Mixtures. ERNST BECKMANN and OTTO LIESCHE (*Z. physikal. Chem.*, 1921, **98**, 438—454).—The authors have combined the Raoult equation $P=P_0[N/(N+n)]$ with Dalton's law $P=B[N'/(N'+n')]$ to form the equation $P_0[N/(N+n)]=B[N'/(N'+n')]$ and shown that this equation may be used generally in the ebullioscopy of binary mixtures, and may be extended to meet complicated cases, since the determination of the absolute boiling point fixes the value of P_0 with the help of vapour pressure tables or formulæ. The introduction of the boiling point difference Δ and the ebullioscopic constant E leads to a special ebullioscopic equation

$\Delta = E(n - n')$, which may only be used for small Δ values. If in either of the above equations n or n' is given the value zero, the two limiting cases are obtained, in which the second component (represented by small letters) is non-volatile or is not soluble in the first component. J. F. S.

A Vapour Pressure Formula with a General Integration Constant. F. A. HENGLEIN (*Z. physikal. Chem.*, 1921, **98**, 1—13).—A theoretical paper in which the constants of a previously published rule (A., 1920, ii, 732) for the comparison of the vapour pressure curves of two substances, $\log T_1 = a \log T_2 + b$, have been brought into relationship with the Trouton constants. From this relationship a vapour pressure formula has been deduced which contains two specific constants and has the form $\log p_{(\text{atm.})} = -k/T^n + 4.6222$. The formula holds, in comparison with other two constant vapour pressure formulæ, over greater temperature ranges and is characterised by the fact that the integration constant is the same for all substances. The index n is shown to be equal to $\lambda/(v - v')p \cdot K$ where K has the same value for all substances, and consequently $\lambda/(v - v')p$ may be calculated from the above formula; on the other hand, n may be determined from $\lambda/(v - v')p$ or λ/RT . To calculate the actual formula, two vapour pressure determinations are necessary, or the knowledge of one vapour pressure point and the molecular latent heat of vaporisation at the same pressure. The formula is shown to be equally true for sublimation pressures, and it may also be applied to decomposition pressures. J. F. S.

Theory of Binary Mixtures. VII. Mixtures of Ethyl Ether and Bromoform. F. DOLEZALEK and M. SCHULZE (*Z. physikal. Chem.*, 1921, **98**, 395—429; cf. A., 1920, ii, 32).—The vapour pressure of a series of mixtures of ethyl ether and bromoform has been determined at 25° and 75°; the contraction on mixing, the coefficient of expansion, and the density of the mixtures have been determined at 25°. The results show that on mixing the components a mutual partial complex formation occurs. The resulting compound consists of one molecule of ether and one molecule of bromoform; it occurs in the solution in a dissociated condition and on heating it decomposes. Bromoform itself is strongly associated, but with decreasing concentration the association decreases. The vapour pressure was determined by a new static method. A theory is developed whereby the molecular constitution may be calculated from the vapour pressure measurements. From two measured vapour pressures the combination constant K and the association constant k were determined, and from these the molecular constitution of the mixture was calculated for 25°. The results show that at 25° bromoform consists of 65% of bimolecules and that in the mixture of 1 mol. of ether and 1 mol. of bromoform, 23% of the equi-molecular compound is present. The vapour pressure for all mixtures has been calculated from the molecular composition, and found to be in good agreement with the experimental values. A marked contraction occurs on mixing

ether and bromoform; the contraction curve is strongly depressed on account of the association of the bromoform. The contraction has been calculated on the basis of the theory and found to agree with the observed contraction. From the coefficient of expansion the contraction at 15°, 20°, and 30° has been calculated. From the contraction at 25°, the density of the mixtures was calculated, and the results show that the measurement of volume change by the differential method is the most exact for the measurement of easily volatile liquid mixtures. J. F. S.

Vapour Pressure of Binary Mixtures. GERHARDT C. SCHMIDT (*Z. physikal. Chem.*, 1921, 99, 71—86).—A new simple static method of measuring the vapour pressure of liquids is described. It is shown that the dynamic method of measuring the vapour pressure of mixtures gives only moderate results and then only when the experiments are made under definite conditions, and it is inferior in every way to the new static method. The vapour pressures of the following mixtures, benzene-ethyl ether, benzene-chloroform, benzene-methyl acetate, methyl acetate-ethyl acetate, benzene-carbon disulphide, benzene-toluene, toluene-carbon disulphide, ethyl alcohol-methyl alcohol, benzene-methyl alcohol, chloroform-carbon disulphide, and acetone-chloroform have been measured up to a pressure of 4 atmospheres. By plotting the molecular compositions as abscissæ and the vapour pressures as ordinates, it is found that at all temperatures (20—100°) mixtures of ethyl alcohol and methyl alcohol give a straight line. Mixtures of benzene and ether and of benzene and chloroform give approximately straight lines up to 30°, but at higher temperature curves which are convex to the abscissa axis, and the higher the temperature the greater the convexity. Mixtures of acetone and chloroform at 0° give a straight line, and at higher temperatures curves convex to the abscissa axis, which become more convex as the temperature is raised. Mixtures of benzene and toluene, ethyl acetate and methyl acetate, and benzene and methyl acetate at low temperatures give straight lines, but at higher temperatures the curves are concave to the abscissa axis and the concavity becomes greater as the temperature is raised. Mixtures of benzene and carbon disulphide, toluene and carbon disulphide, chloroform and carbon disulphide, and benzene and methyl alcohol, give at 0° curves which are concave to the abscissa axis, and the higher the temperature the greater the concavity, this being particularly noticeable in the case of benzene-methyl alcohol. From the fact that the higher the temperature the greater the concavity or convexity, the conclusion can be drawn that for every liquid mixture there is a temperature at which the relationship between the vapour pressure and the molecular composition may be represented by a straight line, generally speaking this occurs at low temperatures. It is shown that a series of deductions from Dolezalek's theory of binary solutions, which refer to the influence of temperature on the course of the isotherms, are not confirmed by the experiments. Consequently the theory cannot be maintained. J. F. S.

Intersecting Vapour Pressure Curves and Deductions therefrom. CARL VON RECHENBERG (*Z. physikal. Chem.*, 1921, 99, 87—104).—A large number of pairs of substances are recorded for which the vapour pressure curves intersect. From a comparison of the intersecting vapour pressure curves the following conclusions are drawn. All liquid and solid substances consist of large molecular complexes of undetermined variable composition of different stability, and present as many classes of compounds as they have different molecular types. Every individual compound behaves in a characteristic manner. The division of liquids into associated and non-associated groups from surface tension measurements is incorrect. All compounds are associated, but the so-called associated compounds are more loosely combined. The sub-division only separates the most divergent compounds, but does not take account of the intermediate and transition compounds. A table is drawn up of the various aggregates according to the increase of vapour pressure with increase of temperature. The table is very similar to Rothmund's solubility table, from which it follows that vapour formation and solubility are parallel phenomena and must be due to the same cause. J. F. S.

Vaporisation of Solutions of Liquid Pairs possessing Intersecting Vapour Pressure Curves. CARL VON RECHENBERG (*Z. physikal. Chem.*, 1921, 99, 105—115; cf. preceding abstract).—The Bancroft rule, that liquids with intersecting vapour pressure curves form solutions with a characteristic point, has been confirmed, when notice is taken of the fact that the property of the characteristic solution only obtains inside a limited pressure region. A large number of homogeneous mixtures with intersecting vapour pressure curves are tabulated with the minimum boiling point and the concentration of the characteristic fraction at 760 mm.

J. F. S.

Distillation and Rectification. L. GAY (*Chim. et Ind.*, 1921, 6, 567—578; cf. this vol., ii, 85).—In order to obtain the maximum efficiency from a column, *ceteris paribus*, the higher the temperature of the initial mixture the lower should be the level of its introduction into the distillation apparatus. This level should be such that an initial liquid or gaseous mixture meets a liquid or gaseous mixture of approximately the same composition in the column. If the liquid mixture is at its boiling point, or rather if the gaseous mixture is at its condensation point, then the composition of the two mixtures is identical. The determination of the minimum intensity of heat and the minimum number of compartments of the column necessary for an initial gaseous mixture has been carried out in a similar manner to that used for an initial liquid mixture (*loc. cit.*), and applied to the separation of practically pure water and alcohol from any gaseous mixture of water and alcohol at 95°. The determination of the minimum intensity of heat necessary to remove a trace of impurity from a liquid has also been carried out.

F. M. R.

Heat of Formation of Silver Iodide. HUGH STOTT TAYLOR and WILLIAM THEODORE ANDERSON, jun. (*J. Amer. Chem. Soc.*, 1921, **43**, 2014—2017).—Braune and Koref's calorimetric measurement of the heat of formation of silver iodide (A., 1914, ii, 536), using *N*-potassium cyanide instead of 3*N*-solutions as solvent for silver iodide, have been repeated. The result 15,100 cal. per mol. of silver iodide has been obtained, which confirms Braune and Koref's value. J. F. S.

Relationship between Heat of Solution and Heat of Fusion of Organic Substances. GEORG GEHLHOFF (*Z. physikal. Chem.*, 1921, **98**, 252—259).—The heat of solution of naphthalene, diphenyl, diphenylamine, azobenzene, α -naphthylamine, β -naphthylamine, urethane, paraffin (wax), nitronaphthalene, nitrophenol, *m*-dinitrobenzene, phenol, menthol, thymol, pyrogallol, resorcinol, citric acid, and chloral hydrate has been determined in 1—3% solutions in the solvents water, benzene, ethyl ether, alcohol, carbon disulphide, acetone, amyl acetate, aniline, chloroform, and acetic acid. The results show that for a series of substances, particularly hydrocarbons, aromatic amines, urethane, and azobenzene, the heat of solution in various solvents is practically identical with the heat of fusion. Organic substances containing the hydroxyl group give very different values for the heat of solution and the heat of fusion, whilst substances containing the nitro-group take up an intermediate position between the other substances. The heat of solution of the sodium, potassium, and ammonium haloids has been determined in aqueous solution, and the results are discussed in connexion with the structures and space lattices of these salts. J. F. S.

Heats of Solution and of Transformation of the Acido- and Aquo-cobalt Pentammines. ARTHUR B. LAMB and JOHN P. SIMMONS (*J. Amer. Chem. Soc.*, 1921, **43**, 2188—2199).—A method of calorimetry has been developed in which only observations on a silver coulometer and of time and electrical resistance are required. It is shown that the same cobalt sulphide, Co_2S_3 , is produced by the action of sodium sulphide on chloro- and aquo-pentamminecobalt chloride in aqueous solution. The solubility of chloro-pentamminecobalt chloride in water at 0°, 30°, and 50° has been determined, and the values 2.244, 6.047, and 10.01, respectively, have been obtained in grams per litre. The heat of solution has been calculated from these data and the value 13,440 cal. obtained, which is in fair agreement with the experimental value, 12,400 cal. The heats of solution of a number of acido- and aquo-pentamminecobalt salts in water have been measured. The following values are found at 25°, in cal., chloro-chloride, —12,420; aquo-chloride, —6,460; bromo-bromide, —12,660; aquo-bromide, —9,220; nitrate-nitrate, —14,900; and aquo-nitrate, —15,300. The heat of reaction of solutions of pentammine salts with solutions of sodium sulphide has been measured at 25° and that of the solid salts with sodium sulphide solutions calculated. The

following values in cal. at 25° are obtained, chloro-chloride, 15,070; aquo-chloride, 12,930; bromo-bromide, 13,290; aquo-bromide, 11,600; nitrate-nitrate, 12,340, and aquo-nitrate, 11,860. From these results the heat of transformation of the acido-salt to the aquo-salt in each case has been calculated, and the values chloride, 2,140 cal.; bromide, 1,690 cal., and nitrate, 480 cal. have been obtained. J. F. S.

Heat of Wetting of Silica Gel. W. A. PATRICK and F. V. GRIM (*J. Amer. Chem. Soc.*, 1921, **43**, 2144—2150).—The heat change occasioned by wetting silica gels with water, ethyl alcohol, benzene, carbon tetrachloride, and aniline, respectively, has been determined at 25° . The quantity of liquid used in each experiment was 50.07 c.c. and the amount of gel 2.3—2.5 grams. The following values in cal./gram of gel were obtained: water, 19.22; alcohol, 22.63; benzene, 11.13; carbon tetrachloride, 8.42, and aniline, 17.54. The heats of wetting have been discussed and found to be in keeping with the changes of surface energy. J. F. S.

Viscosity of Gelatin Sols. ROBERT H. BOGUE (*J. Amer. Chem. Soc.*, 1921, **43**, 1764—1773).—A number of experiments have been effected with gelatin sols to determine the relation between viscosity and concentration. The data obtained have been applied to Hatschek's formula for the viscosity of emulsoids, and it is shown that the value of A'/A , representing the volume occupied per unit weight of dispersed phase, is not a constant with varying concentration, but rises regularly to a maximum and thereafter regularly diminishes with increasing concentration. This behaviour is noticed also in the case of other colloids. A tentative explanation is presented based on the effect which increasing concentrations of dispersed phase will have on the surface tension of the dispersion medium. Assuming the equilibrium, surface tension \rightleftharpoons solvation potential, an empirical relation is developed which, with a fair degree of accuracy, defines the equilibrium. At very high concentrations, a reversal of phase probably occurs, at which no expressions yet developed adequately represent the relations involved. A high degree of solvation is shown to be indicated by a high coefficient of viscosity, that is, solvation and viscosity are parallel functions. Isoelectric gelatin at a hydrogen-ion concentration 2×10^{-5} is shown to have the lowest viscosity and the lowest degree of solvation, gelatin chloride at a hydrogen-ion concentration 3.1×10^{-4} the highest, and calcium gelatinate at a hydrogen-ion concentration 2.5×10^{-6} is intermediate. If an excess of acid is allowed to remain in the gelatin solution, even although the acid be of very low concentration, the viscosity and degree of solvation will be reduced. J. F. S.

A New Viscostalagmometer for the Estimation of Surface Tension and Viscosity of Liquids of Very Different Limpidity. I. TRAUBE (*Biochem. Z.*, 1921, **120**, 106—107).—The essential feature consists in the adaptation to the ordinary form of stalagmo-

meter of five interchangeable ground-in mouth-pieces of differing capillary bore, thus allowing measurements to be performed with the same apparatus on liquids of a great range of fluidities.

H. K.

Ionisation and Surface Activity of Aqueous Solutions of Aliphatic Acids. WILH. WINDISCH and PHIL. OSSWALD (*Z. physikal. Chem.*, 1921, **99**, 172—188).—The connexion between ionisation and surface activity of organic acids has been investigated. It is shown that of *N*/10-acid or alkali when added to an aqueous solution acts only as a diluent, that is, the surface activity is independent of the hydrogen-ion concentration. Experiments have been made to determine the concentration of acids of different strengths, such as hydrochloric, formic, and acetic acids, which must be added to solutions of nonoic acid so that the same size of drops may be obtained, and also the concentrations of these acids which will produce the same colour with methyl-orange solution. It is shown that free nonoic acid in aqueous solution is 10% dissociated, and therefore the addition of acid increases its surface activity. The simultaneous presence of sodium chloride is without action on the activity. With continued addition of acid, the size of the drops sinks to a constant minimum. A solution of sodium nonoate exhibits a small activity, because through hydrolysis a small quantity of acid exists in the free condition. By the addition of a small quantity of alkali, the free molecules are ionised and the size of the drop sinks to that of water. An addition of hydrochloric acid produces fresh acid molecules, and the size of the drop sinks to a minimum, which is reached when all the aliphatic acid ions have disappeared. Consequently it follows that the surface activity of aqueous solutions of aliphatic acids is due to ionisation processes, and the possibility of calculating the size of the drops due to the action of various additions is pointed out.

J. F. S.

High Pressure due to Adsorption, and the Density and Volume Relations of Charcoal. WILLIAM D. HARKINS and D. T. EWING (*J. Amer. Chem. Soc.*, 1921, **43**, 1787—1802).—The present paper furnishes evidence in favour of the hypothesis previously expressed (A., 1921, ii, 87) by the authors, which states that the liquids which penetrate into charcoal are compressed by a force due to molecular attraction, which acts as a pressure of many thousand atmospheres (20,000 or more). The present paper shows that it is the liquid in the micro-pores and not the macro-pores which is compressed, and consequently the pressure would probably be much greater than the figure mentioned. Not only charcoal but other porous substances and fine powders should exert this compressive effect, but to a much smaller extent. A number of experiments are described in which the compression is demonstrated by volume changes, but the values measured have not exceeded 72 atms. Ethyl ether, which is much more compressible than water, occupies a volume in charcoal which is

about 10% less than that occupied by the amount of water which outside the charcoal is equal in volume to the ether. It is probable that the water in the micro-pores is compressed by about 25% or more, whilst the ether is compressed by 40%. The liquids in the macro-pores of the diameter 1.2×10^{-3} cm. are not compressed sufficiently to produce a noticeable effect on the volume. The true volume relations in 1 c.c. of a characteristic coconut shell charcoal are 0.28 c.c. micro-pores, 0.18 c.c. macro-pores, 0.54 c.c. carbon, which give a density of 1.60 for the carbon. The density of the lumps of such a charcoal is 0.866. Charcoals which are inactive as adsorbents of gases do not exert a compressive effect on the adsorbed liquids of a sufficiently high magnitude to be very evident, although there appears to be a slight effect of this nature. The densities of the carbon in the two inactive wood charcoals investigated are 1.65 and 1.50. When coconut-shell charcoals alone are considered, it is found that the lower the apparent density in an organic liquid, the less is the adsorptive action on vapours, and it is indicated that this relation may be expected to hold better the more compressible the liquid which is adsorbed, so that either ethyl ether or pentane or another highly compressible liquid should be used in such tests. Simple thermodynamic equations are given for the heat of immersion or adsorption of a plane surface. Whilst there is probably no definite area of surface inside a lump of charcoal, a definition for an apparent area may be given. The one chosen here is that the apparent area with respect to the heat of immersion is the area of the plane surface of carbon which will develop the same amount of heat on immersion as is equal to that developed by the immersion of 1 gram of the charcoal in the same liquid. Since the film in the charcoal is probably a number of molecules thick, this apparent area is probably larger than corresponds with the carbon surface. This method indicates that the area of 1 gram of charcoal is 120 sq. metres. The magnitude of the heat of immersion of liquids on mercury is 3.3×10^{-6} cal. for octane and 3.25×10^{-6} cal. for isobutyl alcohol.

J. F. S.

The Origin of the Potential Differences Responsible for Anomalous Osmosis. JACQUES LOEB (*J. Gen. Physiol.*, 1921, 4, 213—226).—If a collodion bag, coated on the inside with protein (gelatin) separate two identical acid solutions and a neutral salt be added to the inside, the rate of diffusion inwards through the membrane is a minimum at the isoelectric point of the protein, increases with the acidity to a maximum, and then decreases. The potential difference between the two solutions varies similarly. In the absence of protein, these characteristic variations are not obtained. The anomalous variation of the potential difference is apparently a consequence of the Donnan equilibrium between solution and protein, and this potential difference causes electrical endosmosis, and hence the irregular rates of diffusion. The potential difference is also influenced by the diffusion potential, but this exists although no protein is present.

W. O. K.

Penetration of Electrolytes into Gels. III. Influence of the Concentration of the Gel on the Coefficient of Diffusion of Sodium Chloride. WALTER STILES and GILBERT SMITHSON ADAIR (*Biochem. J.*, 1921, **15**, 620—626).—The coefficient of diffusion from normal solution into gelatin and agar gels was measured by the indicator method previously described (A., 1920, ii, 235). With increasing concentration of gel, the coefficient of diffusion at first decreases rapidly according to an exponential relation, but with concentrations above 2% the curve connecting coefficient of diffusion and concentration is approximately a straight line. It is shown how this result can be harmonised with the relation between diffusion and viscosity found by Einstein, Sutherland, and von Smolukowski. The diffusion coefficients found when extrapolated for diffusion in water are about 7.5% higher than those obtained from the results of Öholm (A., 1905, ii, 147). This is attributed to the fact that in Öholm's experiments the salt concentration refers to ionised + un-ionised salt, whereas the authors measure only the rate of penetration of the ions, which diffuse about twice as fast as the un-ionised salt.

The resistance which even a stiff jelly offers to salt diffusion is quite small; the rate is reduced by less than 2% for each gram of gelatin added to 100 c.c. when the concentration exceeds 2%.

G. B.

Penetration of Electrolytes into Gels. IV. Diffusion of Sulphates. WALTER STILES (*Biochem. J.*, 1921, **15**, 629—635).—In 0.5% agar, ammonium, potassium, sodium, and magnesium sulphates diffuse almost as fast as in pure water. In 10% gelatin, the rate is decreased by about 25%. The diffusion coefficient of copper sulphate in agar is considerably greater than in water, and in 10% gelatin less than in water, but still greater than the values for other sulphates indicate. The abnormal results of von Fürth and Bubanović (A., 1920, ii, 94) have not been confirmed. The comparatively small uptake of sulphates by plant tissue is not to be explained on the basis of retarded diffusion through a gel.

G. B.

A General Theory of Solutions of Electrolytes. JNANENDRA CHANDRA GHOSH (*Z. physikal. Chem.*, 1921, **98**, 211—238).—A theoretical paper in which the author develops a new theory of electrolyte solutions on the basis (i) that in solutions of strong electrolytes only ions exist, and (ii) in solutions of weak electrolytes or those of medium strength there exists an equilibrium between a non-polar form (non-electrolyte) and a polar form (which behaves as a strong electrolyte). This hypothesis is examined in connexion with the data obtained in recent years on electrical conductivity, activity coefficients, conductivity in non-aqueous solvents, influence of salts on solubility relations, absorption of light by salt solutions, and the relation between osmotic pressure and activity coefficients.

J. F. S.

Theory of Strong Electrolytes. H. KALLMANN (*Z. physikal. Chem.*, 1921, **98**, 433—437).—A number of criticisms of Ghosh's

hypothesis of solutions of electrolytes (T., 1918, 113, 449, 627, 707, and preceding abstract) are put forward. J. F. S.

Solubilities in Mixtures of Two Solvents. GEORGE PUCHER and WILLIAM M. DEHN (*J. Amer. Chem. Soc.*, 1921, 43, 1753—1758; cf. A., 1917, ii, 445).—The solubility of forty-five organic substances has been determined at 20—25°, in ethyl alcohol, quinoline, and equimolecular mixtures of the two solvents. In some cases, the solubility in the mixed solvent lies either above or below that in the individual solvents; this is most marked in the case of carbamide, "saccharin," *p*-nitrophenol, acetanilide, resorcinol, piperine, cinnamic acid, and chloral hydrate and in all these cases compound formation is indicated. The solubility of carbamide, "saccharin," brucine, and *o*-nitrophenol in a series of mixtures of alcohol and quinoline has been determined at 25°, and the solubility of lactose at 1° and 25° and raffinose at 25° in a series of mixtures of water and pyridine has also been determined. It is shown that the solubility of carbamide decreases quite regularly as the concentration of quinoline increases, but at 60% quinoline a break occurs and the compound of one molecule of quinoline and three molecules of carbamide is formed, m. p. 154°. Compound formation is indicated in the case of "saccharin," brucine, lactose, and raffinose, but no definite compound was isolated. J. F. S.

Compound Formation and Viscosity in Solutions of the Types Acid-Ester, Acid-Ketone, and Acid-Acid. JAMES KENDALL and ELIZABETH BRAKELEY (*J. Amer. Chem. Soc.*, 1921, 43, 1826—1834; cf. Kendall and Gross, this vol., ii, 32, 33).—The viscosity-composition curves at 25° have been determined for the systems trichloroacetic acid-ethyl acetate, acetic acid-ethyl acetate, trichloroacetic acid-ethyl benzoate, acetic acid-ethyl benzoate, trichloroacetic acid-acetone, acetic acid-acetone, trichloroacetic acid-acetophenone, acetic acid-acetophenone and trichloroacetic acid-acetic acid. The results obtained indicate extensive compound formation in solutions of the esters and ketones with a strong acid (trichloroacetic). The same substances with a weak acid (acetic) give viscosity curves which are much less abnormal, although compound formation is still evident. The curve for the system acetic acid-trichloroacetic acid exhibits considerable compound formation and an examination of the results of previous workers on systems of the types acid-acid and acid-base shows that this behaviour is general except when the components are of similar acidic strength. The rules formulated in previous papers relating to the extent of compound formation with diversity in character of the components are confirmed by the present work. J. F. S.

Compound Formation and Conductivity in Systems of the Types Formic Acid-Metal Formate and Sulphuric Acid-Metal Sulphate. JAMES KENDALL, HOWARD ADLER, and ARTHUR W. DAVIDSON (*J. Amer. Chem. Soc.*, 1921, 43, 1846—1853; cf. preceding abstract).—Electrical conductivity determinations

have been made of solutions of various concentrations of barium, magnesium, and lead formates in anhydrous formic acid at 25°, and of solutions of sodium, barium, calcium, magnesium, zinc, lead, and silver sulphates in anhydrous sulphuric acid. In this case, the solutions contained 0.04 equivalent of solid sulphate. Comparing the results for the formates with those obtained for other formates in formic acid by Schlesinger (A., 1919, ii, 91; 1920, ii, 72, 73), it is shown that a definite parallelism exists between the degree of ionisation and the extent of compound formation. In the case of the sulphates, however, the uncertainty of the correction to be applied for the solvent is so great as to obscure the results. Variations in compound formation, solubility, and ionisation in systems of the general type $HX-RX$ are all more extreme the weaker the acidic radicle X . Hydroxides in aqueous solution differ more widely than formates in formic acid, and these are more diverse than sulphates in sulphuric acid solution. J. F. S.

The Photography of Opaque Crystals. M. FRANÇOIS and CH. LORMAND (*Bull. Soc. chim.*, 1921, [iv], 29, 1056—1059).—The application of the apparatus previously described for the photography of transparent crystals (cf. A., 1921, ii, 626) to the photography of opaque crystals is given in detail. W. G.

Stereoscopic Photography of Crystals. M. FRANÇOIS and CH. LORMAND (*Bull. Soc. chim.*, 1921, [iv], 29, 1059—1063).—For this purpose, a microscope, the tube of which can be inclined successively to the left and right, is used. It is fitted with the apparatus previously described for the photomicrography of crystals (cf. A., 1921, ii, 626, and preceding abstract). A photograph is taken with the tube inclined to the left and then one with it inclined equally to the right. The examination of the two photographs in a stereoscope gives a stereoscopic picture of the crystals in relief. W. G.

Ionic Properties and Crystallo-chemical Relationships. I. The Properties of the Ions which appear in Crystals. H. GRIMM (*Z. physikal. Chem.*, 1921, 98, 353—394).—A theoretical paper in which it is shown that the electrostatic action of the ions in crystals is due to the following ionic properties, (i) the charge of the ions, (ii) the radius of the ions, (iii) the structure of the ions, particularly the surface and number of exterior electrons. The ions are divided into five principal groups depending on the number of exterior electrons. (i) Ions of the helium type (2 exterior electrons), (ii) ions of the Ne, Ar, Kr, Xe, and emanation type (8 exterior electrons), (iii) ions of the Cu^+ , Ag^+ , Au^+ type (probably with 18 exterior electrons), (iv) ions of the Te^{+} and Pb^{++} type, (v) ions of the type Mn^{++} , Fe^{++} , Co^{++} , Ni^{++} (transition ions). It is shown from many compounds and elements that the expression $\phi_A - \phi_{Ne} > \phi_{Xe} - \phi_{Kr} > \phi_{Kr} - \phi_A$ holds for many physical properties where ϕ is the numerical value of the property and the index is that of the inactive gas the structure of which comes nearest to that of the ion concerned. This inequality is due to an analogous inequality of the ionic radii. The ionic radii of O^{--} , S^{--} , Se^{--} , Te^{--} ; Mg^{++} , Ca^{++} , Sr^{++} , Ba^{++} have been calculated and that

of Cs^+ has been approximated. The series order of the other ionic radii has been deduced from the molecular volumes of isomorphous compounds in which the interchangeable ions have the same number of exterior electrons. Ions with different structures and different exterior sheaths show a similar electrostatic action when the difference in the ionic radius compensates the other properties.

J. F. S.

Structure of Organic Crystals. SIR W. H. BRAGG (*Proc. Physical Soc.*, 1921, **34**, 33—50).—The author has determined the X-ray spectra of naphthalene, α -naphthylamine, benzoic acid, acenaphthene, β -naphthol, and α -naphthol by the powder method. To interpret the results, he has made the assumption that the benzene and naphthalene rings are actual structures having definite size and form, and that they are built as a whole into the organic substances in which they occur. It is shown from crystallographic and other data that this hypothesis is an extremely probable one, and it leads to results which are in excellent agreement with crystallographic data. It is shown that the unit cell of naphthalene contains two molecules and has a mass of 213 Å.U., where 1 Å.U. = 10^{-24} grams, the linear dimensions of the cell are $a=8.34$, $b=6.05$, and $c=8.69$ Å.U. Two molecules of anthracene occupy the unit cell, and this has the linear dimensions $a=8.7$, $b=6.1$, and $c=11.6$ Å.U. The unit cell of acenaphthene contains four molecules, and has linear dimensions 8.32, 14.15, and 7.26 Å.U., respectively, whilst α -naphthol has a unit cell which also contains four molecules and has linear dimensions $a=13.1$, $b=4.9$, and $c=13.4$ Å.U.; the same number of molecules occupy the unit cell of β -naphthol and here the linear dimensions are $a=5.85$, $b=4.28$, and $c=8.7$ Å.U. The unit cell of α -naphthylamine also contains four molecules, and has the dimensions $a=8.62$, $b=14.08$, and $c=7.04$ Å.U. Benzoic acid has a wide spacing between the planes, the unit cell contains four molecules and has the dimensions $a=5.44$, $b=5.18$, and $c=21.8$ Å.U. In a note the author stated, "It is convenient in this work to extend the Ångström system of units so that an Å.U. of area is 10^{-16} cm.², of volume 10^{-24} cm.³ and of mass 10^{-24} grams." J. F. S.

Röntgen Spectroscopic Investigation of Organic Compounds. I. and II. K. BECKER and W. JANCKE (*Z. physikal. Chem.*, 1921, **99**, 242—266, 267—274).—In the first part an account is given of the X-ray examination of the structure of a number of organic substances. The substances were examined in the form of compressed pastilles by a method which is a combination of that due to Bragg and Debye-Scherrer. In the case of indigotin it is found that the unit cell is an hexagonal parallelopiped with a rhombus as base of edge 19.55 Å.U. and height 11.80 Å.U. This contains 12 indigotin molecules. The figures refer to indigotin which has been subjected to a pressure of 4000—5000 atoms. Indigotin which has not been so compressed has a unit crystal cell with the linear dimensions $a=b=20.20$ Å.U., $c=12.15$ Å.U., which means that there is a volume contraction of 9.8%, the base decreases 3.2% and the height 2.9%. Carbamide has a unit cell

of dimensions $a=b=8.75 \text{ \AA.U.}$, $c=7.24 \text{ \AA.U.}$, and contains 8 molecules. The unit cell of succinic acid contains 2 molecules and has dimensions $a=5.00 \text{ \AA.U.}$, $b=8.20 \text{ \AA.U.}$, $c=5.40 \text{ \AA.U.}$, $\beta=94.70^\circ$. Compression reduces all values, the c value relatively most, the values being: volume 10.3%, a 2.2%, b 4.8%, and c 5.4%. Measurements are recorded for quinol, quinone, anthraquinone, anthracene, naphthalene, phenanthrene, resorcinol, phthalic anhydride, phthalic acid, cinnamic acid (*trans*), β -phenylpropionic acid, azobenzene, hydrazobenzene, lithium oxalate, maleic acid, succinic acid, maleic acid, *d*- and *l*-tartaric acids, pentaerythritol, α -methylglucoside, and acetylenedicarboxylic acid. The results show that the number of molecules in the unit crystal cell is always greater than one, and is not the same for nearly related substances such as maleic acid and succinic acid. In the second paper, the results of X-ray examination of a large number of aliphatic acids are given. The results are arranged in four groups. I. Acids with an odd number of carbon atoms, formic, propionic, valeric, heptonic, nonic, undeconic. II. Acids with an even number of carbon atoms, acetic, butyric, octic, lauric, myristic, palmitic, stearic (also $\alpha\alpha'$ -distearin). III. Isomeric acids, *isobutyric*, *isovaleric*, trimethylacetic. IV. Unsaturated acids, crotonic, undecenoic, oleic, and elaidic. In many cases, the acids were measured as their lithium salts. It is shown in the case of the even-number saturated acids apart from the first two members that they possess an hexagonal symmetry with 72 molecules in the unit crystal, or possibly rhombohedral with 24 molecules; the uneven-number acids are tetragonal with 24 or 48 molecules in the unit cell. There is no fundamental difference between the free acids and the lithium salts.

J. F. S.

Mixtures of Anisotropic Liquids and the Identity of Grandjean's Stratified Liquids with Liquids of the Azoxyphenetole Type. G. FRIEDEL and L. ROYER (*Compt. rend.*, 1921, 173, 1320—1322; cf. Grandjean, A., 1921, ii, 91).—In the case of mixtures of substances capable of furnishing anisotropic liquids, the two phases, the conic and thread-like (*liquides à coniques et liquides à fils*), are perfectly distinct and separated from one another by an absolute discontinuity. Mixtures of Grandjean's stratified liquids with other anisotropic liquids always show an absolute discontinuity between the stratified liquid and the conic phase. On the other hand, these mixtures do not show any discontinuity between the thread-like phase, and the stratified liquid of Grandjean. It is suggested, therefore, that Grandjean's stratified liquids are only a special aspect of the thread-like liquids of the type of azoxyphenetole.

W. G.

Some Fundamental Conceptions of Colloidal Chemistry. RICHARD ZSIGMONDY (*Z. physikal. Chem.*, 1921, 98, 14—37).—A theoretical paper in which the nature of matter in the colloidal condition is considered. The views put forward by Nägeli ("Gärung," Munich, 1879) on the nature of micellæ are considered, and it is shown that in general these views are in keeping with

experimental data. The conceptions to be generally adopted are expressed as follows: by micellæ in its broadest sense is to be understood a molecular complex of the dispersed material, which is not permeated by the dispersion medium. In the narrower sense, micellæ are crystalline, ultramicroscopic particles of the dispersed material. Micellar complexes are formed by the association of micellæ, and are ultramicroscopic particles generally, but in isolated cases may be microscopic. According to the form of the association, micellar complexes form, on the one hand, microscopic or ultramicroscopic particles which are permeated by the dispersion medium, or, on the other, ultramicroscopic or microscopic swelling crystals.

J. F. S.

An Interesting Colloid Gel. ROSS AIKEN GORTNER and WALTER F. HOFFMAN (*J. Amer. Chem. Soc.*, 1921, **43**, 2199—2202).—Dibenzoylcystine is insoluble in water and in the crystalline state has no hydrophilic properties, but it can give rise to rigid gels which do not contain more than 0.2% of dibenzoyl-*l*-cystine. The 0.2% gel is prepared by dissolving 0.2 gram of dibenzoyl-*l*-cystine in 5 c.c. of 95% alcohol. The solution is heated and water added to make the solution up to 100 c.c. After cooling for two to three hours, the solution sets to a gel comparable with that of a 5% gelatin gel. The gel is transparent, but after several days opaque nuclei are formed, due to crystallisation, which is accompanied by syneresis, and after several weeks most of the dibenzoyl-*l*-cystine has separated in definite crystals. On applying strong suction, the liquid may be drained from the gel, thus showing the coarse dispersion. The gel has a fibrillar structure.

J. F. S.

Coagulation of Colloidal Solutions of Arsenious Sulphide by Electrolytes. E. F. BURTON and E. D. MACINNES (*J. Physical Chem.*, 1921, **25**, 517—525).—The coagulation of solutions of arsenic sulphide sols of concentrations 0.027 gram per c.c. to 0.00337 gram per c.c. by means of potassium, lithium, magnesium, barium, aluminium, and zirconium chlorides, lanthanum sulphate, and cerium nitrate of various concentrations has been investigated. It is shown in the case of aluminium chloride that the volume of the electrolyte required for coagulation of a given amount of the disperse phase varies inversely as the concentration of the electrolyte solution, provided the final concentration of the colloid is kept constant. For univalent ions, it is shown that the concentration of ion necessary to produce coagulation increases with decreasing concentration of the colloid, whilst for bivalent ions the concentration of ion required to produce coagulation is almost constant and independent of the concentration of the colloid. With trivalent ions, the concentration of ion required to produce coagulation varies almost directly with the concentration of the colloid, whilst quadrivalent ions necessary for coagulation decrease much more rapidly than the concentration of the colloid. These results are in keeping with earlier results of Burton and Bishop (*A.*, 1921, ii, 176). It is also shown that the coagulation curve for barium chloride shows

a tendency to resemble the curve for tervalent ions as given by aluminium chloride, whilst the curve for the quadrivalent zirconium ion differs from that of the ceric ion, which is similar to that for tervalent ions.

J. F. S.

Acidity and Basicity. RUDOLF KELLER (*Z. physikal. Chem.*, 1921, **98**, 338—351).—A theoretical paper in which the terms acidity and basicity are considered. It is shown for the determination of the acidity of a combination solute-solvent, or the sense of the electric charge, not only the inner chemical constitution of the dissolved substance is to be considered, but also the chemical constitution of the solvent, which may, in the case of substances which are nearly amphoteric, be determinative. Further, the difference in the dielectric constants of the solvent and solute must be considered; this quantity makes its influence noticeable in the case of amphoteric, non-ionised, and associated solutes. The so-called basic dyes in aqueous solution usually migrate toward the anode, that is, they are acid according to the ruling terminology; this is particularly so in the case of the slightly dispersed and non-dissociated colour colloids; the so-called acid dyes are for the greater part basic or amphoteric. Certain acid dyes, such as picric acid, Martius-yellow, aurantia, are really acid, that is, negative, and wander to the anode. The capillary rule of Fichter-Sahlbom is generally correctly expressed in the literature, but incorrectly defined, since it places the dyes in the incorrect position in the electro-polarity series. All the experimental capillarity experiments show that immediately on dipping the paper strips, the neutral and positive dyes rise with the solvent. In this correct form, the rule holds, not only for colloids, but also for ion-dispersoids. Gobbelsröder ("Kapillaranalyse," Dresden, 1910) has actually found the strongest acids below in the anode region. The strongest acids and bases, such as hydrochloric and sulphuric acids and potassium hydroxide in suitable solvents, migrate in directions which are opposed to their nature. Concentration cells may be built up in which the strongest acids behave as bases. J. F. S.

Homogeneity and Dispersity. WA. OSTWALD (*Z. physikal. Chem.*, 1921, **99**, 155—159).—A theoretical paper in which the conception specific surface is investigated on the basis of the phase rule.

J. F. S.

Reactions in Heterogeneous Systems. The Systems $K_2CO_3|BaSO_4-K_2SO_4|BaCO_3$; $K_2CO_3|CaC_2O_4-K_2C_2O_4|CaCO_3$ and $K_2CrO_4|AgIO_3-KIO_3|AgCrO_4$. E. RAMANN and H. SALLINGER (*Z. physikal. Chem.*, 1921, **98**, 103—150).—The systems named in the title have been experimentally investigated. By the addition by barium chloride solution to an excess of a mixture of potassium carbonate and potassium sulphate solution, the relation in which barium divides itself between the carbonate and the sulphate ions has been approximately determined. This ratio, $[CO_3'']:[SO_4'']$, is termed the precipitation equilibrium. In the

case of the addition of silver nitrate solution to an excess of the mixed solutions of potassium iodate and chromate, the original equilibrium partition of the silver takes place according to the anion ratio, $[\text{IO}_3'] : [\text{CrO}_4''/2]$, as in the previous case, but the two equilibria differ to an extraordinary degree in stability. Whilst the first can be approximately fixed by the rapid addition of alcohol, the second can only be fixed by a special experimental procedure. In the system $x\text{K}_2\text{CO}_3 + y\text{K}_2\text{C}_2\text{O}_4 + z\text{CaCl}_2 (z < x + y)$, the precipitation equilibrium could not be fixed by the addition of alcohol. The precipitation equilibrium in general is labile, inasmuch as immediately after the precipitation a reaction is set up which brings about a change in the relationship of the salts in the solid phase and leads to the formation of one of the salts (solution equilibrium). The solution equilibrium has been determined for various concentrations for the system $\text{K}_2\text{CO}_3|\text{BaSO}_4\text{--K}_2\text{SO}_4|\text{BaCO}_3$; for the system $\text{K}_2\text{CO}_3|\text{CaC}_2\text{O}_4\text{--K}_2\text{C}_2\text{O}_4|\text{CaCO}_3$, at various total potassium salt concentrations and various temperatures and for the system $\text{K}_2\text{CrO}_4|\text{AgIO}_3\text{--KIO}_3|\text{Ag}_2\text{CrO}_4$ at various total salt concentrations and one temperature (20°). In the system $\text{K}_2\text{CO}_3|\text{BaSO}_4\text{--K}_2\text{SO}_4|\text{BaCO}_3$, the partition relationship $\text{K}_2\text{CO}_3|\text{K}_2\text{SO}_4$ shows a marked dependence on the total salt concentration. No measurements were made on the temperature influence on this ratio. In the system $\text{K}_2\text{CO}_3|\text{CaC}_2\text{O}_4\text{--K}_2\text{C}_2\text{O}_4|\text{CaCO}_3$, the partition relationship $\text{K}_2\text{CO}_3|\text{K}_2\text{C}_2\text{O}_4$ is but slightly influenced by the total salt concentration but very strongly influenced by temperature. The ratio $\text{K}_2\text{CO}_3|\text{K}_2\text{C}_2\text{O}_4$ is shown to be a strict linear function of the temperature. The data obtained for the systems investigated and those obtained by Knüpfner (A., 1898, ii, 420) for the system $\text{KCNS}|\text{TiCl--KCl}|\text{TiCNS}$ and by Noyes and Kohr (A., 1903, ii, 201) for the system $\text{KOH}|\text{AgCl--KCl}|\text{AgOH}$ have been examined by means of the formula put forward by Nernst and Noyes (A., 1891, ii, 142).

J. F. S.

Studies on Chemical Affinity. XIII. Reaction Affinity in Systems of Solid Salts. J. N. BRÖNSTED (*Z. physikal. Chem.*, 1921, 98, 239—243).—In earlier papers (A., 1920, ii, 290, 298), a method was described whereby the reaction affinity between very soluble solid salts might be determined. This method does not yield the required results when applied to sparingly soluble salts. In the present paper, a method is described for the determination of the reaction affinity in systems of sparingly soluble solid salts. The method has been applied to the reaction $[\text{CoCl}(\text{NH}_3)_5]\text{Br}_2 + [\text{CoBr}(\text{NH}_3)_5]\text{Cl}_2 \rightarrow [\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2 + [\text{CoBr}(\text{NH}_3)_5]\text{Br}_2$ and consists in determining the solubility of the four cobalt complex salts in mixtures of (i) potassium formate and chloride solution, (ii) potassium formate and bromide, (iii) sodium chlorate and chloride, and (iv) sodium chlorate and potassium bromide, where the total alkali concentration is $0.5N$ in each case. Then from the solubility products of the four cobalt complex salts by means of the gas laws the reaction affinity may be calculated. The results of the experiments lead to the value $A_0 = 621$ cal. for $T = 273^\circ$, a value

which is probably accurate to 1%. The system is characterised by the fact that the lighter ions are combined with the lighter ions and the heavier ions with the heavier.

J. F. S.

The Velocity of Decomposition of High Explosives in a Vacuum. III. Mercuric Fulminate. ROBERT CROSBIE FARMER (T., 1922, 121, 174—187).

Sensitiveness of Very Sensitive Explosives. J. EGGERT (Z. Elektrochem., 1921, 27, 547—558).—The sensitiveness of a number of explosives, including the iodides of nitrogen, has been experimentally investigated. The results show that the intermolecular decomposition of nitrogen iodide takes place according to the equation $8\text{NH}_3\text{NI}_3 = 5\text{N}_2 + 6\text{NH}_4\text{I} + 9\text{I}_2$, whether the decomposition takes place in the dark or in light or is occasioned by detonation. Nitrogen iodide is not sensitive to shock, and many effects which were previously attributed to detonation are now shown to be secondary mechanical effects. The sensitiveness of nitrogen iodide and silver amide is not materially changed by lowering the temperature to -190° . Gradual isothermal increase of pressure to 5000 atm. brings about a decomposition in 70% of the cases of nitrogen iodide or silver amide, but all other explosives examined are unchanged by this treatment. An attempt is made to find an explanation of the sensitiveness of explosives; since earlier experiments have shown that the mechanical effects are not to be explained as secondary temperature effects, there only remains the possibility that local increases of pressure occur with all mechanical influences and these are to be regarded as causing the detonation. This view is supported by the present experiments on the behaviour of the sensitiveness with increase of pressure. A consideration of the processes occurring during the decomposition of explosives from the point of view of Herzfeld's theory of velocity of chemical reaction leads to a possible explanation of some of the properties of these substances. In this connexion, the primary, generally very simple, unimolecular decomposition of the explosive, which depends on the persistence of the molecule alone, is to be differentiated from the accompanying, at least bimolecular reaction, due to the collision between the products of reaction of the primary process. If in the primary reaction products are formed which possess more energy and a greater persistence than the original substances, or if, following on the primary process, other processes which are subjected to several negative accelerations occur, then there will be no marked tendency to detonation. But if, on the other hand, the primary reaction leads to the stable end products of the reaction, or if these products undergo other reactions with no retardations or at most only one retardation, then the explosive is one which has a high sensitiveness and a great tendency to detonation. Pressure is the factor which removes the retardation to the reactions, since it causes the atoms, molecules, and atomic groupings which have affinities for one another to come closer together.

J. F. S.

The Autoracemisation of Potassium Chromioxalate. ERIC KEIGHTLEY RIDEAL and WILLIAM THOMAS (T., 1922, **121**, 196—202).

Neutral Salt Action, at Higher Salt Concentrations; the Velocity of Hydrolysis of Ethyl Acetate, and the Hydrogen-ion Activity of the Catalyst. GÖSTA ÅKERLÖF (*Z. physikal. Chem.*, 1921, **98**, 260—292).—The velocity of hydrolysis of ethyl acetate by 0.05*N*-solutions of hydrochloric, sulphuric, and nitric acid at 25° has been determined in the presence of various concentrations of the chlorides of ammonium, potassium, sodium, magnesium, calcium, and barium, the nitrates of ammonium, potassium, sodium, magnesium, and calcium, and the sulphates of ammonium, potassium, sodium, and magnesium. The hydrogen-ion activity of the catalyst in the various reaction mixtures has been determined by means of *E.M.F.* measurements. An attempt is made to ascertain the cause of the neutral salt action on the velocity of hydrolysis at constant acid concentration by combining the velocity measurements with the hydrogen-ion activity. A relationship between these two quantities is furnished by the formula $K = C\alpha \cdot f(n)\sqrt{\alpha}$, in which K is the reaction velocity, n the acid titre, and α the hydrogen-ion activity. The formula holds for all concentrations of catalyst, and is not influenced by the nature or concentration of the added salt, as far as the present experiments go. This formula is probably also true for the inversion of sucrose and allied reactions. The foregoing shows that the hypothesis of the catalytic activity of the non-ionised molecule is incorrect. The salt molecules have no activity of their own, but they are the cause of the change of activity of the catalyst. Exactly how the neutral salt changes the activity of the catalyst is not known with certainty, but the most probable hypothesis is that the water sheath of the hydrogen ion is changed by the addition of neutral salts. The concentration of the hydrogen ion remains constant whilst the activity changes. According to this view, the hydration numbers do not represent definite quantities, but the ions control all the water molecules in the solution. The various neutral salt actions are controlled by the various forces with which the different ions attract the water molecules. J. F. S.

Velocity of Hydrolysis of Acetals. ANTON SKRABAL and ANTON SCHIFFRER (*Z. physikal. Chem.*, 1921, **99**, 290—313).—The velocity of hydrolysis of methylene dimethyl ether, methylene diethyl ether, ethylidene diethyl ether, methylene diacetate, and ethylidene diacetate has been investigated. The reactions were carried out with hydrochloric acid of various concentrations, (0.001—0.3*N*), and also in alkaline solution. It is shown that the measured velocity constants represent the velocity of hydrolysis of the first ether group; the removal of the second group is much more rapid, and is regarded as a water hydrolysis. The velocity constants vary very much for the different cases, thus for the acid hydrolysis the value of k_a is 70,000 for methylene diethyl

ether, whilst for ethylidene diacetate it is 0.00650, whilst in the case of alkaline hydrolysis the value of k is 1,100 for methylene diacetate and 96 for ethylidene diacetate. In the case of the hydrolysis of esters it is shown that the velocity depends largely on the nature of the acid but very little on the nature of the alcohol. These rules are established from the published data of a number of authors.

J. F. S.

Velocity of Hydrolysis of Sucrose. R. H. CLARK (*J. Amer. Chem. Soc.*, 1921, **43**, 1759—1764).—The velocity of hydrolysis of sucrose by hydrochloric, hydrobromic, sulphuric, or nitric acid has been determined at 25°. The experiments were effected in the presence of acids of varying concentration and in the presence of potassium nitrate and dextrose. It is shown that the addition of a neutral substance, to keep the concentration of the water constant while varying the concentration of the acid, has no appreciable effect in producing a numerical proportionality between the quantity of hydrogen ions present and the inversion velocity of sucrose. The increase in the velocity of hydrolysis of sucrose produced by a strong acid in the presence of a neutral salt of that acid over the velocity produced by the acid alone can only to a small extent be attributed to the fact that the volume of the reaction is reduced by the presence of the salt. On the assumption that both the dissociated and undissociated forms of an acid are catalytically active in sucrose inversion, the values of K_i for the hydrogen ion from hydrochloric, hydrobromic, and nitric acids have the same value ($K_i=0.234$); the corresponding value for sulphuric acid is considerably lower ($K_i=0.144$).

J. F. S.

Affinity Dimensions of Weak Acids and Bases in Alcoholic Solution and the Alcoholysis of their Salts. HEINRICH GOLDSCHMIDT, CARL GÖRBITZ, HAAKON HOUGEN, and KRISTIAN PAHLE (*Z. physikal. Chem.*, 1921, **99**, 116—154).—The theory of the alcoholysis of salts of weak acids with bases of the aniline type in anhydrous alcohol and in alcohol containing water is developed. A method of determining the degree of alcoholysis based on electrical conductivity measurements is described. The electrical conductivity of a series of sodium, aniline, and ammonium salts in pure and in aqueous alcohol has been determined. The affinity dimension of several organic acids in alcohol solution has been determined. The alcoholytic constant of eleven aniline salts has been measured and from the results the affinity constant K_β , corresponding with the equilibrium $(\text{Aniline} \times \text{H}^+)/\text{Aniline ion}$, has been calculated. The same quantity has been determined for the three toluidines and mono- and di-methyl anilines. The influence of water and the alcoholytic constants has been investigated.

J. F. S.

The Rate of Solution of Iron in Dilute Sulphuric Acid both when Stationary and under Rotation. JOHN ALBERT NEWTON FRIEND and JOHN HORACE DENNETT (*T.*, 1922, **121**, 41—44).

Theory of Catalysis in Homogeneous Gas Reactions. KARL F. HERZFELD (*Z. physikal. Chem.*, 1921, **98**, 161—174).—A theoretical paper in which an attempt is made to answer the question, "Why does a reaction proceed more rapidly through an intermediate product than by the direct action?" It is shown that since at equal concentration the slowest of all the partial reactions is determinative of the velocity of the whole process, this slowest reaction must proceed more rapidly than the original reaction when catalysis occurs. After a short review of the previously published theoretical work on gas reactions, the author considers such reactions in a way which assumes the existence of a few free atoms. Then for catalysis it is necessary that at not too small concentrations of the catalyst the heat of activation of the intermediate product (that is, practically its heat of formation from atoms) is markedly smaller than that of the starting material; in the best case about one-half. This gives then an upper limit for the acceleration which at not too high concentrations may be reached by a given catalyst. Examples on which to test the hypothesis are not known.

J. F. S.

Catalytic Oxidation of Carbon Monoxide. T. H. ROGERS, C. S. PIGGOT, W. H. BAHLKE, and J. M. JENNINGS (*J. Amer. Chem. Soc.*, 1921, **43**, 1973—1982).—The present work was undertaken with the object of finding a catalyst which will completely oxidise carbon monoxide at ordinary temperatures. A number of such catalysts have been prepared which cause rapid and complete oxidation. The chief of the catalysts obtained is a specially prepared manganese dioxide on which is precipitated the oxide of silver or copper or both. The silver or copper is best precipitated as the carbonate and subsequently hydrolysed to the hydroxide. The presence of water vapour limits the life of these catalysts. The decomposition temperature of silver oxide when simultaneously precipitated with calcium hydroxide is considerably lower than that of silver oxide alone.

J. F. S.

Catalytic Oxidation of Carbon Monoxide at Ordinary Temperatures. DAVID R. MERRILL and CHARLES C. SCALONE (*J. Amer. Chem. Soc.*, 1921, **43**, 1982—2002).—A number of catalysts for use in protective masks against carbon monoxide are described. The most successful are mixtures containing manganese dioxide and basic copper carbonate and manganese dioxide, copper oxide, cobaltic oxide, and silver oxide, respectively. These mixtures oxidise carbon monoxide rapidly and at ordinary temperatures, and, when protected by a drying agent such as calcium chloride, are suitable for use in protective masks against carbon monoxide of all concentrations below those in which an oxygen helmet would be necessary. The factors influencing activity, such as the constituents of the mixtures, the conditions of precipitation, the mechanical treatment of the precipitate, and method of drying, are discussed and a description is given of the efficiency of the mixtures under various conditions.

J. F. S.

Oxidation Catalysis. II. L. KARCZAG (*Biochem. Z.*, 1921, **119**, 16—22).—Experiments with dyes at high dilutions show that the ferrous ion catalyses oxidation with hydrogen peroxide much faster than the ferric ion. The order of mixing is of influence, the controlling factor being whether the ferrous ion is first oxidised to ferric or not.
H. K.

Electronic Theory of the Interior of the Atom. A. D. FOKKER (*Arch. Néerland.*, 1921, **5**, [iiiA], 193—242).—A mathematical paper in which it is shown that the application of the electronic theory to the mutual actions of the electrons inside the atom gives results which are in accordance with experimental observations.
J. F. S.

Theory of Allotropy. MAURICE COPISAROW (*J. Amer. Chem. Soc.*, 1921, **43**, 1870—1888).—Allotropy is defined as the capacity of an element to exist in forms differing in the mode of their intramolecular linking. It is therefore a function of the valency, but it does not imply isomerism or polymerism, since allotropes need not contain the same or a multiple number of atoms in their respective molecules. The number of possible forms in which an element can exist on this basis is indicated for the elements of all valencies. It is theoretically possible for an element to have in certain cases more than one molecular form corresponding with each mode of linking. Regarding allotropes as the most chemically and physically distinct forms of an element, it follows that several molecular forms, each containing a different number of atoms, but all having the power of free rotation, will differ among themselves to a less extent than when compared with a molecular structure of the same element in which all atoms are rigidly fixed. Thus it follows that valency and the saturation or fixation of atoms, and not the actual number of atoms, play the predominant part in the determination of allotropes. In this light, allotropy becomes the capacity of an element to exist in forms differing in the mode of their intramolecular linking. Molecular forms differing in the distribution of their intramolecular linking and in the number of atoms, but all belonging to one type of linking can be termed *allotropoids*. The allotropy of carbon, phosphorus, iron, and nickel are considered from the point of view of the hypothesis.
J. F. S.

Types of Valency. IRVING LANGMUIR (*Science*, 1921, **54**, 59—67; cf. *ibid.*, 1921, **53**, 290; *J. Ind. Eng. Chem.*, 1920, **12**, 386, and A., 1919, ii, 328; also Rydberg, A., 1915, ii, 94).—Recognition of three distinct types of valency, (a) positive valency (the number of electrons an atom can give up), (b) negative valency (the number of electrons an atom can take up), and (c) co-valency (the number of pairs of electrons an atom can share with its neighbours), as well as the numerical values, for most of the elements, of each type are shown by a simpler method than that hitherto employed to be derived from certain postulates regarding the structure of atoms, and the relationships between the different types of valency are thereby further clarified. On the basis of the

Rutherford atom, only three postulates, consistent with those previously proposed, are necessary: (a) The electrons in atoms tend to surround the nucleus in successive layers containing 2, 8, 8, 18, 18, and 32 electrons respectively (the extra electrons, if any, remaining in the outside layer as an incomplete layer or "sheath"). (b) Two atoms may be coupled together by one or more duplets (stable pairs of electrons forming the first complete layers) held in common by the completed sheaths of the atoms. A group of neutral atoms interacting by transfer of electrons gives rise to the conception of electrovalency, including positive and negative valency differing only in algebraic sign, whilst interaction by the sharing of duplets corresponds with co-valency. It is shown that the sum of the electrovalencies and co-valencies for all the atoms in any complete compound is zero, a complete compound being defined as one in which all the atoms possess complete layers of electrons. (c) The residual charge on each atom and on each group of atoms tends to a minimum. The term "residual charge" is employed to express the total charge of an atom or aggregate of proximate atoms regardless of sign. It is pointed out, however, that the first and third postulates are often in conflict, and that in such cases the tendency of the first may prevail against that of the third.

Chemical compounds are therefore classified according to the types of valency exhibited by their atoms as follows: (1) complete compounds, including (a) compounds without co-valency, such as certain simple metallic salts, volatile halogen compounds, silicates, and most minerals, and (b) compounds without electropositive atoms, such as organic compounds; (2) incomplete compounds, including metallic substances, and compounds such as zinc oxide, ferrous-ferrous oxide, lead sulphide, and cupric oxide, which contain both electropositive and electronegative atoms; (3) exceptional cases, including nitrogen, carbon monoxide, nitric oxide, and the cyanogen radical, the structure of which is not accounted for by this theory. These substances may have a single octet structure or possibly a triple bond structure. Other exceptions are boron hydride and certain other compounds forming double molecules.

A. A. E.

The Expression of the Octet Theory of Valence in Structural Formulæ. GRANVILLE A. PERKINS (*Philippine J. Sci.*, 1921, **19**, 1—22).—A system for writing structural formulæ is developed, based on the octet theory of valency as presented by Langmuir.

Electronegative valence, the physical interpretation of which is vacancy for one more electron in the outer shell of the atom, is represented by a line in the usual way. Electropositive valence, on the other hand, is variable and its maximum is represented by the total number of electrons in the shell. It cannot be represented by "unsatisfied bonds" as it never causes direct union between atoms, and is expressed as follows, for example, Na^+ , Ca^{++} . The neutral atoms having electronegative valence may satisfy that valence by acquiring an electron, that is, becoming

a negative ion; this electron may be obtained from the shell of an atom showing positive valence tendencies, and it is then left as a positive ion. These two oppositely charged ions may then form a stable compound by electrostatic attraction. Such a union is termed a salt-forming union and is expressed thus: $\text{Na}^+ \dots \text{Cl}^-$, or $\text{Ca}^{++} :::: \text{O}^{--}$. On the other hand, two atoms may be held together by the shell-completing forces of both atoms acting on one or more pairs of electrons, which are then shared between them. Each shell thus fills one or more electron vacancies by sharing electrons, and thus "satisfies" one or more "bonds." This is expressed in the usual way: $\text{H}-\text{H}$, $\text{H}-\text{O}-\text{H}$, etc., and is termed a direct union. All valency relations cannot, however, be expressed in terms of either of the above unions, and a special feature of the system is the introduction of the conception of a "borrowing direct union," for cases in which both the shared electrons are supplied by the same atom. In this case, the borrowing atom fills two vacancies in its shell, and the lending atom neither gains nor loses electrons; but the union is essentially polar, since the originally neutral borrowing atom has acquired at least an interest in two negative electrons and therefore becomes a negative pole. This relationship is expressed thus: $\text{H} \begin{array}{c} \text{H} \\ \text{H} \end{array} > \text{O} \propto \text{O}, \text{O}=\text{S} \propto \text{O}$,

indicating that the O atom is bound to S, or to O, by virtue of having its two electron vacancies filled by borrowing an interest in two of the shell electrons of the other oxygen atom in hydrogen peroxide, and in the sulphur atom of sulphur trioxide. The mode of application of the system to all the known elements is indicated in the original paper.

G. F. M.

The Thermos Flask in the Chemical Laboratory. CLAUDE W. BOURLET and WALTER THOMAS (*Chem. News*, **123**, 336).—The thermos flask can be utilised advantageously in the laboratory in numerous instances where it is desired to maintain substances above the normal temperature, as, for example, in reactions between liquids, or liquids and solids at elevated temperatures such as hot oxidation by permanganate and other similar reactions which are not strongly exothermic. Oil and water emulsions and similar mixtures are conveniently “split” by warming and keeping overnight in a thermos flask, and flocculent or colloidal precipitates can be dealt with in a similar manner. In carrying out certain colour tests, for example, the Halphen reaction, and reactions in media which gelatinise or become viscous at ordinary temperatures, a water-bath can with great advantage be replaced by the vacuum flask.

G. F. M.

Water Pump. JOHANNES WETZEL (*Chem. Ztg.*, 1921, 45, 1122).—A water pump of improved efficiency is described; particular attention is directed to the relative diameters of the injector tube and outlet tube and to the central position of the jet as regards the outlet tube. W. P. S.

W. P. S.

Inorganic Chemistry.

Separation of the Element Chlorine into Isotopes (Isotopic Elements). The Heavy Fraction from the Diffusion. WILLIAM D. HARKINS and ANSON HAYES (*J. Amer. Chem. Soc.*, 1921, **43**, 1803—1825).—By means of elaborate diffusion a definite increase in the atomic weight of chlorine has been obtained. The increase in atomic weight amounts in different experiments to from slightly less than to considerably more than one part in a thousand (1 in 645). The diffusion experiments were effected with hydrogen chloride, and a considerable amount of the isotopic acid has been obtained. The separation of isotopes by diffusion is discussed in terms of the Rayleigh diffusion equation, which applies to the diffusion into a vacuum. It is shown that for a high efficiency the pressure of the gas on both sides of the diffusion wall should be low, first to secure good mixing, and secondly to insure that the passage through the porous partition shall be entirely molecular. A rapid and precise method for the determination of the atomic weight of isotopic chlorine has been devised. It is found that in the separation of isotopes the percentages of the different isotopes present are as important factors as the atomic weight differences. Thus, contrary to what has been supposed, it is shown, even aside from the greater difficulties involved in obtaining and handling neon, that it is easier to produce a small increase in the atomic weight of chlorine (of the magnitude of 0.05 unit) than to produce the same increase in the atomic weight of neon. J. F. S.

Viscosities of the Hydrogen Haloids. H. HARLE (*Proc. Roy. Soc.*, 1922, [A], **100**, 429—440).—The viscosity of hydrogen chloride, bromide, and iodide has been determined by the method of transpiration through a capillary tube. Measurements were made at temperatures in the neighbourhood of 20° and 100°, and from the results the viscosity is calculated for 0° and 100° respectively. The following values in *C.G.S.* units are recorded: hydrogen chloride, $\eta_0 = 1.332 \times 10^{-4}$; $\eta_{100} = 1.837 \times 10^{-4}$; hydrogen bromide, $\eta_0 = 1.710 \times 10^{-4}$; $\eta_{100} = 2.365 \times 10^{-4}$; hydrogen iodide, $\eta_0 = 1.731 \times 10^{-4}$, $\eta_{100} = 2.403 \times 10^{-4}$. The values of *C*, the Sutherland constant, are 357, 375, and 390 for the three gases respectively. J. F. S.

Numerical Revision of the Data referring to the Density of Gaseous Hydrogen Bromide: Atomic Weight of Bromine. E. MOLES (*J. Chim. Physique*, 1921, **19**, 135—138).—The molecular weight of gaseous hydrogen bromide with reference to oxygen has been calculated to be 80.944, and from this the atomic weight of bromine is 79.936. If, however, the value for the weight of the normal litre of oxygen recently published (cf. following abstract) is used the atomic weight of bromine becomes 79.927. J. F. S.

Critical Study of the Modern Value of the Density of Gaseous Oxygen. E. MOLES (*J. Chim. Physique*, 1921, **19**, 100—120).—A discussion of the modern results for the density of oxygen leads to the value $L_0 = 1.42891 \pm 0.00003$ as the most probable value for the weight of the normal litre of oxygen. The value is deduced from 162 measurements made by nine workers using oxygen obtained from three different sources and by three essentially different methods. If only the most recent measurements by weighing a globe of the gas are considered the mean is $L_0 = 1.42894$. Up to this the value accepted was 1.42905, which can no longer be maintained, and although the difference is only 1 in 10,000, yet it cannot be neglected in the calculation of molecular weights. It is proposed that the value 1.42891 be accepted as the standard, and this in some cases may be rounded to 1.4289. If this value is calculated to the conventional value of g , $g = 980.665$ C.G.S. units then the value of L_{0N} becomes 1.42897, which may be rounded to 1.4290. J. F. S.

Solubility. VII. Solubility Relations of Rhombic Sulphur. JOEL H. HILDEBRAND and CLARENCE A. JENKS (*J. Amer. Chem. Soc.*, 1921, **43**, 2172—2177).—The solubility of rhombic sulphur has been determined in carbon tetrachloride, benzene, toluene, *m*-xylene, heptane, and ethylene dichloride at 0°, 25°, 35°, 45°, and 54°. The results are expressed in molecules of S_8 per 100 molecules of solvent and in grams per 100 grams of solvent. The following values in grams per 100 grams of solvent are recorded: Carbon tetrachloride, 0°, 0.339; 25°, 0.831; 35°, 1.155; 45°, 1.564; and 54°, 2.008; heptane, 0°, 0.124; 25°, 0.362; 35°, 0.512; 45°, 0.698; and 54°, 0.926; toluene, 0°, 0.897; 25°, 2.018; 35°, 2.722; 45°, 3.620; and 54°, 4.85; *m*-xylene, 25°, 1.969; 45°, 3.604; benzene, 25°, 2.074; 54°, 5.165; ethylene dichloride, 25°, 0.826; 40°, 1.380; 79°, 5.43; and 97.5°, 9.97. It is shown that, with the exception of certain minor discrepancies, the solubilities of sulphur accord well with the internal pressure relations of the substances involved. J. F. S.

The Constitution of Selenium. H. PÉLABON (*Compt. rend.*, 1921, **173**, 1466—1468).—The grey selenium previously described (cf. A., 1921, ii, 533), the specific resistance of which may vary from a few ohms to several million ohms, is now shown to consist of two modifications. The α -modification has a very high resistance and is prepared by heating selenium at a temperature only just above its melting point and then allowing it to cool slowly. The specific resistance of this modification diminishes at first very rapidly with rise in temperature and then more slowly. At 200°, the resistance is about 70,000 ohms, and at 218° the substance melts, the melting being accompanied by a sudden rise in resistance. The β -modification has a very small specific resistance. It is obtained by maintaining the molten selenium at a temperature near its boiling point for some time and then allowing it to cool. The β -modification is not stable at low temperatures, and it is

readily changed into the α -form by oscillations of its temperature between 15° and 200° .
W. G.

Influence of Freezing on Colloidal Selenium. II. A. GUTBIE, FR. HEINRICH, and J. HUBER (*Kolloid Z.*, 1921, **29**, 287—293; cf. A., 1921, ii, 693).—A continuation of work previously described (*loc. cit.*) on the effect of freezing on selenium sols. Three new series of experiments are now described in which it is shown that the sensitiveness of undialysed selenium sols, prepared by means of sulphur dioxide, towards cold increases with the time during which they are frozen. The system may be frozen for short periods and will then melt to form a typical colloid, but more prolonged freezing increases the tendency to coagulate to irreversible gels on melting, and very prolonged freezing will even cause coagulation to take place in the solid. In this respect, there is no fundamental difference between dialysed and undialysed sols, but the dialysed system is somewhat more sensitive. The reducing action of sulphur dioxide on solutions of selenious acid is retarded by freezing the mixture. If the mass is kept frozen for a long time the colloid is precipitated in the ice and thereby the reduction process is accelerated. The precipitation appears to exercise a nucleus action, by which the reduction in the solid mass is accelerated, so that eventually more selenium is precipitated in the frozen mass than would be produced in a solution in the same time. In general, the coagulation in the frozen sol commences where the sol is in contact with the air, as is shown by the formation of a coloured ring on the upper surface of the ice. When test-tubes are used for the experiments, the curved lower portion of the tube always shows an increased concentration of selenium. The form of the vessel in which the freezing takes place is shown to exert an influence on the coagulation. When a sol is poured on ice and frozen it is found that the disperse phase diffuses into the ice. It has been found scarcely possible to freeze selenium sols in capillary tubes.
J. F. S.

Metallurgy of Tellurium by the Wet Way. PIERRE HULOT (*Bull. Soc. chim.*, 1921, [iv], **29**, 1070—1071).—The method of reduction of potassium anhydrotellurate by zinc and hydrochloric acid with the precipitation of metallic tellurium (cf. A., 1920, ii, 174) is modified by using aluminium and sodium or potassium hydroxide for the production of nascent hydrogen, with the result that the reduction is completed in one hour instead of ten. The aluminium must be pure and free from copper.
W. G.

Manganese in the Catalytic Oxidation of Ammonia. CHARLES SNOWDEN PIGGOT (*J. Amer. Chem. Soc.*, 1921, **43**, 2034—2045).—The action of manganese dioxide alone and when mixed with copper oxide or silver oxide, and various alloys of manganese, copper, silver, iron, and silica as catalysts in the oxidation of ammonia have been investigated. A mixture of manganese dioxide with 40% of copper oxide at 800° is shown to have an efficiency of more than 90%. All the substances mentioned catalyse the

oxidation of ammonia with various efficiencies which with suitable conditions are about 50%. The physical structure of the oxide catalyst is of great importance, extremely fine subdivision giving a large adsorbing surface with very small pores being conducive to greater activity.

J. F. S.

Attempt to Prepare Nitro-nitrogen Trichloride. II. Behaviour of Mixtures of Nitrogen and Chlorine in a Flaming Arc. WILLIAM ALBERT NOYES (*J. Amer. Chem. Soc.*, 1921, **43**, 1774—1782; cf. A., 1913, ii, 584).—Attempts to prepare nitro-nitrogen trichloride or nitrogen trichloride by passing mixtures of nitrogen and chlorine through a flaming arc were entirely unsuccessful. Passing the same gases through a powerful ozoniser had the same result and no action at all occurred with Strutt's active nitrogen. The results, although negative, confirm Lewis's hypothesis that electrons are held jointly by two atoms rather than the view that electrons are transferred from one atom to another when atoms combine.

J. F. S.

Vapour Pressures of Aqueous Solutions of Nitric Acid. WILLIAM C. SPROESSER and GUY B. TAYLOR (*J. Amer. Chem. Soc.*, 1921, **43**, 1782—1787).—The total and partial vapour pressures of nitric acid solutions of the concentrations 20%, 40%, 56%, 68%, and 80% by weight have been measured at temperatures 0°, 35°, 50°, 65°, and 80°. From the data the vapour pressure for each 10% increase in concentration and each 10° rise in temperature has been calculated and tables drawn up. Attempts to measure the vapour pressure of 90% acid were unsuccessful owing to the decomposition of the acid at all temperatures except 0°.

J. F. S.

Reducing Actions of Arsenious Acid. MORITZ KOHN (*Monatsh.*, 1921, **42**, 221—226).—When copper sulphate is heated with ammonia solution and arsenious anhydride in a sealed tube in a boiling water-bath, it undergoes reduction to cuprous salt with formation of arsenic acid. After the resulting cuprous solution has been oxidised to the cupric condition by atmospheric oxygen, estimation of the arsenic acid reveals more of the latter than corresponds with the equation, $2\text{Cu}^{++} + \text{AsO}_3''' + 2\text{OH}' = \text{H}_2\text{O} + 2\text{Cu}' + \text{AsO}_4'''$. Evidently oxidation of the ammoniacal cuprous solution to the cupric stage activates the atmospheric oxygen for the oxidation of the residual unchanged arsenious acid. Depression of the concentration of hydroxyl ions by addition of ammonium salts retards the reduction of cupric to cuprous salt.

T. H. P.

Catalysis in the Interaction of Carbon with Steam and with Carbon Dioxide. HUGH STOTT TAYLOR and HARVEY A. NEVILLE (*J. Amer. Chem. Soc.*, 1921, **43**, 2055—2071).—The effect of potassium carbonate, sodium carbonate, lithium carbonate, barium carbonate, calcium carbonate, sodium chloride, ferric oxide, copper, sodium silicate, borax, and nickel as catalysts on the interaction of steam on carbon has been investigated, using various forms of

carbon. It has been discovered that the interaction of carbon and carbon dioxide is likewise accelerated by the presence of the same materials, and a striking parallelism between the catalysts for the two reactions has been shown. The probable mechanism of the steam-carbon reaction has been investigated. It has been shown that good catalysts for the water-gas reaction, for example, iron oxide, are ineffective in the steam-carbon and carbon dioxide-carbon reactions. Catalysis of the water-gas reaction thus being excluded from consideration, it has been shown that the acceleration of the reaction $C + CO_2 = 2CO$, and therefore the acceleration of the reaction $C + 2H_2O = CO_2 + 2H_2$, may be ascribed to increased adsorption of carbon dioxide by the carbon surfaces in presence of active catalytic agents. Adsorption measurements confirm this view. The results have been considered in connexion with the suggested existence of a surface complex, C_xO_y , and have been found to agree with this conception. J. F. S.

A Modification of Silicon Soluble in Hydrofluoric Acid.

WILHELM MANCHOT (*Ber.*, 1921, **54**, [B], 3107—3111).—Moissan and Siemens (*A.*, 1904, ii, 560) have isolated specimens of silicon from a silver regulus which suffer loss of weight (up to 99%) when treated with hydrofluoric acid, and subsequently Lebeau (*A.*, 1906, ii, 168) has brought forward evidence to show that a similar modification is present in copper-silicon alloys rich in the latter. The substance, however, does not appear to have been investigated fully.

Considerable difficulty is experienced in preparing silicon which is completely resistant towards hydrofluoric acid; the product obtained by Wöhler's method requires frequently repeated treatment with the acid before a stable specimen is secured. It is shown that an appreciable gain in weight occurs when the latter is melted with silver in an electric furnace in an atmosphere of air, oxygen, or carbon monoxide, but this is in itself insufficient to account for the subsequent solubility of the silicon. The latter, however, is only produced in the soluble condition when the regulus is suddenly cooled. The silver may be replaced by aluminium. It dissolves in hydrofluoric acid with evolution of hydrogen.

It is remarkable that Moissan and Siemens describe their product as exactly resembling crystalline silicon, whereas the author's specimens are dark to pale brown and amorphous; they leave a pale brown powder after being treated with hydrofluoric acid.

H. W.

Organogels of Silicic Acid. B. S. NEUHAUSEN and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1921, **43**, 1844—1846).—Hydrogels of silicic acid have been repeatedly soaked in alcohol, acetone, and benzene for long periods, dried in a vacuum of 5 mm. at 80°, 120°, and 270° successively for periods of one hour, and analysed. The dried products contain: alcogel, 4.23% water, 3.90% alcohol; acetone gel, 4.77% water, 3.75% acetone; benzene gel, 4.31% water, 3.82% benzene. Hence it follows, in opposition to Graham's

statement, that the water of a hydrogel of silicic acid cannot be entirely replaced by a second solvent. It has been previously shown that heating silicic acid gels in a vacuum at 300° for six hours does not reduce the water content below 4.8%, a quantity which is very near the amount of water left in the organo-gel above, and indicates that this water is very firmly combined in the gel.

J. F. S.

Relative Densities of Alkali Metal Amalgams and Mercury.

II. EDGAR C. BAIN and JAMES R. WITHROW (*J. Physical Chem.*, 1921, **25**, 535—544; cf. A., 1916, ii, 431).—The methods of formation and the relative densities of liquid and solid amalgams of sodium, potassium, ammonium, and calcium have been investigated. It is shown that solid amalgams float on the mother-liquor and do not sink as stated by Kerp (A., 1898, ii, 516). The method used by Kerp (*loc. cit.*) produces sodium and potassium amalgams, which are like the amalgams produced by other methods inasmuch as the solid is lighter than the liquid. Oily and pasty amalgams are due to fine crystals incorporated in the liquid. By electrolysis of solutions of potassium chloride, amalgams with concentrations up to 2.31% of potassium were obtained. No difficulties, except those of collection and preservation, were met with in the production of ammonium amalgams by the electrolysis of solutions of ammonium chloride, but crystalline amalgams cannot be obtained in this way. Electrolysis of an acidified solution of calcium acetate is not a satisfactory method for the production of calcium amalgams, but it does produce a dilute calcium amalgam.

J. F. S.

The Production of Potassium Hydrogen Sulphate from Ammonium Hydrogen Sulphate and Potassium Sulphate.

W. DOMINIK (*Przemysl Chem.*, 1921, **5**, 10—15, 37—40, 63—67).—Reaction in the presence of steam superheated at 200 — 400° takes place according to the equation $M_2SO_4 + NH_4HSO_4 = 2MHSO_4 + NH_3$; lack of steam results in the production of pyrosulphates. In the above reaction, $K = [MHSO_4]^2 / [M_2SO_4] \cdot [NH_4HSO_4]$ increases with the temperature according to a logarithmic function. Theoretical consideration is given to the use of a mixture of sodium and potassium sulphates in the reaction. CHEMICAL ABSTRACTS.

Crystal Structures of Sodium Chlorate and Sodium Bromate.

ROSCOE G. DICKENSON and ELBRIDGE A. GOODHUE (*J. Amer. Chem. Soc.*, 1921, **43**, 2045—2055).—A large amount of X-ray spectrometer data for sodium chlorate and bromate has been obtained and tabulated. In agreement with other observers, it has been found that the nature of the crystal surface has a considerable effect on both the absolute and relative intensities of reflection. The ease with which reflections from one face may be mistaken for those from another and the necessary precautions to avoid this have been pointed out. It is shown that the atoms in sodium chlorate and sodium bromate are very

probably arranged with the symmetry of the Schönflies space group T^4 , all oxygen atoms being equivalent. Sets of positions of the atoms in the unit structure, only slightly different for the chlorate and bromate, have been suggested. J. F. S.

Preparation and Study of the Rarer Alkali Bromates. Rubidium Bromate. HAROLD D. BUELL and C. R. McCROSKY (*J. Amer. Chem. Soc.*, 1921, **43**, 2031—2034).—Rubidium bromate was prepared by treating the pure carbonate with an excess of bromic acid and recrystallising the product (cf. A., 1920, ii, 688). The following figures are the solubilities in 100 grams of water at various temperatures: 25°, 2·93; 30°, 3·55; 35°, 4·28, and 40°, 5·08. The corresponding figures for caesium bromate are 25°, 3·66; 30°, 4·53; 35°, 5·32. The following melting points are recorded: potassium bromate, 405°; caesium bromate, 420°; rubidium bromate, 430°. Both rubidium and caesium bromates form small, cube-like crystals, which, however, belong to the hexagonal system; they have a refractive index between 2·144 and 2·22. J. F. S.

Vapour Pressure of some Salts. II. H. VON WARTENBERG and H. SCHULZ (*Z. Elektrochem.*, 1921, **27**, 568—573; cf. Albrecht and Wartenberg, *ibid.*, 162).—Using the method previously employed, the authors have determined the vapour pressures of lithium chloride, caesium chloride, rubidium chloride, lithium bromide, caesium bromide, rubidium bromide, sodium fluoride, potassium fluoride, lithium fluoride, caesium fluoride, rubidium fluoride, sodium iodide, caesium iodide, and rubidium iodide. The measurements were carried in most cases up to the boiling point of the salt in question. The following data are recorded, pressures being in atmospheres: lithium chloride, b. p. 1382°, m. p. 606°, $\log p = -37200/4\cdot57T + 4\cdot923$; caesium chloride, b. p. 1303°, m. p. 626°, $\log p = -37400/4\cdot57T + 5\cdot190$; rubidium chloride, b. p. 1383°, m. p. 717°, $\log p = -37800/4\cdot57T + 4\cdot998$; lithium bromide, b. p. 1310°, m. p. 549°, $\log p = -35600/4\cdot57T + 5\cdot109$; caesium bromide, b. p. 1300°, m. p. 627°, $\log p = -36750/4\cdot57T + 5\cdot113$; rubidium bromide, b. p. 1350°, m. p. 681°, $\log p = -36980/4\cdot57T + 4\cdot964$; sodium fluoride, b. p. 1695°, m. p. 988°, $\log p = -56600/4\cdot57T + 6\cdot299$; potassium fluoride, b. p. 1505°, m. p. 846°, $\log p = -41900/4\cdot57T + 5\cdot138$; lithium fluoride, b. p. 1676°, m. p. 842°, $\log p = -55100/4\cdot57T + 6\cdot190$; caesium fluoride, b. p. 1251°, m. p. 684°, $\log p = -34700/4\cdot57T + 4\cdot982$; rubidium fluoride, b. p. 1410°, m. p. 775°, $\log p = -40000/4\cdot57T + 5\cdot243$; sodium iodide, b. p. 1300°, $\log p = -37000/4\cdot57T + 5\cdot130$; lithium iodide, b. p. 1170°, $\log p = -40300/4\cdot57T + 6\cdot105$; caesium iodide, b. p. 1280°, $\log p = -36600/4\cdot57T + 5\cdot165$; and rubidium iodide, b. p. 1305°, $\log p = -37000/4\cdot57T + 5\cdot148$. The results show that the heats of formation of the haloids of potassium, rubidium, and caesium lie very close together, whilst that of the lithium salts is much higher and that of the sodium salts much lower. J. F. S.

Catalytic Influence of Foreign Oxides on the Decomposition of Silver Oxide, Mercuric Oxide, and Barium Peroxide.

JAMES KENDALL and FRANCIS J. FUCHS (*J. Amer. Chem. Soc.*, 1921, **43**, 2017—2031).—The effect of foreign oxides on the temperature and rate of decomposition of silver oxide, mercuric oxide, and barium peroxide under an oxygen pressure of one atmosphere has been experimentally investigated. In almost all the systems examined the added oxides (CuO , MnO_2 , Fe_2O_3 , CeO_2 , SiO_2 , CrO_3) induce a considerable change in the decomposition temperature. Most commonly, there is a marked lowering in this point; thus, quoting an extreme case, an equimolecular mixture of barium dioxide and cupric oxide has an oxygen equilibrium pressure of 1 atm. at 322° , a temperature which is approximately 500° below the decomposition temperature of pure barium dioxide. In a few systems a comparatively small rise in the decomposition temperature is indicated. In all cases, however, the rate of oxygen evolution is markedly increased. The decomposition temperatures recorded refer to true equilibrium conditions, concordant values being obtained with rising and falling temperature. The results are tentatively ascribed to the formation of unstable intermediate compounds between the two oxides present. The increased rates of decomposition may be referred to adsorption effects, but the large temperature changes point strongly to the actual participation of the added oxide in the reaction. Direct evidence was given in certain mixtures of the production of stable complexes.

J. F. S.

Physical Chemistry of the Oxides of Lead. III. Hydrated Lead Monoxide. SAMUEL GLASSTONE (*T.*, 1922, **121**, 58—66).**Reactions in Fused Salt Media. I. Basic Lead Chromates.**

J. F. G. HICKS (*J. Physical Chem.*, 1921, **25**, 545—560).—The reaction between lead monoxide and sodium chromate in fused sodium chloride and a 50% mixture of sodium and potassium nitrates has been investigated and the equilibrium diagram of the system $\text{PbO}-\text{PbCrO}_4$ constructed. It is shown that reactions in fused salts can be brought about in such a way as to yield products analogous to those prepared from the same initial substances in aqueous solution. The chief difference between these reactions and their analogues in aqueous solution lies in the smaller velocity of the former, probably due to the relative insolubility of the reacting substances in the fluxes as compared with water. There is in several cases a reaction between the flux and the dissolved substance, similar to hydrolysis. This analogy would appear to indicate that these solvolytic reactions are ionic, but the second phase of the reaction forming basic lead chromates points to a non-ionic reaction. It may be a purely molecular (additive) reaction, resulting in the formation of compounds of higher orders. Such a conclusion explains satisfactorily the slowness of the reactions, aside from the low solubility of the solutes in the fused salt medium. Whilst at least one basic lead chromate,

$\text{PbO}, \text{PbCrO}_4$, may be prepared by alkaline hydrolysis, it does not follow that the basic lead chromates formed in fused salt media are formed by an entirely analogous process. Two new basic chromates have been prepared by the present method which have not been obtained by the wet process; these have the formulæ, $2\text{PbO}, \text{PbCrO}_4$ and $3\text{PbO}, \text{PbCrO}_4$ respectively. A fourth compound, $\text{PbO}, 2\text{PbCrO}_4$ is readily prepared by the fusion process and has been stated to be formed by the wet process, but the author has been unable to prepare it by this method. The existence of the four basic lead chromates named is confirmed by the equilibrium diagram of the system $\text{PbO}-\text{PbCrO}_4$. Other basic lead chromates described in the literature are shown to be mixtures or solutions of the compounds named above in one another. Salts of ortho-chromic acid are shown not to exist; whilst the salt Pb_2CrO_5 may be the salt of the monohydrate of ordinary chromic acid, it could equally well be a true basic salt or a compound of a higher order, so far as the present work is concerned. At the temperature ($225-800^\circ$) the stable form of lead monoxide is yellow in colour. This, combining with yellow lead chromate yields red compounds, all of which point to compounds of a higher order. The red compound formed by alkaline hydrolysis of normal lead chromate could well be considered a basic salt, but the addition of lead oxide and lead chromate molecules to form a compound of higher order might as easily take place in aqueous solution as in the nitrate flux used to form a compound of very closely the same composition. The reddening of lead monoxide in the nitrate flux has been shown to be due to change in crystalline form, and not, as might be supposed, to the formation of red lead.

J. F. S.

Reduction of Copper Oxide by Hydrogen. ROBERT N. PEASE and HUGH STOTT TAYLOR (*J. Amer. Chem. Soc.*, 1921, **43**, 2179—2188).—An investigation of the characteristics of the reduction of cupric oxide by hydrogen and the effect on the reaction of adding metallic copper to the oxide and water vapour and oxygen to the hydrogen has been carried out. It is pointed out that the reaction is auto-catalytic, copper being the auto-catalyst. The reaction appears to take place at the copper-copper oxide interface. This is shown by the character of the reduction curve and the fact that the addition of metallic copper accelerates the reaction. It is shown that the presence of water vapour in the hydrogen markedly interferes with the formation of the original copper nuclei from which the reaction zone, that is the copper-copper oxide interface, spreads out; it does not markedly affect the subsequent reaction at the interface, however. The presence of oxygen in the hydrogen strongly inhibits the reaction at the interface, but in all probability has no marked effect on the primary reaction, that is, the formation of the original copper nuclei.

J. F. S.

The Oxidising Properties of Sulphur Dioxide. III. Copper Chlorides. WILLIAM WARDLAW and FREDERICK WILLIAM PINKARD (*T.*, 1922, **121**, 210—221).

Behaviour of Ammoniacal and Alkaline Copper Solutions.

MORITZ KOHN (*Monatsh.*, 1921, **42**, 83—87).—When arsenic is heated in a sealed tube with ammoniacal copper solution, the cupric compound undergoes reduction, first to cuprous salt and subsequently to copper, $3\text{Cu}^{++} + \text{As} + 3\text{OH}' = \text{AsO}_3''' + 3\text{Cu}' + 3\text{H}'$ and $3\text{Cu}' + \text{As} + 3\text{OH}' = \text{AsO}_3''' + 3\text{Cu} + 3\text{H}'$; the copper liberated unites with the excess of arsenic to form greyish-black copper arsenide. Exactly similar changes occur when antimony is heated with ammoniacal copper solutions containing tartaric acid, the solid deposited being then reddish-black and containing the copper and the excess of antimony. With bismuth and ammoniacal copper solutions containing tartaric acid, rapid action occurs, but the reduction proceeds only as far as the cuprous compound. Alkaline solutions of copper salts, such as Fehling's solution or an aqueous solution containing copper sulphate, glycerol and potassium hydroxide, are rapidly reduced by arsenic, antimony, or bismuth, with separation of copper, $2\text{As}(2\text{Sb}) + 3\text{Cu}^{++} + 6\text{OH}' = 2\text{AsO}_3(\text{SbO}_3)''' + 6\text{H}' + 3\text{Cu}$ or $2\text{Bi} + 3\text{Cu}^{++} = 2\text{Bi}''' + 3\text{Cu}$. T. H. P.

Separation of the Isotopes of Mercury. J. N. BRÖNSTED and G. VON HEVESY (*Z. physikal. Chem.*, 1921, **99**, 189—206, and *Phil. Mag.*, 1922, **43**, [vi], 31—49).—A partial separation of the isotopes of mercury has been achieved by two processes. (1) Evaporation method (ideal distillation) based on the difference in the velocities of evaporation of the isotopes. The distillate was found to be richer and the remainder poorer in the lighter isotope than the original substance. (2) Effusion method. A fraction of the mercury vapour penetrates through narrow openings into a condensation chamber where the lighter isotope is found in a relatively larger amount than in ordinary mercury. The results of the experiments agree with the hypothesis, according to which the evaporation, as well as the effusion velocity of the isotopes, is inversely proportional to the square root of their molecular weights; they are further in conformity with Aston's results, obtained by means of mass spectrographic observations. The partial separation achieved was proved by measurements of density. The density difference found between the heaviest and lightest mercury amounts to 0.49%, corresponding with a difference of 0.1 unit in the atomic weight of mercury. J. F. S.

Physico-chemical Analysis of Aluminium Oxy-salts and Aluminium Oxide Sols. MONA ADOLF, WOLFGANG PAULI, [with FRANZ JANDRASCHITSCH] (*Kolloid Z.*, 1921, **29**, 281—287; cf. A., 1917, ii, 563; 1921, ii, 700).—The composition and nature of aluminium oxy-chloride sols have been investigated by means of measurements of the concentration of hydrogen and chlorine ions, the total chlorine concentration, and the electrical conductivity. A number of transport determinations have also been made. It is shown that it is impossible to remove all the chlorine from the products of hydrolysis of aluminium chloride by washing. A quantity of chlorine, which is greatly in excess of that contained

in the hydrochloric acid required for peptisation, always remains. On boiling well washed aluminium hydroxide with dilute hydrochloric acid, sols of various compositions are obtained up to a limiting composition represented by the formula $[\text{Al}(\text{OH})_3]_2\text{AlOCl}$. Of these two have been investigated. Aluminium oxy-dichloride $\text{AlCl}_2\cdot\text{OH}$ behaves as a ternary electrolyte and on dilution is strongly dissociated, the process being complete at a dilution $0\cdot00106N$. This compound shows a remarkably small hydrolysis, which amounts to $0\cdot1\%$ at $0\cdot068N$, and in a $0\cdot00106N$ solution is only $0\cdot25\%$. The compound aluminyl monochloride, $\text{Al}(\text{OH})_2\text{Cl}$ or AlOCl , behaves as a binary electrolyte. The conductivity data indicate that a complex ionisation occurs in this case of the type $\text{Al}(\text{OH})_2\text{Cl}|\text{AlO}$, indicating a compound in which one aluminium atom of the complex acts as the central atom of a negative complex, whilst the other furnishes a stable univalent positive ion. The peptisation of aluminium hydroxide leads to a sol of the composition $2[\text{Al}(\text{OH})_3]|\text{Al}(\text{OH})_2\text{Cl}$, and this on dilution undergoes complex ionisation represented by the formulæ (1) $10\text{Al}(\text{OH})_3, 4\text{AlOCl}, \text{AlO}|\text{Cl}$; (2) $12\text{Al}(\text{OH})_3, 5\text{AlOCl}, \text{AlO}|\text{Cl}$; (3) $16\text{Al}(\text{OH})_3, 7\text{AlOCl}, \text{AlO}|\text{Cl}$. On the other hand, no complex ionisation of the form $\text{Al}(\text{OH})_4|\text{AlO}$ has been observed in the case of aluminium hydroxide. J. F. S.

Germanium. I. Extraction from Germanium-bearing Zinc Oxide. Non-occurrence in Samarskite. L. M. DENNIS and JACOB PAPISH (*J. Amer. Chem. Soc.*, 1921, **43**, 2131—2144).—A method of extracting germanium residues obtained in the smelting of certain American zinc ores has been investigated and is described. The residue contains zinc oxide, considerable quantities of lead, arsenic, and cadmium, and small quantities of indium, tin, and antimony, in addition to the germanium. A kilogram of the crude oxide is placed in a 5-litre Pyrex flask, which is fitted with a two-holed rubber stopper carrying a bent glass tube for connexion to a Liebig condenser, and a second short glass tube for introduction of the acid. The condenser leads under the surface of water contained in a 4-litre bottle which acts as receiver. Two and a half litres of hydrochloric acid ($d\ 1\cdot18$) are added to the ore and the flask is heated until 2 litres of distillate have been collected. The distillate at this point contains all the germanium and a great deal of the arsenic from the ore. The distillate is poured into a 15-litre bottle until 10 litres have been accumulated, carefully acidified with sulphuric acid until it is $6N$ (this must be carefully done to prevent loss of germanium chloride), and treated with washed hydrogen sulphide. The precipitate is at first yellow, due to arsenic, but later becomes whiter, due to the germanium. When precipitation is complete, the bottle is stoppered and kept for twenty-four hours. The solution is filtered by suction and washed with $3N$ -sulphuric acid which has previously been saturated with hydrogen sulphide. The filtrate is kept for forty-eight hours, when usually a small quantity of a white precipitate (corresponding with 2 mg. of germanium) separates, the majority of the supernatant liquid is siphoned off, and the small amount of liquid and

precipitate worked up with the filtrate from the next lot of precipitate. At this point two different methods of procedure are possible.

(1) The moist sulphides are added to hot 50% sodium hydroxide until a small quantity remains undissolved; this is then just dissolved by the addition of a little more sodium hydroxide. The solution is made strongly alkaline by the addition of 8 grams of solid sodium hydroxide and placed in a large Pyrex flask fitted with a rubber stopper carrying a delivery tube, a separating funnel, and a glass tube reaching almost to the bottom of the flask. The flask is connected to a condenser and receiver as before. Washed chlorine is passed in to oxidise the arsenic to the quinquevalent condition. When the solution is saturated with chlorine, the rate of entry of the chlorine is reduced and concentrated hydrochloric acid is added in large excess from the funnel. The flask is heated until half the liquid has distilled. The germanium chloride passes over and is hydrolysed by the water in the receiver, forming white, hydrated germanium dioxide. Should oily drops form in the receiver, more water is added to reduce the acid concentration and so allow the hydrolysis to proceed. The receiver is now replaced by a second one, the distilling flask is filled up again with concentrated hydrochloric acid, and the distillation continued as before. Most of the germanium chloride passes over in the first distillation, but for a complete separation the distillation must be repeated several times. The hydrated oxide is filtered, washed first with dilute sulphuric acid and then with water, and dried at 110° . It is pure white, and contains traces of sodium, calcium, and iron, but no arsenic. The filtrates from the hydrated oxide are treated with hydrogen sulphide and the germanium sulphide is recovered. The impurities mentioned are removed by dissolving in a slight excess of sodium hydroxide, saturating with chlorine, and distilling with hydrochloric acid, hydrolysing the distillate as before.

(2) This process is generally superior to the former in its greater economy of reagents. The wet sulphides are washed with 3*N*-sulphuric acid until free from chlorine and dried at 110° . They are then roasted in shallow iron dishes at temperatures not exceeding 500° . This removes a great deal of the arsenic. The roasted material is dissolved in sodium hydroxide (50%), chlorinated, and distilled with twice its weight of concentrated hydrochloric acid. A repetition of the distillation removes the last trace of arsenic. Either process gives a very pure germanium dioxide; the yield is better by the first, but the second is more rapid and economical.

Germanium in ores is estimated by grinding 20–100 grams of the finely ground, dried, and weighed ore into a paste with water and pouring into a solution of sodium hydroxide in a hard flask, the proportions being 2 of ore : 1 sodium hydroxide : 5 of water. The flask is fitted with a delivery tube for leading in chlorine, a fractionating column, and a small tap funnel. It is connected with a Liebig's condenser which leads to two Erlenmeyer flasks in series containing water to the depths of 3 cm. and half full respectively. The receivers are cooled with ice. The distilling flask is surrounded

by ice and the contents are saturated with chlorine; the solution is then neutralised by hydrochloric acid and an excess equal to twice the weight of the ore added. The ice is removed and a slow distillation in chlorine carried out until one-half the liquid in the flask has passed over. An equal volume of hydrochloric acid is added to the distilling flask and the distillation continued until its volume is again reduced by one-half. This is then repeated once more. The receivers are disconnected, acidified with sulphuric acid to make the solutions 6*N*, saturated with hydrogen sulphide, and kept for twenty-four hours. In a successful experiment there will be no germanium in the second flask. The precipitate is brought on to an ashless paper and washed with 3*N*-sulphuric acid, saturated with hydrogen sulphide until free from chloride, then washed with alcohol to remove the acid, and dried. The bulk of the precipitate is placed in a porcelain crucible and dried, moistened with 1 : 1 nitric acid, and warmed to drive off all the liquid, allowed to cool, treated with concentrated nitric acid, dried, and ignited. The filter-paper is incinerated in a second crucible, treated with concentrated nitric acid, and ignited. The filtrate from the germanium sulphide is kept forty-eight hours and the small precipitate formed filtered and treated as above. The weight of the germanium dioxide in the crucibles represents the germanium in the ore. Using this method, the amount of germanium in the material used for the extraction of germanium was found to be: sample I 0.247%, sample II 0.19%. Samarskite has been analysed by this method and found not to contain germanium. J. F. S.

Crystalline Structure of Iron and Steel. ARNE WESTGREN and AXEL E. LINDH (*Z. physikal. Chem.*, 1921, **98**, 181—210).—Various types of iron and steel have been subjected to Röntgen ray spectrographic examination. It is shown that the results of Hull (*Phys. Review*, 1917, **9**, 84, **10**, 661), that pure iron at ordinary temperatures (α -iron) possesses a space-centred cubic lattice, is in keeping with the present work. At 800—836°, that is, within the so-called β -iron region, the atoms are grouped in exactly the same way as in α -iron. Since in the authors' opinion allotropy and polymorphy are synonymous, β -iron can only be regarded as a particular modification of α -iron. In austenite and in pure iron stable at 1000°, the crystals possess a face-centred cubic lattice. This is also characteristic of γ -iron, and thereby a fundamental difference is established between α -iron and γ -iron. In martensite, the iron occurs in its α -modification. This is also the case with high speed tool steel which has been hardened at 1275°. Photomicrographs of some of the preparations examined are included in the paper. J. F. S.

Alloys of Iron and Uranium. E. P. POLUSHKIN (*Iron and Steel Inst., Carnegie Schol. Mem.*, 1920, **10**, 129—150; cf. *Rev. Metal.*, 1920, **17**, 421).—Alloys of iron with uranium are pyrophoric, this property varying directly with the content of uranium. Alloys containing carbon are decomposed by water, but this effect is not

exhibited by silicon, except when present in very large amount, or by vanadium. A polished sample placed on the emulsion of a photographic plate leaves an impression which, after development by the usual process, represents the structure of the specimen. Iron-uranium alloys contain the uranium carbides UC , U_2C_3 , and U_3C_8 , the compound Fe_3C, U_2C_3 , as well as the compounds V_2C , Fe_6U , and $FeSi$. Neither uranium nor any of its compounds already mentioned forms solid solutions with iron. Vanadium has a greater affinity for uranium than for carbon. CHEMICAL ABSTRACTS.

Equilibria in the System Fe-C-O: the Equilibrium Fe_β -Martensite-Ferrous Oxide-Gas. W. REINDERS and P. VAN GRONINGEN (*Rec. trav. chim.*, 1921, **40**, 701—706).—A considerable number of determinations of points of univariant equilibrium for this system have been carried out. The conclusion is drawn that the transition temperature for $Fe_\beta \rightarrow Fe_\gamma$ is 905° ; this is in accord with previous results obtained by different methods. By extrapolation of the graphic results, the quintuple point of the system is found at 740° and 2300 mm. H. J. E.

Researches on the Metallic Carbonyls. ROBERT LUDWIG MOND and ALBERT EDWARD WALLIS (T., 1922, **121**, 29—32).

The Action of Nitric Oxide on the Metallic Carbonyls. ROBERT LUDWIG MOND and ALBERT EDWARD WALLIS (T., 1922, **121**, 32—35).

Expansion of Chromium and of Nickel-Chromium Alloys over a Wide Range of Temperatures. P. CHEVENARD (*Compt. rend.*, 1922, **174**, 109—112).—Between 0° and 100° the expansion of chromium is exactly reversible, the curve showing no singular point. The true coefficient of expansion, which is 6.8×10^{-6} at 0° , increases rapidly with the temperature, but the curve shows a slight concavity towards the increasing temperature.

Nickel-chromium alloys containing up to 16% of chromium and from 0.5 to 2.5% of manganese were examined over the temperature range 0° to 1000° . The addition of chromium leads to a very rapid weakening of the anomaly of dilatation of nickel, and when the chromium content reaches 5% the anomaly disappears. The addition of chromium to nickel affects the expansion of this metal very little at the ordinary temperature, but tends to increase it at higher temperatures; this effect being probably due to the presence of the compound Ni_2Cr_3 . W. G.

Zirconium. J. W. MARDEN and M. N. RICH (*Bur. Mines Bull.*, 1921, **186**, 146 pp.; cf. A., 1920, ii, 547).—The work is divided into four parts, dealing successively with an historical review of zirconium minerals, the salts of zirconium, and the metal; experimental work on zirconium; the furnaces used; and a bibliography of zirconium and its compounds. Analytical methods are given for the estimation of zirconium in ferrozirconium, steel, alloys such as nickel-zirconium, and a method of separation of titanium, columbium, tantalum, and zirconium. The physical and chemical

properties of amorphous and coherent zirconium are described. The cupferron method is the only one effecting complete separation of zirconium from aluminium.

CHEMICAL ABSTRACTS.

Polymorphic Transformations of Antimony Trisulphide.

SAMUEL WILSON and C. R. McCROSKY (*J. Amer. Chem. Soc.*, 1921, **43**, 2178—2179).—The rate of transformation of the red, amorphous variety of antimony trisulphide into the black variety has been determined in the presence of *N*-, 7*N*-, 12*N*-hydrochloric acid, 7*N*-phosphoric acid, 7*N*-sulphuric acid, glacial and *N*-acetic acids, and a saturated ethereal solution of hydrochloric acid. Of these acid solutions, only the aqueous solution of hydrochloric acid gave any appreciable transformation at 18—22°, even after two months. With the aqueous hydrochloric acid, the time necessary for complete transformation was 0.5 day, 1 day, and 10.5 days for 12*N*, 7*N*, and *N*, respectively. The action is due to a solution of the red variety and a reprecipitation of the less soluble black variety. The effect of temperature was investigated with a 20% aqueous hydrochloric acid. Complete conversion at 26.5° required forty-four hours; at 30°, twenty-nine hours; 35°, sixteen hours; 40°, nine hours; 68.5°, sixty-two minutes, and 75°, thirty-two minutes. A 20% solution of hydrobromic acid gave no change after twenty hours at 75°.

J. F. S.

Mineralogical Chemistry.

The Ultimate Composition of British Coals. THOMAS JAMES DRAKELEY [with FREDERICK WILLIAM SMITH] (T., 1922, 121, 221—238).

Kasolite, a New Radioactive Mineral. ALFRED SCHOEP (*Compt. rend.*, 1921, 173, 1476—1477).—This occurs together with curite (this vol., ii, 77) and torbernite at Kasolo, Katanga, Belgian Congo. It forms compact, crystalline aggregates, with sometimes tufts and radiating groups of prismatic crystals on the surface. The colour is ochre-yellow to brownish-yellow and the streak ochre-yellow. The crystals are monoclinic, with the optic axial plane perpendicular to the plane of symmetry, and the acute bisectrix of the optic axes nearly perpendicular to a perfect cleavage. $d^{17} 5.962$, H. 4—5. Analysis I is of translucent crystals showing no sign of alteration, II of less fresh massive material, and III of clear crystals :

	SiO ₂ .	PbO.	UO ₃ .	H ₂ O.	Fe ₂ O ₃ .	CaO.	MgO.	CO ₂ .	Total.
I.	9.42	36.20	49.28	3.59	0.41	0.06	0.03	0.85	99.84
II.	9.14	34.44	49.00	3.77	0.58	—	—	0.53	—
III.	9.00	32.16	48.26	3.28	0.40	—	—	—	—

The simplest formula corresponding with the mean of these analyses is $3\text{PbO}, 3\text{UO}_3, 3\text{SiO}_2, 4\text{H}_2\text{O}$. The mineral is decomposed by acids with the separation of gelatinous silica and of lead chloride or sulphate. Heated in the reducing flame on charcoal it fuses to a black glass with beads of lead. Its radioactivity is less than that of curite.

L. J. S.

Melanovanadite, a New Mineral from Peru. WALDEMAR LINDGREN (*Proc. Nat. Acad. Sci. U.S.A.*, 1921, 7, 249—251).—This occurs as bunches of black needles on a black shale from Minasragra, Cerro de Pasco. The crystals are monoclinic with a perfect cleavage parallel to the plane of symmetry. The streak is dark reddish-brown, d^{15} 3.477, H. $2\frac{1}{2}$. Only the thinnest splinters are brown and translucent under the microscope, and the optical characters are masked by the strong absorption. Analysis by L. F. HAMILTON gives the formula $2\text{CaO}, 3\text{V}_2\text{O}_5, 2\text{V}_2\text{O}_4$.

V_2O_5	V_2O_4	CaO	MgO	$\text{Al}_2\text{O}_3, \text{Fe}_2\text{O}_3$	SiO_2	Total
52.61	33.34	9.89	0.27	1.89	1.66	99.66

Before the blowpipe the mineral readily fuses to a brown liquid. It is readily soluble in acids, giving an apple-green solution, and in potassium hydroxide with a brown colour.

L. J. S.

Some Natural and Synthetic Melilites. A. F. BUDDINGTON (*Amer. J. Sci.*, 1922, [v], 3, 35—87).—To test Schaller's hypothesis regarding the composition of the melilite group of minerals, comprising akermanite, gehlenite, humboldtilite, sarcolite, fuggerrite, and other varieties (A., 1916, ii, 632) more than one hundred synthetic crystalline mixtures of $2\text{CaO}, \text{MgO}, 2\text{SiO}_2$ (akermanite), $2\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ (gehlenite), and $3\text{R}'\text{O}, \text{R}_2\text{O}_3, 3\text{SiO}_2$ ($\text{R}' = \text{Ca}$ or Na , $\text{R} = \text{Fe}$ or Al) were prepared from appropriate glasses at temperatures above 1000° . The quenching method was used (cf. Ferguson and Buddington, A., 1920, ii, 621), and the glasses were crystallised by annealing at a temperature just below the melting point or the dissociation point. The homogeneity, optical characters, and melting points were determined, and the synthetic materials compared with the natural minerals. The gehlenite of Velardeña consists approximately of 76% of gehlenite, 17% of akermanite, and 7% of ferric and ferrous compounds, and agrees very closely with artificial gehlenite, having the same ratio of akermanite to gehlenite, but free from iron compounds. Other natural gehlenites examined confirm the opinion that the artificial series of solid solutions of $2\text{CaO}, \text{MgO}, 2\text{SiO}_2$ and $2\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$ are pure synthetic analogues of the akermanite-gehlenite series of minerals. Mixtures of akermanite and gehlenite form a complete series of solid solutions with $3\text{CaO}, \text{Al}_2\text{O}_3, 3\text{SiO}_2$ (grossularite) plus 10% of $3\text{Na}_2\text{O}, \text{Al}_2\text{O}_3, 3\text{SiO}_2$, except for a trace of inhomogeneity in some preparations high in akermanite. These mixtures when crystallised correspond in their properties with the humboldtilites, which are interpreted as isomorphous mixtures of positive uniaxial akermanite and a negative, uniaxial, tetragonal, moderately birefringent form of grossularite, with minor amounts of gehlenite, a

ferrous compound, and $3R'O, R_2O_3, 3SiO_2$ compounds. The compositions of the humboldtilites lie in a zone which exhibits the lowest temperatures of complete melting for the components involved. Artificial crystalline mixtures containing ferric iron ($3CaO, Fe_2O_3, 3SiO_2$) were found to be quite different from the natural melilites of similar composition rich in ferric iron. The latter probably were formed at temperatures lower than those of the present experiments, since some of them were found to decompose or invert at temperatures as low as 850° . A new specimen of melilite rich in ferric iron, from Capo di Bove, differs in composition from any hitherto known. It contains :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	CaO.	Na ₂ O.	K ₂ O.	Total.
40.03	5.66	7.76	0.4	9.43	32.17	2.83	1.72	100.0

The crystals have a tabular or pseudo-cubic habit and are intimately associated with nephelite and pyroxene.

E. H. R.

Analytical Chemistry.

The Graphical Representation of the Composition of Chemical Compounds. JULIUS HÜBSCHER (*Chem. Ztg.*, 1922, 46, 19—20).—The repeated calculation of the percentage of the various constituents of chemical compounds in mixtures can be avoided by calculating once and for all the percentage of the required constituent (for example, anhydrous sodium carbonate in the decahydrate) and dividing a vertical line in these proportions. A square is then described with this line as its right-hand side and the points marked off joined to the left-hand top corner. From this co-ordinate system the weight of any constituent corresponding with a given weight of any other constituent can be rapidly read off with sufficient accuracy for practical purposes. Should the given weights not lie between 0 and 100 they can be divided by a suitable factor and the corresponding weight read off the diagram and subsequently multiplied by the same factor. H. C. R.

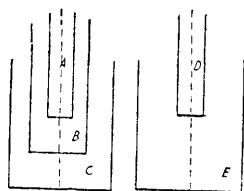
The Sensitiveness of Coloured Indicators at Temperatures above the Ordinary. I. M. KOLTHOFF (*Rec. trav. chim.*, 1921, 40, 775—785; cf. Schoorl, A., 1907, ii, 388).—Indicators which are themselves weak acids are almost all as sensitive to hydrogen ions at higher temperatures as at ordinary temperatures. Those which are weak bases become less sensitive to hydrogen ions, but retain the same sensitiveness to hydroxyl ions. Theoretical deduction of these facts is given in addition to experimental evidence. The suggestion is made that the results obtained may be of service in providing a colorimetric method of studying variations in dissocia-

tion constant and of hydrolysis constant with change of temperature and may also be of use in analytical work. H. J. E.

Further Elaboration of the Indicator Method without Buffers. L. MICHAELIS and R. KRÜGER (*Biochem. Z.*, 1921, **119**, 306—327).—The salt error and temperature coefficient of *m*-nitrophenol have been determined, and a new one-colour indicator, 2 : 5-dinitrophenol, described. A theoretical and practical treatment of the effect on the P_H of a solution of the addition of an indicator is given, and instructions for the colorimetric estimation of P_H in solutions weak in buffers, for example, sea and river waters. A discussion of the theory of the salt-error and of the activity theory of ions is also given. H. K.

A Stable Single Buffer Solution, p_H 1 to p_H 12. S. F. ACREE, R. R. MELLON, PAULINE M. AVERY, and E. A. SLAGLE (*J. Infect. Dis.*, 1921, **29**, 7—10).—The components of the buffer solution are: (1) One mol. of potassium dihydrogen phosphate, with dissociation constant, K_a 1.1×10^{-2} ; (2) 0.625 mol. of sodium formate, K_a 2×10^{-4} ; (3) 0.375 mol. of sodium acetate, K_a 2×10^{-5} ; (4) the second group of dipotassium hydrogen phosphate, K_a 2×10^{-7} ; (5) 1 mol. of sodium phenolsulphonate, K_a 10^{-10} (approx.); (6) 0.005 molar thymol to saturation (for water, 0.08), K_a 0.5×10^{-10} (approx.); (7) the third group of phosphoric acid, K_a 10^{-12} . A curve is given from which the amounts of 0.5 molar hydrogen chloride or sodium hydroxide necessary to produce a given p_H may be directly determined. CHEMICAL ABSTRACTS.

Colour Standards for the Colorimetric Measurement of Hydrogen-ion Concentration. LOUIS J. GILLESPIE (*J. Bact.*, 1921, **6**, 399—405).—The recently published studies of Medalia are in disagreement with other published data (cf. *ibid.*, 1920, **5**, 441—468). A colorimeter for two-coloured indicators is described for the measurement of the hydrogen-ion exponent of indicators. The optical assumptions underlying its use are practically the same



as those on which ordinary colorimetry are based. The instrument is used as follows. The glass vessels A and C are fixed in position, and B can be moved up and down, the motion being measured by a pointer (not shown) fixed to B and moving on a scale divided into 100 parts. The pointer moves from 0 to 100 when B moves from contact with C to contact with A. The acidified indicator solution may be placed in B and the alkaline indicator solution of the same strength in C. A is left empty. If the scale reads 70, the path of light along the left dotted line passes through the alkaline form of the indicator for 10% of its path and the acid form for 30%. The light along the right-hand dotted line traverses an indicator solution in tube E, again of the same strength, and over a path equal in length to the total path on the left. The

solution, the p_H of which is unknown, is placed in tube *E*, in which titrations may be made.

CHEMICAL ABSTRACTS.

A New Apparatus for Colorimetric Estimations. O. MANNEBACH (*Chem. Ztg.*, 1922, 46, 20).—The apparatus consists of a wooden box open at the top the inside of which is painted black. Into this fits a glass vessel filled with water. The bottom of the box has a hole cut in it allowing light to come up through the glass vessel, and below is a rotating frame carrying a dead-white porcelain plate. The solutions to be compared are placed in glass tubes 16 mm. in diameter and 300 mm. long, which are placed in the glass vessel in a slanting position. The apparatus is suitable for the colorimetric estimation of carbon in iron. H. C. R.

A Gas Receiver of Convenient and Practical Form for Sampling Expired Air for Analysis. CHARLES CLAUDE GUTHRIE (*J. Biol. Chem.*, 1921, 48, 373—378).—Whilst less efficient than the mercury receiver, the apparatus described has the advantage of being inexpensive. Expired air, after storage in it for some hours, gave results, on analysis, with an error of about 1% for carbon dioxide and considerably less for oxygen. E. S.

Apparatus for Estimation of the Gases in Blood and Other Solutions. DONALD D. VAN SLYKE (*Proc. Nat. Acad. Sci.*, 1921, 7, 229—231).—Essentially a much simplified form of the apparatus described in A., 1917, ii, 422, and this vol., ii, 78. The upper part of a large pipette (for instance, 50 c.c.) ends in a tap funnel. The stem above the wide portion has a mark, indicating a definite volume *a* from there to the tap (for instance, 2 c.c.), and below the wide portion another mark indicating a volume *A* (for instance, 50 c.c.) from it to the tap. The pipette is joined below to a tube of 800 mm. connected with an open manometer and through a tap, with a mercury reservoir. A definite volume of solution (for instance, 1 c.c. of blood) is sucked in through the tap funnel and then the necessary reagent (for instance, acid for a carbonate solution), making a total solution of *S* c.c. (for instance, 2.5 c.c.) and the mercury is allowed to fall to the lower mark. The lower tap is closed, and the pipette is shaken for one to two minutes to establish equilibrium. Mercury is then let in through the lower tap until the gas volume is *a* c.c. and the pressure is read (*m* mm.). The zero point is then determined by expelling the gases or after absorbing one or more of them by introducing small, measured volumes of gas-free absorbent solutions. The pressure is then lowered until the space above the solution is again *a* c.c. and read (*n* mm.). The volume at *N.T.P.* of the gas given off is $V = a(m-n)/760 \cdot \{273/T + S\alpha/(A-S)\}$. The term $S\alpha/(A-S)$, in which α is the volume of the gas dissolved in 1 c.c. of the solution at *N.T.P.* corrects for the portion of the gas remaining dissolved when equilibrium is reached. It is negligible for oxygen and nitrogen, but not for carbon dioxide. The solubility of the latter gas also imposes an empirical correction for reabsorption of the gas while undergoing reduction from 50-*S* to *a* c.c. With *S*=50 c.c. *a*= 2 c.c. the factor is 1.020, that is 2% of the carbon dioxide is reabsorbed. G. B.

The Use of Mercuric Nitrate instead of Silver Nitrate in the Estimation of the Halogens. I. M. KOLTHOFF and ADA BAK (*Chem. Weekblad*, 1922, **19**, 14—16).—The method proposed by Votoček (A., 1918, ii, 238, 272, 330), in which mercuric nitrate is used with sodium nitroprusside as indicator, gives very accurate results for chlorides (and for bromides, cyanides, and thiocyanates) if a correction is applied for the excess of mercuric salt necessary to produce a precipitate under given conditions of composition and volume of solution. Tables of corrections are given. Neither dilute acids nor the common metals (except copper, cobalt, nickel, and cadmium) interfere. The method estimates accurately chlorides in conductivity water, and gives good results for as little as 9 mg. of chlorine per litre; it is suitable for the estimation of chlorides in urine. S. I. L.

Use of Perchloric Acid as an Aid to Digestion in the Kjeldahl Nitrogen Estimation. BRAINERD MEARS and ROBERT E. HUSSEY (*J. Ind. Eng. Chem.*, 1921, **13**, 1054—1056).—In the estimation of nitrogen in such substances as milk, urine, casein, gelatin, dried blood, etc., by the Kjeldahl method, the time required for the digestion with sulphuric acid is reduced to about twenty minutes if perchloric acid is added to the mixture. For each gram of sample, 25 c.c. of sulphuric acid, 1 gram of copper sulphate, and 2 c.c. of 60% perchloric acid should be used, but the presence of an excess of perchloric acid causes loss of nitrogen. W. P. S.

Micro-Kipp Apparatus for the Preparation of Air-free Carbon Dioxide for Use in the Micro-estimation of Nitrogen by Pregl's Method. A. SCHOELLER (*Z. angew. Chem.*, 1921, **34**, 586).—The apparatus consists of two small cylindrical bulbs, one above the other; the upper one contains fused potassium-sodium carbonate and is provided with a tapped delivery tube, whilst a side tube on the lower bulb connects with an upper acid reservoir. The apparatus is made all in one piece. W. P. S.

Estimation of Very Small Quantities of Arsenic in Silicate Rocks. O. HACKL (*Chem. Ztg.*, 1921, **45**, 1169).—Ten grams of the finely-powdered sample are heated at 250° in a tube through which a current of dry carbon dioxide saturated with bromine vapour is passed; the outlet end of the tube is connected with a receiver containing 10 c.c. of dilute nitric acid and the receiver may be connected with a vessel containing sodium hydroxide solution to absorb the excess of bromine. The contents of the receiver are subsequently evaporated with the addition of a small quantity of sulphuric acid, the residue is dissolved in water, and the arsenic in this solution estimated by the Gutzeit method. W. P. S.

Method for Direct Estimation of Carbon Dioxide and Oxygen in the Berthelot Bomb and its Importance for the Metabolic Balance of Herbivora. W. KLEIN and MARIA STEUBER (*Biochem. Z.*, 1921, **120**, 81—89).—An extension of the

work of Zuntz and co-workers on the use of the Berthelot bomb calorimeter for the analysis of organic substances, the main feature now introduced being the determination of the oxygen used, by weighing. It may prove useful for the analysis of the metabolic excreta of herbivora.

H. K.

Micro-elementary Analysis by Pregl's Method. A. SCHOELLER (*Z. angew. Chem.*, 1921, **34**, 581—583).—A short review of the method, with a detailed description of the apparatus used.

W. P. S.

Simplified Construction of the Metal Parts of the Apparatus used in Pregl's Micro-analytical Method. A. SCHOELLER (*Z. angew. Chem.*, 1921, **34**, 587).—Convenient methods of attaching the heating apparatus for the lead peroxide, the micro-burner, the drying chamber, etc., to the stand are described, the parts being provided with brass rods which fit into a boss on the stand.

W. P. S.

Solid Sodium Hydroxide as an Absorbent for Carbon Dioxide in Steel Analysis. G. L. KELLEY and E. W. EVERS (*J. Ind. Eng. Chem.*, 1921, **13**, 1052).—Powdered sodium hydroxide, which will pass through a 5-mesh sieve but be retained on a 20-mesh sieve yields satisfactory results when used to absorb carbon dioxide in the estimation of carbon.

W. P. S.

The Separation of Silver from Mercurous Salts. I. M. KOLTHOFF (*Pharm. Weekblad*, 1921, **58**, 1680—1683).—The treatment of the mixed chlorides precipitated in Group I with ammonia will not separate small quantities of silver from mercurous chloride. A better method is to treat the mixed chlorides, after exhaustive washing with boiling water to remove lead, with 2% potassium cyanide solution. Silver and mercuric cyanides dissolve in the reagent, whilst black metallic mercury is precipitated. After filtering, silver is again precipitated by means of hydrochloric acid; mercuric chloride remains in solution, and may be detected, after filtering, by means of sodium sulphide. The test detects 0.05 mg. of silver in presence of 50 mg. of mercurous mercury, and will also detect 0.5 part of mercury in presence of 100 parts of silver.

S. I. L.

The Titration of Zinc. E. MONASCH (*Pharm. Weekblad*, 1921, **58**, 1652—1656).—The thiocyanate method of Kolthoff and van Dijk (*ibid.*, 538) has been applied to the estimation of zinc in alloys. The potassium mercuric thiocyanate solution is prepared by dissolving 23.7 grams of mercuric thiocyanate in a concentrated aqueous solution of 14.4 grams of potassium thiocyanate, and is stable for many months. Compounds of all the common metals interfere, but ferric and aluminium salts do not affect the reaction. Since the author uses aluminium in the separation of zinc from alloys, the method is suitable for the estimations, but iron salts must first be oxidised by means of peroxide.

S. I. L.

Estimation of Minute Amounts of Lead in Water, with Notes on certain Causes of Error. D. AVERY, A. J. HEMINGWAY, V. G. ANDERSON, and T. A. READ (*Proc. Austral. Inst. Min. Met.*, 1921, 173—199).—By the following method it is possible to detect and estimate with considerable accuracy 1 part of lead in 100,000,000 parts of water. A known volume of the water is filtered, and 2·5 to 5 litres of the filtrate are evaporated to about 100 c.c., just neutralised with hydrochloric acid, and 2 c.c. excess of acid are added, the liquid is filtered and the filtrate cooled and made up to 250 c.c. Hydrogen sulphide is passed into the solution for one hour and, after remaining over-night, the precipitate, which is usually barely visible, is collected and washed with cold water containing hydrogen sulphide in solution. Two portions of 2 c.c. of hot nitric acid (*d* 1·2) are then successively poured over the filter to dissolve the sulphides, and the filter is washed with hot water. The filtrate is evaporated with 1 c.c. of sulphuric acid until the latter fumes strongly, and the liquid, after cooling, is treated with 20 c.c. of cold water and 10 c.c. of absolute alcohol, and the mixture set aside over-night. The precipitated lead sulphate is collected and washed with a mixture of 65 vols. of water, 32 vols. of absolute alcohol, and 3 vols. of sulphuric acid. It is dissolved off the paper by dropping successively two portions of 5 c.c. of hot 33% ammonium acetate solution round the edges and then washing the paper thoroughly with hot water. The solution is transferred to a 50 c.c. Nessler tube and treated with 1 c.c. of 10% potassium cyanide solution, 1 c.c. of ammonia solution, and six drops of freshly-prepared ammonium sulphide solution. Into the standard tube are placed the same reagents in the same quantities; the liquid, which must be absolutely colourless, is diluted to 45 c.c., and a standard solution of lead acetate (1 c.c. = 0·00001 gram of lead) is added until the tint matches that of the assay. If more than 8 c.c. of the standard are required, a proportionately smaller quantity of the sample should be used. To estimate the lead in the sediment, it is evaporated to dryness with hydrochloric acid, the residue is taken up with 2 c.c. of the same acid, the solution filtered, and the assay finished in a similar way to that of the water.

The estimation of lead in urine is carried out by evaporating 1 litre of the sample with 50 c.c. of nitric acid to dryness, first on a water-bath, then on the hot-plate. The dish is then placed in a cool, electrically heated muffle and gradually heated to 450—500° to destroy organic matter and nitrates. The residue is dissolved in water, the liquid just neutralised with hydrochloric acid, 2 c.c. more acid are added, and the solution is filtered. The filtrate is treated for lead as described above.

All the materials used in the above work should be redistilled from lead-free glass apparatus, the ammonium acetate should be made by neutralising freshly distilled ammonia with acetic acid, and the ammonium sulphide must be made immediately before use. All filter-papers before use must be washed with hot dilute hydrochloric acid, hot ammonium acetate solution, and hot water

successively to remove the minute amounts of lead introduced by the acid washing process of rendering them ashless. A blank test must be made, using the same quantity of redistilled water as that used for the assay and putting it through the whole of the operations.

A. R. P.

New Method for the Volumetric Estimation of Copper.

S. MINOVICI and AL. IONESCU (*Bul. Soc. Chim. România*, 1921, 3, 89—93).—The salt $\text{CuSO}_4 \cdot 4\text{NH}_3$ is quite stable at the ordinary temperature, and is quantitatively precipitated from aqueous solution by addition of eight volumes of 98% alcohol. The precipitate, after thorough washing with alcohol, is redissolved in water, and titrated with *N*/10-sulphuric or oxalic acid, with methyl-red as indicator.

J. K.

Rapid Estimation of Mercury in Ores.

ALFRED HEINZELMANN (*Chem. Ztg.*, 1921, 45, 1226—1227).—The author has made comparative tests on the estimation of mercury in ores, using a modification of Whitton's method (*U.S. Bureau of Mines, Bull.* 78, 1918) which consists in heating the ore with a mixture of 3 grams of fine iron filings and 3 grams of good lime and collecting the mercury on a cooled silver plate previously weighed, and his own method (A., 1921, ii, 521) and finds that both methods give equally satisfactory results. [Cf. *J. Soc. Chem. Ind.*, 1922, 61A.]

A. R. P.

The Analysis of Aluminium Alloys.

H. MENDE (*Chem. Ztg.*, 1922, 46, 49—50).—One gram of the alloy is heated with 5 c.c. of water and 12 c.c. of strong potassium hydroxide solution (the latter added gradually) on a water-bath until nothing further dissolves. The liquid is diluted with water, the clear liquor decanted through a small filter-paper, and the precipitate washed by decantation, first with dilute potassium hydroxide solution, then with hot water. The filter-paper is burnt in a platinum spiral, the ash added to the metallic residue in the beaker, and the whole dissolved in 5 c.c. of strong nitric acid and 15 c.c. of water; 75 c.c. of water are added, the liquid is boiled and the precipitate collected, washed, ignited, and weighed as tin dioxide. It should be tested for traces of silica. The filtrate is evaporated with 5 c.c. of sulphuric acid until the latter fumes strongly, the mass is treated with 150 c.c. of water, and the precipitated lead sulphate estimated in the usual way. The filtrate is electrolysed with a current of 0.5 ampere at 2.0—2.2 volts for one and a half hours at 75°, using a spiral anode and a gauze cathode. The gain in weight of the latter represents copper. The solution is neutralised with sodium hydroxide after adding any zinc found by treating the potassium hydroxide solution of the alloy with sodium sulphide, and 50 c.c. of a 50% solution of sodium hydroxide are added in excess. The solution is again electrolysed, using the same anode and cathode (the latter being coppered or silvered) for two to three hours at 70°, using a current of 1—1.5 amperes at 4 volts. The gain in weight of the cathode represents zinc. Silicon is estimated in a separate

trial in which 3 grams of the alloy are evaporated with 50 c.c. of a mixture of 2 parts of sulphuric acid, 3 parts of hydrochloric acid, 1 part of nitric acid, and 4 parts of water. After the metal has dissolved, the solution is evaporated with 30 c.c. of strong sulphuric acid until the latter fumes strongly, the liquid is treated with 300 c.c. of water, and the silica, which separates in an easily filterable, flocculent form, is collected, washed, ignited, and weighed as usual. Iron is determined by treating 3 grams of the alloy in potassium hydroxide solution, collecting the insoluble residue, and dissolving it, after thorough washing, in nitric acid. The solution is evaporated to dryness, the nitric acid destroyed by evaporation with hydrochloric acid, the copper and heavy metals are removed by hydrogen sulphide, the iron is precipitated from the oxidised solution by ammonia, redissolved in acid, reprecipitated as before, and the final precipitate either weighed as Fe_2O_3 after ignition, or dissolved in sulphuric acid, reduced, and titrated in the usual way.

For the estimation of traces of iron in pure aluminium, 3 grams of the metal are heated with 50 c.c. of strong potassium hydroxide solution, 200 c.c. of 50% sulphuric acid are added, the solution is heated until everything has dissolved, then quickly cooled, and titrated with *N*/10-potassium permanganate. Copper and silicon are estimated as described above for alloys. A. R. P.

Germanium. II. Identification of Germanium by its Visible Arc Spectrum. JACOB PAPISH (*Chem. News*, 1922, 124, 3).—Photographs of the arc spectrum of germanium were obtained by means of a Hilger constant deviation spectrograph fitted with a flint glass prism ($n_D=1.7537$), the arc being made between carbon electrodes, the lower positive one carrying the material to be tested. Under these conditions, the little-known germanium line in the blue, λ 4686, is very sharp and intense, and very suitable for the identification of the metal. The line overlaps the prominent zirconium line of wave-length 4688.

G. F. M.

The Carrying Down of Calcium Oxide by Precipitates of Ferric Oxide. A. CHARRIOU (*Compt. rend.*, 1921, 173, 1360—1362; cf. Toporescu, A., 1920, ii, 450).—In order to get the minimum co-precipitation of calcium hydroxide with ferric hydroxide, the concentration of the calcium salt should be as small as possible and the minimum amount of ammonium hydroxide requisite for the precipitation of the ferric hydroxide should be used. W. G.

Estimation of Nickel in Steels. H. RUBRICIUS (*Chem. Ztg.*, 1922, 46, 26).—From 2 to 5 grams of the borings are dissolved in 40—80 c.c. of nitric acid (d 1.2), and the solution is cooled and treated with 250 c.c. of ammonia (d 0.91). It is transferred to a graduated flask and diluted to 500 c.c. of which 250 c.c. are filtered through a dry paper, diluted to 500 c.c., and the solution, heated at 40° , is treated with 20—30 c.c. of a 1% alcoholic solution of dimethylglyoxime. After half an hour the precipitate is filtered

on a 15 cm. paper, washed with hot water, dried, and ignited to nickelous oxide in a platinum crucible and weighed. $0.7858 \times \text{NiO} = \text{Ni}$.
A. R. P.

Estimation of Chromium in Ferrochromium by Electro-metric Titration. G. L. KELLEY and J. A. WILEY (*J. Ind. Eng. Chem.*, 1921, **13**, 1053—1054).—Twenty grams of sodium carbonate are fused in a nickel crucible and then cooled, the crucible being rotated during the cooling so that the carbonate forms a lining. A mixture of 16 grams of sodium peroxide and 1 gram of the sample is then fused for three minutes in this crucible, the heat being so regulated that the sodium carbonate lining is not fused; when cold, the contents of the crucible are dissolved in 300 c.c. of water, the solution is boiled for thirty minutes, cooled, 80 c.c. of sulphuric acid (d 1.58) are added, the solution is boiled for a further five minutes, cooled, filtered, and the filtrate diluted to 1 litre. One hundred c.c. of this solution are treated with 25 c.c. of sulphuric acid and titrated with ferrous ammonium sulphate solution, using the apparatus described previously by the authors and Adams (*A.*, 1917, ii, 512).
W. P. S.

Tungsten. HERBERT LAVERS (*Proc. Austral. Inst. Min. Met.*, 1921, 101—152).—The paper contains a short description of the chemistry and metallurgy of tungsten together with a summary of the various processes that have been described for the estimation of tungsten in low grade ores. A volumetric method is recommended in which the tungsten is precipitated with cinchonine hydrochloride from acid solutions, and the precipitate dissolved in ammonium acetate, an excess of lead acetate added, and the excess determined by titration with ammonium molybdate. [Cf. *J. Soc. Chem. Ind.*, 1922, Feb.]
A. R. P.

Estimation of Thorium in Monazite Sand by an Emanation Method. HOMER H. HELMICK (*J. Amer. Chem. Soc.*, 1921, **43**, 2003—2014).—A method of estimating thorium in monazite sand is described. The sample is sieved through a 40 per cm. mesh and dried at 115—120°. Two grams are well mixed with 5 grams of potassium hydrogen fluoride and 5 grams of anhydrous, recently fused, metaphosphoric acid, and slowly brought to the highest temperature obtainable with a Méker burner in a 35 c.c. platinum crucible. A further 5 grams of metaphosphoric acid are slowly added during the heating; when the mass is clear, it is allowed to cool. After cooling, 20 c.c. of 80% orthophosphoric acid are added, and the crucible is heated in an air-bath at 250—255° for three hours, the solution being automatically stirred with a platinum wire; in this way a viscous solution is obtained. A small vessel made of glass and fitted with a ground stopper and inlet and outlet tubes is suspended in a vessel of concentrated sulphuric acid at 190—200° and the liquid from the crucible poured in. The solution vessel is removed from the acid, allowed to cool, and the remaining contents of the crucible are washed in with two quantities of 20 c.c. of water, the total volume made up to 75 c.c.,

and the vessel closed in an air-tight manner. The electroscope measurements are made, (i) with a blank, prepared in exactly the same way as the sample except that the monazite is omitted, (ii) with a standard solution containing a known amount of thorium, and (iii) with the sample solution. The percentage of thorium is calculated by means of the expression $X = AT_s(T_b - T_u)/T_s(T_b - T_s)$ in which X is the percentage of thorium in the sample, A the percentage in the standard, T_s the time of discharge of the electroscope by the standard, T_b by the blank, and T_u by the sample under investigation. The main sources of error of Cartledge's emanation method (A., 1919, ii, 120) were adsorption of thorium X by suspended matter in final solutions, by filters, and by the walls of the vessels used. These errors are avoided in the present method by producing a complete solution of the sand without filtration and in a single vessel. Other improvements made use of are a highly efficient form of vessel to contain the solution during de-emanation; the use of an automatic regulator to maintain constant pressure in the ionisation chamber during measurements; maintenance of optimum pressure gradient along the air current line through the measuring apparatus, thus assuring a minimum error on account of pressure variations, and maximum speed of measurement; protection of the insulation of the electroscope by means of a current of dry air. Analyses by this method gave results agreeing very well with results obtained by gravimetric methods, and required much less time for each determination.

J. F. S.

Detection of Bismuth in Urine. PIERRE AUBRY (*J. Pharm. Chim.*, 1922, [vii], 25, 15—18).—Following the administration of bismuth salts the metal is at least to some extent eliminated in the urine. In certain cases, it manifested its presence as a black precipitate of bismuth sulphide, but in other cases no precipitation occurred, and the metal was detected by evaporating to dryness, calcining the residue, dissolving the ash in hot dilute nitric acid, and adding a reagent containing 1% of quinine sulphate and 2% of potassium iodide dissolved in slightly acidified water, which produces an orange-red coloration or precipitate, according to the amount of bismuth present. This reagent is sufficiently sensitive to detect 1 part of Bi_2O_3 in 600000 parts of water. G. F. M.

Estimation of Alcohols by Acetylation. H. WOLFF (*Chem. Umschau*, 1922, 29, 2—3).—The acetylation is carried out by weighing out 0.5 gram of the sample in a test-tube 0.6—0.8 cm. wide and 10 cm. long. One c.c. of acetic anhydride is added and the tube sealed, the lower end being kept in cold water the while. The tube is heated for one hour in a boiling water-bath, removed, and allowed to cool. It is then placed in a well-stoppered, thick-walled flask, and broken by vigorous shaking. The stopper is bound on and the flask heated at about 50° for half an hour on the water-bath with constant shaking, cooled, and neutralised to phenolphthalein. Twenty-five c.c. of $N/2$ -alcoholic potash are

added and enough alcohol to make a clear solution. The flask is either left over-night or warmed for a quarter to half an hour at 50–60°, cooled, and titrated back with *N*/2-acid. The results obtained are within less than 1% of the theoretical. Solvents such as light petroleum or benzene have no effect on the result. If esters are present, their saponification value must be allowed for.

H. C. R.

New Methods of Blood Sugar Estimation. Estimation of the True Sugar Content of Urine. D. G. COHEN-TERVAERT (*Nederl. Tijdschr. v. Geneesk.*, 1921, 65, ii, 857–864, 3065–3069).—I. The methods of Schaffer and Hartmann (A., 1921, ii, 417), Folin and Wu (A., 1919, ii, 308), and of Ponder and Howie (A., 1921, ii, 417) deserve full recommendation. The first-named has been worked out for 0.1–0.2 c.c. of blood.

II. Sumner's method (A., 1921, ii, 564) has been compared with a fermentation method due to Nagasaki (*Nederl. Tijdschr. v. Geneesk.*, 1915, ii, 1478) and found to be very accurate. A few small modifications were introduced.

G. B.

A Source of Error in Testing Urine for Dextrose with o-Nitrophenylpropionic Acid. GEORGES RODILLON (*J. Pharm. Chim.*, 1922, 25, 56–57).—Dextrose is not the only reducing agent likely to be found in urine which will reduce o-nitrophenylpropionic acid to indigotin. The presence of hydrogen sulphide will both show this reaction and give a positive result in the sodium nitroprusside reaction for acetone. It does not reduce Fehling's solution. If the tests are carried out after clarifying the sample with lead acetate, these misleading results are avoided.

H. C. R.

The Identification of Lævulose in Presence of Aldoses. I. M. KOLTHOFF (*Chem. Weekblad*, 1922, 19, 1–2).—To 2 c.c. of the 1% sugar solution are added in succession 4 c.c. of *N*/10-iodine solution and 5 c.c. of 2*N*-sodium hydroxide. This order of addition must not be reversed. The mixture after shaking is left for one to one and a half hours and the excess of iodine removed by addition of a few drops of *N*-thiosulphate. Two c.c. of Fehling's solution No. II and 2 c.c. of Fehling's solution No. I are added, the tube is shaken, and warmed in a boiling water-bath for not more than five minutes. A red coloration in one minute shows 5% fructose in presence of glucose; in two minutes, 2½%, and in four minutes 1% of fructose. After five minutes, glucose alone gives the red colour.

The test detects 0.2 mg. of lævulose in presence of 10 mg. of dextrose, 10 mg. of sucrose, and 10 mg. of lactose.

S. I. L.

Estimation of Sugar by Titration with Alkali of the Cuprous Oxide Precipitated from Fehling's Solution. A. HANAK (*Z. Unters. Nahr. Genussm.*, 1921, 42, 248–250).—The cuprous oxide obtained from the inverted sugar solution containing not more than 0.5% of invert-sugar, and 50 c.c. of Fehling's solution is washed, dissolved in aqua regia, diluted to 250–300 c.c. with water free from carbon dioxide, and carefully neutralised with

sodium hydroxide so that it gives a pale greenish-yellow colour with methyl-orange. Phenolphthalein is added and $N/2$ -sodium hydroxide run in until the red colour remains for three minutes in the boiling solution. One c.c. of $N/2$ -sodium hydroxide = 0.0159 gram of copper.
H. C. R.

Detection of Traces of Lactose in Urine by Formation of Formaldehyde. KURT HERZBERG (*Biochem. Z.*, 1921, **119**, 81—92).—The injection of lactose for testing the functioning capacity of the kidney necessitates a ready method for its recognition in urine. Concentrations of 0.2% can be recognised by isolation of the osazone, oxidation of the latter with permanganate to formaldehyde which can be detected by a colour test, for example, the reaction with peptone and ferric chloride.
H. K.

Polarisation of Normal Sucrose Solution. VLAD. STANĚK (*Z. Zuckerind. čechoslov.*, 1921, **45**, 417—423; 425—431).—After correction for water, ash, invert-sugar, error of the polarimeter, etc., a normal solution of sucrose (recrystallised) polarised 99.9° Ventzke, using a dichromate filter, or 100.1° Ventzke, when a filter was not used.
W. P. S.

Use of Invertase for Sucrose Estimation. T. SWANN HARDING (*Sugar*, 1921, **23**, 546—547).—Errors in acid hydrolysis of sucrose by the Clerget method include the hydrolysis of other sugars present and the effect of the acidity on optical non-sugars. Using invertase, no effect is found on compounds present other than sucrose. Invertase can be obtained of sufficient strength to invert a 10% sucrose solution in two hours. The activity of invertase may be retained for a year and a half.

CHEMICAL ABSTRACTS.

Detection of Fatty Acids by the Formation of their Sodium Uranyl Salts. J. BARLOT and (MLLE) M. T. BRENET (*Compt. rend.*, 1922, **174**, 114—116).—Streng's reaction for the micro-chemical detection of sodium (cf. *Ber. oberhess. Ges. Nat. Heilkunde*, 1883, **22**) based on the formation of a characteristic crystalline precipitate of sodium uranyl acetate with uranyl acetate in the presence of acetic acid, gives positive results if acetic acid is replaced by its homologues in which there is an even number of carbon atoms in the straight chain. In the case of derivatives of acetic acid, the reaction depends on the nature of the substituent. The chloroacetic acids do not give the reaction, but sodium phenylacetate and uranyl nitrate give, at once, crystals of the double salt, $\text{CH}_2\text{Ph}\cdot\text{CO}_2\text{Na}, (\text{CH}_2\text{Ph}\cdot\text{CO}_2)_2\text{UO}_2$.
W. G.

[**Estimation of Arachidic Acid.**] J. PRITZKER and R. JUNG-KUNZ (*Z. Unters. Nahr. Genussm.*, 1921, **42**, 232—241).—See this vol., i, 208.

A rapid Method for Determining the Acetyl Value of Oils and Fats. ALEXANDRE LEYS (*J. Pharm. Chim.*, 1922, **25**, 49—56).—The following values are determined: the saponification

value S of the oil or fat, the saponification value S' of the acetylated oil or fat and the ratio K between the weight of the acetylated matter and that of the oil or fat from which it has been prepared. The acetyl value A is given by $A = S' - S/K$. To determine K , a weighed quantity of the oil or fat is boiled with ten times its volume of acetic anhydride under a reflux condenser for two hours, cooled, diluted with benzene, and transferred to a tared dish. The benzene and excess of acetic anhydride are evaporated on a water-bath and the acetylated oil or fat is weighed. The acetyl value of an oil or fat dissolved in a neutral solvent having no acetyl value may be obtained without evaporating off the solvent as follows. One weighed portion (P') of the mixture is acetylated and the excess of acetic anhydride removed as above. The saponification value S' of this is then obtained. A further portion is saponified without acetylating, giving a saponification value S . $S' - S = A_0$ represents the quantity of potassium hydroxide required to neutralise the acetic acid which has combined with 1 gram of the mixture. This has increased its weight by $42 \times A_0 / 56 = 0.75 A_0$. Therefore P' grams of fat has become $P'' = P'(1 + 0.75 A_0)$ grams of acetylated fat. A saponification value S'' can therefore be calculated, based on the weight of acetylated oil or fat. The acetyl value $A = S'' - S/K$.

H. C. R.

Detection of Vegetable Oils in Animal Fats. The Phytosteryl Acetate Test. C. F. MUTTELET (*Ann. Falsif.*, 1921, **14**, 327—333).—The cholesteryl acetate obtained from butter, lard, or beef fat (by treating the fatty acids at 70° with alcoholic digitonin solution, collecting the precipitated compound, converting it into the acetate and recrystallising the latter twice from alcohol) has m. p. 114.0° to 114.3° , whilst the phytosteryl acetate obtained in a similar way from coconut oil or earthnut (arachis) oil has m. p. 124.5° to 126.5° . This method will detect the presence of 10% of vegetable oil in an animal fat.

W. P. S.

Presence and Estimation in the Total Lipoid Ether-soluble Phosphorus of Phosphorus Compounds other than Phosphatides. (MLLE) ELIANE LE BRETON (*Bull. Soc. Chim. Biol.*, 1921, **3**, 539—546).—The ordinary indirect method of estimating lecithins as ether-soluble phosphorus is subject to an error, unless the material is purified by precipitation with acetone, according to MacLean (A., 1914, i, 1197). About 20% of impurities remain in the acetone, which contains free and combined glycerol as well as phosphorus. These impurities are not formed by hydrolysis of lecithin during extraction.

G. B.

Titrimetric and Spectrometric Analysis of Keto-Enol Mixtures. KARL VON AUWERS and HELENE JACOBSEN (*Annalen*, 1922, **426**, 161—236).—The general plan of the series of researches of which this paper forms a part has already been fully described (A., 1918, ii, 381), and it is now shown that by following the method of computation previously indicated spectrochemical data may be employed to estimate with moderate certainty the proportion

of enol in a keto-enol mixture. It is true that the method breaks down in certain cases owing to the difficulty of estimating the optical constants for one or other of the pure constituents; K. H. Meyer's titration method also gives somewhat uncertain values in particular cases. However, when the indications of both methods are definite they are in remarkably good agreement.

The following substances have been examined. The percentages represent the enol-content estimated spectrochemically, whilst the figures in brackets are the values determined by titration with bromine: ethyl acetylmalonate, 70% (69); ethyl propionylmalonate, 43% (44); ethyl *n*-butyrylmalonate, 55% (55); ethyl isobutyrylmalonate, 47% (47); ethyl isovalerylmalonate, 57% (55); ethyl hydroxymethylenemalonate, 100% (94); ethyl hydroxymethylene-ethyl ketone, ?% (<100); hydroxymethylenecyclohexanone, assumed 100% (100); 3-methyl-6-hydroxymethylenecyclohexanone, <100% (91%); 3:4-dimethyl-6-hydroxymethylenecyclohexanone, ?% (89); hydroxymethylenementhone, ?% (97); acetylacetone, 82% (84); propionylacetone, 76% (72); methylacetylacetone, 33% (36); ethylacetylacetone, 31% (29); propylacetylacetone, 31% (32); benzoylacetone, 100% (100); propionylacetophenone, 93% (94); butyrylacetophenone, 88% (90); isovalerylacetophenone, 89% (85); methylbenzoylacetone, 6% (9); methyl benzoylacetate, 20% (19); ethyl benzoylacetate, 24% (21); ethyl α -benzoyl-*n*-butyrate, 2% (4). C. K. I.

Colour Reactions of Phenacetin and Acetanilide. L. EKKERT (*Pharm. Zentr.-h.*, 1921, 62, 735—737).—Under definite conditions, phenacetin and acetanilide give different colorations when hydrolysed with sulphuric acid and then oxidised with potassium dichromate. If 0.1 gram of phenacetin is boiled for one minute with 5 c.c. of 10% sulphuric acid, the solution then cooled, diluted to 5 c.c., and treated with 2 drops of 1% potassium dichromate solution, a violet-red or red coloration is obtained. Acetanilide under similar treatment, but when boiled for two minutes, yields gradually a greenish-blue coloration. W. P. S.

Alkalimetric Estimation of Amino-acids and Peptides. RICHARD WILLSTÄTTER and ERNST WALDSCHMIDT-LEITZ (*Ber.*, 1921, 54, [B], 2988—2993).—The acid of ammonium salts can be estimated alkalimetrically with phenolphthalein as indicator if the aqueous solution of the salt is mixed with a sufficient amount of alcohol, since ammonia does not affect the indicator in alcoholic solution. It is essential that the solution should contain about 97% of alcohol and that relatively much indicator should be used. Amino-acids and polypeptides show a similar behaviour. Characteristic differences are shown, however, in the concentration of the alcohol which is necessary for the elimination of the action of the amino-groups or of hydroxyl ions. The polypeptides, peptones, and proteins behave in the same manner as the ordinary carboxylic acids in solutions containing 40% of alcohol, whereas amino-acids of the aliphatic series or of aliphatic character require an alcoholic

concentration of about 97% to produce this effect. Ethyl alcohol can be replaced by propyl alcohol, which appears to be even more effective, but not by methyl alcohol. The behaviour enables amino-acids and polypeptides to be estimated simply in mixtures of the substances by titrating with alkali hydroxide solution to neutrality towards phenolphthalein in 50% and 97% alcoholic solution. If a and b are the volumes of alkali solution used, the proportion, x , required by the amino-acids (since the majority of the latter and, in any case, those which predominate in the general mixtures neutralise in 50% alcoholic solution 28% of the amount required for complete neutralisation) is $100(b-a)/72$ and the proportion used by the polypeptides is $b-x$.
H. W.

Estimation of Urea. F. MEZGER (*Pharm. Zentr.-h.*, 1921, 62, 719—721).—A simple gasometric method is described. One c.c. of the urine is placed in a small tube and this in turn is placed in a reaction bottle containing 30 c.c. of hypobromite solution and connected with the top of a burette; the latter is filled with water to the zero point by means of a levelling reservoir and serves as a measuring vessel for the nitrogen evolved when the urine and hypobromite solution are mixed. A definite volume (for example, 1 c.c.) of 2% urea solution is treated in the same way and at the same time in an exactly similar apparatus. This is taken as the standard and the amount of urea in the urine is calculated from the ratio of the two volumes of nitrogen obtained. W. P. S.

Quantitative Gravimetric Micro-analysis of Urea. Application to the Estimation of Urea in 1 c.c. of Blood. MAURICE NICLOUX and GEORGES WELTER (*Compt. rend.*, 1921, 173, 1490—1493).—The use of Fosse's xanthidrol reagent (cf. A., 1914, i, 859; ii, 506) is combined with Pregl's micro-methods of analysis (cf. *Die quantitative organische Mikroanalyse*, Berlin, 1917). To 1 c.c. of solution containing not more than 0.2 mg. of urea are added 1 c.c. of glacial acetic acid and 0.2 c.c. of 5% xanthidrol solution in methyl alcohol. The mixture is stirred, and after thirty minutes the precipitate is collected in a Neubauer micro-crucible and washed alternately with saturated solutions of xanthylcarbamide in alcohol and water and finally with two drops of distilled water. The precipitate is dried at 105—110° and weighed on a micro-balance. For the estimation of urea in serum, 1.0 c.c. or 0.5 c.c. is used. It is diluted with exactly five times its volume of water, and a volume of Tanret's reagent equal to the original volume of the serum is added. After five minutes the precipitate is filtered off and, in 1 c.c. of the filtrate, the urea is precipitated as above. The weight of xanthylcarbamide obtained is thus just equal to the weight of urea present in 1 c.c. of the original serum.
W. G.

Estimation of Uric Acid in Blood. CH. O. GUILLAUMIN (*J. Pharm. Chim.*, 1922, [vii], 25, 5—15).—The following *modus operandi* is recommended for the colorimetric estimation of uric

acid in blood: The blood or serum is first freed from albuminous substances by mixing 4 c.c. with 4 c.c. of 10% sodium tungstate solution, 28 c.c. of distilled water, and 4 c.c. of 2.7% sulphuric acid, shaking vigorously, and filtering until a clear filtrate is obtained. For ordinary clinical work, the uric acid may then be estimated directly in the filtrate by adding to 20 c.c. 1.5 c.c. of 40% solution of crystallised sodium carbonate, 0.5 c.c. of the sodium phosphotungstate reagent, and sufficient water to make 25 c.c.; and comparing in a colorimeter with a standard sulphite solution of uric acid prepared according to the directions of Folin and Wu (A., 1919, ii, 308). For a more exact estimation, it is preferable to separate the uric acid from the dealbuminised blood by means of silver lactate as described by Folin (*loc. cit.*). This separation of the uric acid is, however, always necessary if working with a solution containing red corpuscles, and by so doing it was demonstrated that blood usually contains a slightly lesser quantity of uric acid than serum. The author does not favour the dealbuminisation of the blood by Grigaut's method, using 20% trichloroacetic acid.

G. F. M.

Detection and Estimation of Morphine and Other Alkaloids in Animal Excreta and Organs. CURT WACHTEL (*Biochem. Z.*, 1921, 120, 265—283).—Previous methods for the estimation of morphine in animal tissues are very laborious and time-consuming. A new process is described which takes about one and a half days. Urine is submitted to a preliminary purification by basic lead acetate and the morphine, in the lead-free filtrate, precipitated by phosphotungstic acid in weakly acid solution. The washed precipitate is decomposed in alkaline solution by sodium potassium tartrate and the morphine, in solution, oxidised to ψ -morphine by an excess of a standard solution of potassium ferricyanide. The excess of the latter is estimated iodometrically. When the morphine is present in tissues a preliminary extraction is made by means of acidified alcohol. The extract from brain and muscle in addition to purification by basic lead acetate has to be submitted to a further purification by boiling with copper sulphate, the copper-free filtrate being then precipitated with phosphotungstic acid. The process is applicable to other alkaloids provided they are not adsorbed by the basic lead acetate precipitate. H. K.

The Bliss Method for the Separation of Strychnine from Quinine. L. E. WARREN and A. H. CLARK (*J. Amer. Pharm. Assoc.*, 1920, 10, 267—270; cf. A., 1920, ii, 276).—The method is shown to be untrustworthy. The quinine fractions invariably contained strychnine. In most cases the strychnine fraction was comparatively free from quinine so that the method may have a qualitative value in detecting the presence of strychnine in mixtures.

CHEMICAL ABSTRACTS.

The Estimation of Proteins in Blood—a Micro-method. PAUL E. HOWE (*J. Biol. Chem.*, 1921, 49, 109—113).—The author

uses 0.5 c.c. of blood and the micro-Kjeldahl method. For the fibrinogen and non-protein nitrogen, he follows the technique of Cullen and Van Slyke (A., 1920, ii, 398). For the rest, the method indicated in the following abstract.

G. B.

The Use of Sodium Sulphate as the Globulin Precipitant in the Estimation of Proteins in Blood. PAUL E. HOWE (*J. Biol. Chem.*, 1921, **49**, 93—107).—In order to apply the Kjeldahl method more readily, the author substitutes sodium sulphate for the ammonium salt. At 37°, critical zones in the precipitation are observed when 13.5, 17.4, and 21.5% of sodium sulphate are present in solution. These correspond respectively with the precipitation of euglobulin (as usually separated by carbon dioxide or saturated sodium chloride) and of that of two ψ -globulins I and II.

G. B.

Reaction for Blood with Hydrogen Peroxide in statu nascendi. A. PATZAUER (*Chem. Ztg.*, 1921, **45**, 1056).—A small quantity of magnesium peroxide is dissolved in very dilute acetic acid and, when violent evolution of gas ceases, guaiacum tincture or benzidine dissolved in acetic acid is added, followed by the ethereal extract of the blood.

W. P. S.

Measuring Soil Toxicity, Acidity, and Basicity. R. H. CARR (*J. Ind. Eng. Chem.*, 1921, **13**, 931—933).—The acidity or basicity of a soil and the amount of soluble iron and aluminium in the same may be estimated as follows: 50 grams of the soil are shaken for two minutes with 30 c.c. of a saturated solution of potassium thiocyanate in 95% alcohol; if, after settling, the liquid has a red colour, *N*/10-alcoholic potassium hydroxide solution is added until the colour disappears. Each c.c. of the alkali solution required is equivalent to 200 lbs. of calcium carbonate per acre. Should a red colour not appear on the addition of the thiocyanate, the mixture is titrated with *N*/10-alcoholic hydrochloric acid until a pink coloration is obtained. The relative amount of aluminium in solution is indicated by the depth of the blue colour produced when the thiocyanate extract of the soil is treated with a few drops of logwood tincture. Soluble iron and aluminium salts seem to be toxic to plants.

W. P. S.

The Estimation of Tannin in Wines. PHILIPPE MALVEZIN (*Bull. Soc. chim.*, 1921, [iv], **29**, 1087—1088; cf. A., 1912, ii, 612).—A reply to Clarens (cf. A., 1921, ii, 719).

W. G.

General and Physical Chemistry.

Visible Refraction and Dispersion in Aqueous Solutions of Salts, particularly Coloured Salts. G. LIMANN (*Z. Physik*, 1921, 8, 13—19).—The refractive indices for the D , H_α , H_β , and H_γ lines have been measured for 0.3, 0.5, 1.0, 2.0, and 4.0*N* solutions of ferrous chloride, bromide and nitrate, copper nitrate and chlorate, ferric chloride, manganous chloride, bromide and nitrate; nickel chloride, bromide, nitrate and chlorate, cobalt chloride, bromide, nitrate and chlorate, aluminium chloride and nitrate; potassium chromate, dichromate, ferrocyanide and ferricyanide, chromic chloride and bromide, lithium sulphate, chromate and dichromate, magnesium chromate, caesium bromide and nitrate, glucinum chloride and nitrate, mercuric chloride, lead nitrate, and sodium chromate. Two constants are deduced from the measurements by means of which the refraction of a solution may be calculated if the equivalent conductivity for the particular concentration is known. The influence of temperature on the refraction and dispersion has been determined in the case of potassium bromide over the range 6—30°. The results show that the dispersion decreases markedly with decrease of temperature, but the refraction is not much influenced. Thus over the measured range of temperature the refraction changes only 1/1500 for a change of 1°.

J. F. S.

Eisenlohr's Refractometric Constants. WOJCIECH SWIENTO-SLAWSKI (*Roczniki Chemji*, 1921, 1, 104—115).—A theoretical paper in which the author attempts to prove the constancy of atomic refraction of the atoms of organic substances. An analysis of the experimental data leads the author to the conclusion that the method employed by Brühl and Eisenlohr is not a rational method. This method of determination of the atomic refraction, based on the calculations of the mean value obtained from a large number of compounds, only serves to cancel the individual differences of the compounds investigated. The author has used a different method. For the calculation of the atomic refractions he takes the molecular refractions of the eight compounds, pentane, isopentane, hexane, octane, diisobutyl, diisoamyl, cyclohexane, and cyclopentane, and has calculated the most probable mean value of the refractivity of the group CH_2 , ζ_{CH_2} , and that of hydrogen, ζ_{H} , by the method of least squares, the equations employed being of the type $M_D = n\zeta_{\text{CH}_2} + 2\zeta_{\text{H}} + \Sigma\Delta\zeta$, and $M'_D = n\zeta_{\text{CH}_2} + \Sigma\Delta\zeta$. In the solution of the equations, it is assumed that the increment $\Sigma\Delta\zeta = 0$. The values thus obtained are compared with those of Eisenlohr, $\zeta_{\text{C}} = (2.418) 2.490$, $\zeta_{\text{H}} = (1.100) 1.066$, $\zeta_{\text{CH}_2} = (4.618) 4.622$, Eisenlohr's values being bracketed. The results show an agreement for the value of ζ_{CH_2} , but a difference of about 3% for ζ_{H} . In the case of compounds containing oxygen, the equation $M_D = n\zeta_{\text{CH}_2} + \zeta_{\text{O}} + \Sigma\Delta\zeta$ is used. The figures obtained show considerable deviations of the

value $\Sigma\Delta\zeta$, that is to say, this increment cannot be regarded as zero. Similar results are obtained for both alcohols and ethers. The agreement obtained on comparing the author's value with those of Eisenlohr is explained by the dominant rôle of $n\zeta_{\text{CH}_2}$ and the insignificant influence of $\Sigma\zeta_x$, which corresponds with a residual refraction of the molecule in the equation $M_D = n\zeta_{\text{CH}_2} + \Sigma\zeta_x + \Sigma\Delta\zeta$. The author concludes that the methods employed by Brühl and Eisenlohr to determine the atomic refractivity mask the variability of this quantity and scarcely give any real knowledge of the refraction of the atoms. J. F. S.

Molecular Coefficients of Refraction. K. VON AUWERS and H. KOLLIGS (*Ber.*, 1921, **55**, [B], 21—45).—In recent publications, Eisenlohr (*A.*, 1920, ii, 717; 1921, ii, 1, 229) has pointed out that the "molecular coefficient of refraction" $M \times n_D^{20}$ is more sensitive to constitutive changes than the generally employed molecular refraction, and has calculated values for aliphatic, benzenoid, and polymethylene compounds; this work is now exhaustively criticised.

A protest is raised against Eisenlohr's method of deriving corrected values. Thus in the case of the *cyclohexane* series, he has assumed that the E values for the hydrocarbons may be derived from those of the corresponding, analogously constituted, alcohols and ketones by the deduction of 0.35. This rule is not fulfilled by 1-methyl*cyclohexan*-4-ol or 1-methyl*cyclohexan*-4-one, and the values for these substances have therefore been recalculated from the relationships that are supposed to exist among position-isomeric *cyclohexane* derivatives. It is shown, however, that these recalculated values lead to data for the refractive index which differ so widely from the experimental values that the latter could only have been obtained by the use of grossly impure material and that this assumption is devoid of experimental basis.

The work on the benzenoid hydrocarbons has been examined in detail. In correcting the observed values for the refractive index to a temperature of 20°, Eisenlohr has preferred the factor 0.00065 or 0.00060 for each degree to the generally employed factor 0.00045. An exhaustive survey shows that this is generally unjustifiable. In the cases of benzene, toluene, and, to a less extent, of ethylbenzene, the higher factor is to be preferred, but in the cases of seventeen other hydrocarbons it is shown experimentally that the lower factor is in very close agreement with the observations. Since the bulk of Eisenlohr's data for the constants of aromatic hydrocarbons are based on von Auwers's observations which have been regarded as erroneous when they do not harmonise with the theory, the values have been redetermined with more particular reference to *m*-ethyltoluene, *m*-propyltoluene, *p*-ethyltoluene, *p*-propyltoluene, and *p*-diethylbenzene. The previous specimens were obtained by the reduction of the corresponding ketones by Clemmensen's method. The latter are prepared by the Friedel-Crafts method and also according to the scheme $\text{C}_6\text{H}_4\text{MeBr} \rightarrow \text{C}_6\text{H}_4\text{Me}\cdot\text{CHMe}\cdot\text{OH} \rightarrow \text{C}_6\text{H}_4\text{Me}\cdot\text{COMe}$, and the

physical constants of the products obtained in either manner are found to be identical. The constants of the hydrocarbons obtained by their reduction are in good harmony with those observed previously. A second method of preparation consists in replacing the hydroxyl group of the carbinols, $C_6H_4Me \cdot CHR \cdot OH$, by bromine and reduction of the bromides by sodium in the presence of moist ether; the indices of refraction of these preparations are mostly lower than those of the first group, practical identity being encountered only with *p*-propyltoluene. Thirdly, the Fittig synthesis is employed which gives specimens having refractive indices lower by 0.002—0.003 than those of the Clemmensen preparations. The discrepancies are far beyond the limits of experimental error. It appears impossible to decide which preparations have the greater claim to purity, since, on the one hand, the Clemmensen products are generally obtained smoothly and in good yield, whereas the "Fittig" specimens, although isolated from more complex mixtures, have constants which harmonise better with Eisenlohr's rules.

Examination of the new data obtained for the benzenoid hydrocarbons in accordance with Eisenlohr's principles leads the author to the following conclusions. Ortho-derivatives can be easily recognised by the markedly higher refractive coefficient, but this does not represent any advance, since it has been shown previously that they are differentiated so sharply from their position isomerides by density, refractive index, and specific exaltation that any of these factors is alone suitable for this purpose. The older methods do not allow the distinction between meta- and para-compounds and in this respect Eisenlohr's constant appears also to be useless; thus in the cases of *m*- and *p*-xylene the refractive indices do not differ by more than one part in a thousand parts and this position is not improved by multiplying them by their molecular weights. Position isomeric tri-derivatives are easily distinguished from one another by their different molecular refractive coefficients, but this was easily possible previously. The relationships of substances with four side chains cannot yet be elucidated.

The molecular coefficient of refraction cannot replace the spectrochemical constants, particularly the specific exaltation, but can only serve as an amplification of them. If it is desired to assign a substance to a particular group or to elucidate the general character of a group of substances, the most trustworthy data are to be derived from the specific exaltation, since in this the influence of homology or position isomerism is but little noticeable. When, on the other hand, it is desired to elucidate questions of structure within a group of substances, the molecular refractive coefficients are likely to be extremely valuable.

The following new data are recorded. Benzene, n_D^{20} 1.50092. Toluene, $n_D^{19.9}$ 1.49653, n_D^{20} 1.49647. Ethylbenzene, n_D^{20} 1.49606. Propylbenzene, n_D^{20} 1.49241. *iso*Propylbenzene, n_D^{20} 1.49199. *m*-Xylene, n_D^{20} 1.49782. *p*-Xylene, $n_D^{19.9}$ 1.49685, n_D^{20} 1.49680. 1-Methyl-2-ethylbenzene, n_D^{20} 1.50381. 1-Methyl-2-propylbenzene, n_D^{20} 1.49931. *o*-Cymene, n_D^{20} 1.501, n_D^{20} 1.50188. *p*-Cymene (from camphor), $n_D^{20.2}$

1.48885, whence n_D^{20} 1.48894 (from cymene-*p*-sulphonic acid), $n_D^{24.1}$ 1.48942, whence n_D^{20} 1.49122. *p*-Diethylbenzene, n_D^{20} 1.49671. ψ -Cumene, $n_D^{19.9}$ 1.50527, whence n_D^{20} 1.50523. Mesitylene, n_D^{20} 1.49981. Prehnitol, n_D^{20} 1.51865. Ethyl- ψ -cumene, $n_D^{15.75}$ 1.51047, whence n_D^{20} 1.50856. 1 : 3 : 5-Methyl-2-ethylbenzene, n_D^{20} 1.51167. *m*-Tolylmethylcarbinol (from magnesium *m*-tolyl bromide and acetaldehyde), b. p. 112°/12 mm. 1-Methyl-3- α -bromoethylbenzene, $C_6H_4Me \cdot CHBrMe$, a colourless liquid, b. p. 101°/12 mm. ($\beta\gamma$ -*Di-m-tolylbutane*, $C_6H_4Me \cdot CHMe \cdot CHMe \cdot C_6H_4Me$, crystallises in slender, lustrous needles, m. p. 97°.) 1-Methyl-3-ethylbenzene (from *m*-methylacetophenone by Clemmensen's method), b. p. 159.7—160.5°, $d_4^{19.9}$ 0.8669, d_4^{20} 0.867, $n_a^{19.9}$ 1.49575, $n_D^{19.9}$ 1.49966, $n_\beta^{19.9}$ 1.51102, $n_\gamma^{19.9}$ 1.52056; (from 1-methyl-3- α -bromoethylbenzene), b. p. 159°, $d_4^{19.8}$ 0.8622, d_4^{20} 0.862, $n_a^{19.8}$ 1.49279, $n_D^{19.8}$ 1.49650, $n_\beta^{19.8}$ 1.50767, $n_\gamma^{19.8}$ 1.51678. *p*-Tolylmethylcarbinol, b. p. 108/12 mm., is oxidised to *p*-methylacetophenone, b. p. 105—106°/13 mm., $d_4^{18.4}$ 1.0045, d_4^{20} 1.003, $n_a^{18.4}$ 1.52880, $n_D^{18.4}$ 1.53391, $n_\beta^{18.4}$ 1.54835, $n_\gamma^{18.4}$ 1.56127, n_D^{20} 1.5332, which is identical with a product prepared by the Friedel-Crafts reaction. 1-Methyl-4- α -bromoethylbenzene, a colourless liquid, b. p. 105—106°/12 mm. 1-Methyl-4-ethylbenzene (from *p*-methylacetophenone by Clemmensen's method), b. p. 160.5°, $n_D^{21.5}$ 1.49424, n_D^{20} 1.49490; from the Friedel-Crafts ketone), b. p. 161°, $d_4^{18.4}$ 0.8650, whence $d_4^{15.9}$ 0.8657, d_4^{20} 0.862, $n_a^{18.4}$ 1.49372, $n_D^{15.9}$ 1.49775, $n_\beta^{15.9}$ 1.50889, $n_\gamma^{15.9}$ 1.51833; (from 1-methyl-4- α -bromoethylbenzene), b. p. 160°, $n_D^{21.4}$ 1.49287, n_D^{20} 1.49481. *m*-Tolylethylcarbinol, b. p. 114°/12—13 mm. 1-Methyl-3- α -bromopropylbenzene, a colourless liquid, b. p. 114°/14 mm. 1-Methyl-3-propylbenzene (from the bromide), b. p. 180°, $d_4^{17.6}$ 0.8646, d_4^{20} 0.863, $n_a^{17.6}$ 1.48968, $n_D^{17.6}$ 1.49340, $n_\beta^{17.6}$ 1.5038; (from *m*-bromotoluene, propyl bromide, and sodium), b. p. 177—178.5°, d_4^{20} 0.8601, n_a^{20} 1.48978, n_D^{20} 1.49321, n_β^{20} 1.50392. *p*-Tolylethylcarbinol is a colourless liquid, b. p. 114°/12—13 mm. 1-Methyl-4- α -bromopropylbenzene, a colourless liquid, b. p. 108°/13 mm. *p*-Propionyltoluene, b. p. 114°/14 mm. 1-Methyl-4-propylbenzene (from the corresponding bromide), b. p. 182°, $d_4^{18.8}$ 0.8620, d_4^{20} 0.861, $n_a^{18.8}$ 1.49278, $n_D^{18.8}$ 1.49655, $n_\beta^{18.8}$ 1.50765, $n_\gamma^{18.8}$ 1.51687; (from *p*-propionyltoluene, according to Clemmensen), b. p. 183°, d_4^{20} 0.860, $d_4^{18.8}$ 0.8617, $n_a^{18.8}$ 1.49269, $n_D^{18.8}$ 1.49641, $n_\beta^{18.8}$ 1.50752; (by reduction of the ketone prepared by the Friedel-Crafts method), b. p. 182.5°, n_D^{20} 1.49542; (from *p*-bromotoluene, propyl bromide, and sodium), b. p. 181—181.5°, $d_4^{23.7}$ 0.8554, d_4^{20} 0.858, $n_a^{23.7}$ 1.48706, $n_D^{23.7}$ 1.49065, $n_\beta^{23.7}$ 1.50119. 1-Methylcyclohexan-4-ol, b. p. 172—173°, $d_4^{16.3}$ 0.9192, d_4^{20} 0.916, $n_a^{16.3}$ 1.45742, $n_D^{16.3}$ 1.45959, $n_\beta^{16.3}$ 1.46558, $n_\gamma^{16.3}$ 1.47025, n_D^{20} 1.4579. 1-Methylcyclohexan-4-one, b. p. 169.2°, $d_4^{19.9}$ 0.91685, d_4^{20} 0.917, $n_a^{19.9}$ 1.44285, $n_D^{19.9}$ 1.44509, $n_\beta^{19.9}$ 1.45110, $n_\gamma^{19.9}$ 1.45595, n_D^{20} 1.4450. H. W.

Occurrence of Spark Lines (Enhanced Lines) in the Arc.

I. Lead and Tin. G. A. HEMSALECH and A. DE GRAMONT (*Phil. Mag.*, 1922, **43**, [vi], 287—306).—A convenient method is

described for obtaining the arc spectra of volatile metals. This consists in placing a piece of the metal on a sheet of copper (5 cm. \times 10 cm. \times 1 mm.) and connecting to the positive pole. The negative pole is a pointed carbon rod; the arc is struck by lowering the point until it touches the metal and then withdrawing it a little. The metal melts and forms a globule and the arc between it and the carbon point burns steadily. The heat generated is dissipated by the copper plate. Experiments are described which seem to indicate that spark lines are brought out in the arc when the degree of ionisation is reduced, as, for example, by blowing air through the arc. The effect of liquid media on the character of the arc spectrum of the metal has been studied by placing a drop of the liquid between the poles before striking the arc. The spark lines, or so-called high temperature lines, disappear from the arc when the cathode is formed by white-hot carbon, but they are brought out prominently when the electrodes are cooled down to about -190° by immersion in liquid air. A detailed account is given of the observations on the relative behaviour of various types of lead and tin lines in the arc under various conditions of discharge. It is definitely shown that the presence of hydrogen is not essential for the excitation of spark lines. Spark lines attain a high degree of development only in a medium which offers a comparatively high resistance to the flow of electricity. When hydrogen is present in the medium, either free or in combination, its spectrum resembles that which is only observed with high tension condenser discharges; namely, its lines are symmetrically broadened as though under the influence of a strong electric field (Stark effect).

J. F. S.

Röntgen Absorption Spectrum of Chlorine. AXEL E. LINDH (*Z. Physik*, 1921, 6, 303—310).—The Röntgen absorption spectrum of chlorine has been examined, using free chlorine and the compounds lithium, sodium, potassium, and thorium chlorides, potassium chlorate, potassium perchlorate, ammonium stannichloride and dichlorotetra-aquochromium chloride, $(\text{Cr}[\text{H}_2\text{O}]_4\text{Cl}_2)\text{Cl}$. It is shown that with univalent chlorine in all cases the absorption edge has the same wave-length, within the limits of the experimental error. In the case of quinque- and septa-valent chlorine, a displacement of the absorption edge toward shorter wave-lengths is observed which is greatest in the case of septavalent chlorine. A metallic Röntgen tube and new apparatus for photometric measurements both designed for measurements of the above-named type are described.

J. F. S.

Series Regularities in the Resonance Spectrum of Iodine. R. MECKE (*Z. Physik*, 1921, 7, 73—85).—A theoretical paper in which, on the basis of Wood's measurements of the resonance spectrum of iodine (A., 1911, ii, 82, 950; 1912, ii, 325, 1018; 1913, ii, 994; 1914, ii, 233; "Researches in Physical Optics," II, 1919), which is shown to consist of a series of doublets of the band type and is expressed by the series formula $\nu = A + Bm + Cm^2 + Dm^3$, the author has examined the series regularities of this spectrum.

It is shown that the first constant is given invariably by the exciting line, whilst the two final coefficients, C and D , maintain their values at all exciting lines. On the other hand, the second factor varies, but this may be represented in the form $B=b_0-b_1n$, in which n is a whole number, so that a number of partial series can be differentiated. In the case of the most accurately investigated resonance spectrum, that of the green mercury line, eight such series of doublets can be characterised, which can also, according to the position of the components of the doublets, be divided into two groups. In one group, b_1 has the value 0.655, and, in the other, 0.75, and n can have the values 0, 1, 2, and 3. For $n=0$ an apparent triplet is indicated. Further regularities are probable in the series, but they cannot be definitely characterised. It appears that the value of m represents an azimuth quantum number. In consequence of the very small moment of inertia, however, the rotation cannot be ascribed to the molecule itself; it is therefore assumed that the moment of inertia is due to a rotating electron ring. On this assumption, the series formula can be developed, and resolved into the two energy terms. Further, it is shown that resonance spectra, in the same way as line spectra, are brought into existence by electron springs.

J. F. S.

Divergence from Stokes's Law during the Excitation of the Fluorescence of Iodine Vapour. PETER PRINGSHEIM (*Z. Physik*, 1921, 7, 206—216).—The resonance spectrum of iodine vapour has been examined. It is shown that on heating the vapour from the ordinary temperature to 320°, the intensity of the anti-Stokes members increases many times, and at the same time also that of the members of positive order number some become stronger whilst the majority become less bright. It is thought probable that these oppositely behaving resonance lines belong to series which originate from some of the seven iodine absorption lines covered by the mercury line.

J. F. S.

Difference between the Absorption Spectrum and the Complete Fluorescence Spectrum of Iodine Vapour indicated by Lenz's Theory. PETER PRINGSHEIM (*Z. Physik*, 1921, 8, 126—131).—Theoretically, it is to be expected that the members of higher order number in the resonance spectrum of cold iodine vapour will not be markedly absorbed; this conclusion is fully confirmed by experiment. Correspondingly, the fluorescence spectrum of iodine vapour excited by white light is not a simple reversal of the absorption spectrum, but is considerably richer in lines, and so the colour change of the fluorescence of iodine vapour of high density is explained by a partial reabsorption of the fluorescence light. In iodine vapour at higher temperatures, resonance lines of higher order number are also strongly absorbed. The colour change in the emission spectrum of iodine vapour of constant density, occasioned by fluorescence or electric discharge at higher temperatures is considered, and it is shown that the cause cannot, at present, be indicated theoretically.

J. F. S.

Ultra-red Reflection Power of Silica. CLEMENS SCHAEFER and MARTHA SCHUBERT (*Z. Physik*, 1921, 7, 313—315).—The reflection spectra of various varieties of silica has been measured; the varieties include quartz, chrysoprase, hornstein, chalcedony, opal, and quartz-glass. It is shown that all varieties except the last two exhibit an identical quantitative reflection power. The reflection maximum at about 9μ exhibits about 90% of the metallic reflection. In the case of opal and quartz-glass, the reflection maximum lies in the same position as in the other varieties, but the reflection power has fallen to 40—50%. This result is attributed to a distortion of the space lattice in the amorphous varieties of silica. It is remarkable that the water maximum, which lies at 3.2μ , is not observed in the case of opal and it is suggested that this is to be attributed to the probable fact that the water is not arranged in the space lattice in opal. J. F. S.

The L Doublet of Neon. WALTER GROTRIAN (*Z. Physik*, 1921, 8, 116—125).—From a consideration of the recent work on the systematics of examination of Röntgen spectra, the view is put forward that only one permanent condition of unexcited atoms exists, and that the different absorption band edges are to be explained, not by different initial conditions, but by different final conditions. From this, the conclusion is drawn that of the inactive gases helium has one ionisation-potential, neon three, argon five, and krypton seven. In the case of neon, it is shown that the doublet difference, $L_2 - L_1$, is identical with the constant A found by Paschen for the neon spectrum, $A = 782 \text{ cm}^{-1}$. The absolute value of the ionisation potential of neon has as yet not been determined with certainty. J. F. S.

Characteristic Ultra-red Frequencies of Selenates and Chromates. CLEMENS SCHAEFER and MARTHA SCHUBERT (*Z. Physik*, 1921, 7, 297—308).—The reflection spectra of potassium, manganese, nickel, copper, zinc, and cadmium selenates, an isomorphous mixture of lithium and sodium selenate, magnesium ammonium selenate, manganese ammonium selenate, nickel ammonium selenate, cobalt ammonium selenate, nickel potassium selenate, and zinc potassium selenate have been determined in the region of the ultra-red, using ordinary light. It is shown that all selenates exhibit in the region 11μ a definite maximum of the reflection power, which is to be attributed to the vibrations of the selenate radicle. This maximum is analogous to the maximum at 9μ exhibited by the sulphates (cf. A., 1916, ii, 505, 506; 1918, ii, 282, 315). In those cases where the selenates contain water of crystallisation, the water bands previously recorded (*loc. cit.*) are also observed. The crystals have also been examined in polarised light, and it is shown that the reflection maximum at about 11μ can be resolved into two groups of characteristic vibrations in the case of uni-axial crystals and into three in the case of bi-axial crystals. Similar measurements were made with potassium chromate, sodium potassium chromate, magnesium ammonium chromate, and potassium dichromate. In the first three cases

using ordinary light, a single well-developed maximum is found, which lies respectively at 11.16μ , 11.2μ , and at complex maximum 11.3μ and 11.42μ . In the case of potassium dichromate, three maxima are observed, the first two of which are complex and lie at 10.44μ and 11.1μ , 12.14μ and 13.22μ , and 18.12μ . Magnesium ammonium chromate has been examined in polarised light and exhibits a maximum at 11μ which falls into three groups: 11.46μ parallel to the a axis, 11.28μ parallel to the b axis, and 10.36μ parallel to the c axis.

J. F. S.

Characteristic Ultra-red Frequencies of Chlorates, Bromates, and Iodates. CLEMENS SCHAEFER and MARTHA SCHUBERT (*Z. Physik*, 1921, 7, 309—312).—The reflection spectra of sodium, potassium, silver, and barium chlorates, sodium, silver, cadmium, and barium bromates and potassium iodate have been measured. It is shown that in all cases but that of sodium bromate, where a single maximum is observed, two reflection maxima are exhibited. The maxima have the following wave-lengths: sodium chlorate, 10.04μ , 16.04μ ; potassium chlorate, 10.12μ , 16.22μ ; silver chlorate, 10.76μ , 16.38μ ; barium chlorate, 10.24μ , 19.6μ ; sodium bromate, 12.24μ ; silver bromate, 12.62μ , 13.10μ ; cadmium bromate, 12.32μ , 13.20μ ; barium bromate, 12.3μ , 12.64μ , and potassium iodide, 12.48μ , 13.16μ . The values are discussed in connexion with those found for other acid radicles (cf. preceding abstract).

J. F. S.

Röntgen Spectra. ELIS HJALMAR (*Z. Physik*, 1921, 7, 341—350).—Röntgen spectra of the elements copper to tantalum have been measured. It is shown to be probable that the β_1 lines of the K series of the lighter elements are not simple. This has been established in the case of sulphur. The new line is regarded by the author as the continuation of the β_2 line of the next higher element, and the theoretical significance of this is discussed. The valency of sulphur appears to have no action on the emission spectra, but the experimental difficulties experienced in the work make it advisable to leave this question open. Exact measurements of a number of lines of the K -series are recorded, and the earlier measurements of lines of the L series are controlled. Two long tables of wave-lengths measured in the present work are included in the paper.

J. F. S.

Systematics of Röntgen Spectra. D. COSTER (*Z. Physik*, 1921, 6, 185—203).—The author has measured the Röntgen spectra of the elements tantalum, tungsten, osmium, iridium, platinum, gold, thallium, lead, bismuth, thorium, and uranium, using the method adopted by Hadding (*ibid.*, 1920, 3, 369). The object of the work was to obtain measurements of the very weak lines and from these to examine various relationships and regularities obtaining among X-ray spectra. Tables of the lines measured are given in the paper and also of the L doublets; a table of the constant wave-length differences $\beta_2 - \beta_5$, $\gamma_1 - \gamma_6$, $\gamma_2 - \gamma_3$, $\beta_4 - \beta_5$, $\beta_2 - \beta_8$, and $\beta_2 - \beta_7$ is drawn up. The relationship $(L_3 - L_1) - M\gamma = L\beta_3 - L\beta_2$, put forward

by Smekal (A., 1921, ii, 615), is evaluated and found to be only in moderate agreement with the experimental data; the divergences between the two sets of values are attributed to errors in the $(L_3 - L_1)$ values.
J. F. S.

Systematics of Röntgen Spectra. ADOLF SMEKAL (*Z. Physik*, 1921, 7, 410—412).—A reply to Coster (preceding abstract). The author points out that Coster's criticism is based on a misunderstanding of his method of treatment.
J. F. S.

Fluorescence of Cadmium Vapour. J. STEPH. VAN DER LINGEN (*Z. Physik*, 1921, 6, 403—404).—Light from cadmium sparks was allowed to pass through an evacuated quartz globe at 280° containing a scrap of cadmium. It is found that an absorption line 2288 Å.U. appears at this temperature, and with changing vapour density a band symmetrical with this line appears. When the band extends to 2307 Å.U. a second absorption line, 3260 Å.U. is observed. To ascertain whether the emitted light is due to resonance or fluorescence, the cadmium light around 2288 Å.U. was isolated and passed through the globe. It was found that at a density corresponding with that at which the line 2288 Å.U. is emitted, the vapour shows an ultra-violet fluorescence band which is sharply terminated at 2288 Å.U. and fades at 2314 Å.U. At higher densities the head disappears at 2288 Å.U., and the band is then terminated at 2313 Å.U. and extends to 3005 Å.U., where it also ends sharply. Between 2745 and 3005 Å.U. the band contains sixteen lines which are closer together the smaller the wave-length.
J. F. S.

Dependence of the Intensity of the Fluorescence of Dyes on the Wave-length of the Exciting Light. S. I. VAVILOV (*Phil. Mag.*, 1922, [vi], 43, 307—320).—It has been shown by Nichols and Merritt (*Physical Rev.*, 1910, 31, 376, 381) that the specific fluorescence of resorufin and eosin increases toward long wave-lengths. The present paper describes experiments with fluorescein, eosin-S extra, and rhodamine-B extra, designed to test how far this result is general. It is shown that within the limits of the errors of observation the specific fluorescence of the dyes mentioned is independent of the wave-lengths of their absorption bands. This result is equivalent to the conclusion that the absorption curves of the dyes are physically simple ones. Einstein's theory is not confirmed, but the deviations required by this theory are so small that they are only a little greater than the experimental errors, and consequently no very definite statement can be made. The intensity of fluorescence radiated by a definite molecular resonator depends only on the value of the absorbed energy and on the mechanism of the resonator. In the case of excitation by white light, the intensity of fluorescence F can therefore be expressed by the equation

$$F = K \int_{\lambda_1}^{\lambda_2} I_\lambda \cdot xc \cdot e^{-xc} \cdot d\lambda, \text{ where } I_\lambda \text{ is the energy of the exciting source in the wave-length interval } \lambda \dots \lambda + d\lambda, xc \text{ the coefficient of absorption of the solution over the same wave-length interval, } C \text{ the}$$

concentration, and K the specific fluorescence. The result of Nichols and Merritt (*loc. cit.*) probably only shows the physical complexity of the bands of the dyes examined by them. J. F. S.

Ionisation brought about by Quinine Salts. GERHARD C. SCHMIDT (*Z. Physik*, 1921, 8, 160—164).—It is shown that quinine nitrate as well as quinine sulphate (Le Bon, *Compt. rend.*, 1900, 130, 891) emits light on warming and makes the surrounding air a conductor; other salts of quinine have no such action. All quinine salts when heated to just above the melting point change into a modification which gives intensely green fluorescent solutions instead of the usual violet fluorescent solutions. Quinine hydrogen sulphate in aqueous or chloroform solution gives a violet fluorescence, but when heated at 50° for an hour the fluorescence is light blue; when heated to the melting point this changes to an intense green which is maintained at very high dilutions. In the case of quinine valerate, the green colour changes back to violet on dilution when in water solution; in chloroform solution the heated salt gives a green fluorescence, but a violet fluorescence in benzene. The absorption spectrum of the green fluorescing solution is different from that of the violet fluorescing solution. The following hypothesis is advanced to explain the luminescence of the nitrate and sulphate when warmed, and its absence in other salts. On heating, these two salts pass into a new modification, which on stronger heating passes into the green, fluorescing variety; the change into the intermediate modification is accompanied by the emission of electrons or ions. In the case of the other salts, there is no intermediate compound formed, but a direct change into the green, fluorescing variety without emission of ions or electrons. J. F. S.

Action of Light on Silver Chloride, Bromide, and Iodide. PETER PAUL KOCH and FRITZ SCHRADER (*Z. Physik*, 1921, 6, 127—131).—The results of experiments, made to ascertain the loss of weight of particles of silver chloride, silver bromide, and silver iodide on illumination, previously published (A., 1921, ii, 289) and a large number of other experiments made by the same method are collected and considered. The experiments were made with the suspended particles in air, dried air, dry nitrogen, moist nitrogen, moist argon, and dry argon, and a number of improvements were made in the technique of the method. The results show that silver chloride illuminated by intensities up to 3,000,000, silver bromide up to 12,000,000, and silver iodide up to 5,600,000 candle metre seconds (the light coming from the positive crater of an arc through 80 cm. of 1% copper sulphate solution) do not undergo a change in weight greater than 1—2%. The larger changes previously recorded are attributed to disturbances in the earlier experiments, among which the secondary reaction of silver bromide with the surrounding gas is mentioned. The rate of colouring of the silver haloids by light has also been determined; it is shown that silver bromide, after an illumination of 5 seconds by a light of intensity 3200 candle metre seconds, shows a definite coloration, silver chloride shows a coloration in three minutes when illuminated by

940 candle metre seconds, and silver iodide after ten minutes' illumination by the same light shows only a weak greyish-black coloration. In all cases the coloration increases with the duration of the illumination. J. F. S.

Luminous Path of α -Rays in Crystals. H. GEIGER and A. WERNER (*Z. Physik*, 1921, 8, 191—192).—An experiment is described which answers the question, "Is the number of metallic centres, which are excited by an α -particle on its entry into a crystal, sufficiently great in every case to bring about a visible scintillation?" A thin, highly polished section of artificial willemite was arranged in the field of a microscope so that the α -rays from a polonium preparation should strike it at a small angle. At a magnification of 400, point scintillations were not seen, but luminous lines of 0.02 mm. length. These represent the path of the α -particle in the crystal, and show that the number of centres is extremely large, and in the case of perfect crystals sufficient to ensure a scintillation for every α -particle hitting the crystal. J. F. S.

The Meitner Nuclear Model of the Radio-elements as the Basis of a Relationship between the Range and Total Number of Nuclear Particles of the α -Radiators. MAXIMILIAN CAMILLO NEUBURGER (*Z. physikal. Chem.*, 1921, 99, 327—331).—A theoretical paper in which, on the basis of the Meitner nuclear model, a relationship between the range and the total number of nuclear particles of the α -radiators is deduced. The range of most of the α -radiators of the uranium, thorium, and actinium families is calculated by means of this new relationship and found to be in good agreement. The divergence of the two sets of values lies between $\pm 0.8\%$ and $\pm 1.8\%$. Applying this relationship to the hypothetical elements uranium III and uranium IV, it is found that the former is practically inactive whilst the latter has a much shorter life than uranium I. This is further evidence against the existence of these hypothetical isotopes (cf. this vol., ii, 85). J. F. S.

Beta Rays and Atomic Number. J. L. GLASSON (*Phil. Mag.*, 1922, [vi], 43, 393—396).—A theoretical paper in which the relationships between the atomic absorption, α , and the atomic scattering, β , of β -rays respectively and the atomic number are considered. The values of α , β , the atomic absorption $a = \alpha A/D$, the atomic scattering $b = \beta A/D$, the atomic weight A , the density D , and the atomic number N are tabulated for a number of elements from magnesium to bismuth. It is shown from the table that the values of a are approximately constant for elements of the same period of the periodic system; the elements examined fall into four groups which have values for a in the ratio 1 : 2 : 3 : 4. These groups are magnesium and aluminium, $a = 89$; iron, cobalt, nickel, copper, and zinc, $a = 172$ —196; palladium, silver, and tin, $a = 260$ —268; and platinum, gold, lead, and bismuth, $a = 348$ —372. It therefore seems likely that the value of a is a periodic function of the atomic number. The value of b increases with the atomic number of the element and on plotting $\log b$ against $\log N$ a curve is obtained

which is represented by $\log b = 2.09 \log N - 0.44$ and therefore $b = 0.36 \times N^{2.09}$. J. F. S.

Scattering of Röntgen Rays by the Atoms of a Crystal. W. L. BRAGG, R. W. JAMES, and C. H. BOSANQUET (*Z. Physik*, 1921, 8, 77—84).—A theoretical paper in which the experimental results previously published (A., 1912, ii, 477) on the scattering of Röntgen rays by the sodium and chlorine atoms of rock-salt crystals have been used in connexion with the arrangement of the electrons inside the atom. In the case of the sodium atom, the expected amplitude curve has been calculated for the case that of the eight exterior electrons four vibrate in di-quantic circular orbits and four in di-quantic elliptical orbits, and it is shown that such a model has a very satisfactory agreement with the experimental facts. J. F. S.

Characteristic X-Rays from Boron and Carbon. A. LL. HUGHES (*Phil. Mag.*, 1922, [vi], 43, 145—161).—The photoelectric effect of the radiation from carbon and boron bombarded by electrons has been measured as a function of the energy of the electrons. Two slight but definite breaks in the curves for both carbon and boron were obtained. These are considered to correspond with the *K*- and *L*-absorption wave-lengths. The breaks occur at 215 volts ($\lambda = 57.5$) and 34.5 volts ($\lambda = 358$) for carbon and 148 volts ($\lambda = 83.5$) and 24.5 volts ($\lambda = 505$) for boron. The *L* point for carbon is in good agreement with the measured values recently obtained by Millikan (*Astrophys. J.*, 1920, 52, 47) for the *L* emission lines of carbon vapour. The *K* points for carbon and boron are approximately where they would be expected on extrapolating the known values of the *K_a* critical absorption wave-lengths for elements heavier than magnesium. J. F. S.

Absorption of the *K* X-Rays of Silver in Gases and Gaseous Mixtures. P. W. BURBIDGE (*Phil. Mag.*, 1922, [vi], 43, 381—389).—The total absorption coefficient of silver *K* radiation has been measured in air, carbon dioxide, sulphur dioxide, and methyl iodide vapour. Using the same silver *K* radiation, it has been shown with mixtures of sulphur dioxide and air, carbon dioxide and air, sulphur dioxide and carbon dioxide, and methyl iodide and air that the absorption in gases is atomic (as in the case of solids and liquids) and therefore additive in mixtures and compounds. J. F. S.

Experimental Decision of the Question of the Radioactivity of all Elements. II. G. HOFFMANN (*Z. Physik*, 1921, 7, 254—259; cf. A., 1920, ii, 575).—Making use of the very sensitive method of measuring α -ray activity previously described (*loc. cit.*), the author has extended his measurements to platinum. The measuring instrument itself shows an α -ray activity represented by 0.3—0.5 α -particle per hour. Using a cleaned platinum dish of 39 sq. cm. surface, an activity of 14.6 per hour for the whole dish is recorded, or 0.39 per sq. cm. The measurements were made over a period of about fifty hours. The results are analysed for α -rays which

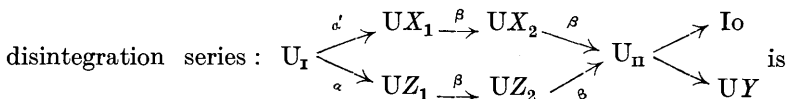
may come from known α -radiators of all ranges uniformly distributed through the mass of the platinum and for α -radiators situated on the surface of the platinum, and the analysis indicates a definite α -ray activity of platinum.

J. F. S.

Protactinium Content of Pitchblende Residues and the Branching Relationship of the Actinium Series. OTTO HAHN and LISE MEITNER (*Z. Physik*, 1921, 8, 202—204).—A criticism of the value put forward by St. Meyer (*Mitt. Inst. Rad. Forsch.*, 1920, 127) for the branching relationship of the actinium series. The value, 4.2%, is about 25% higher than that found by the present authors, $3 \pm 0.3\%$. It is shown to be probable that Meyer's preparation contained 1—2% of ionium, which would explain the difference in the two figures.

J. F. S.

Existence of Isotopes of Uranium and the Meitner Nuclear Model. MAXIMILIAN CAMILLO NEUBURGER (*Z. physikal. Chem.*, 1921, 99, 321—326).—The author discusses the position of uranium- Z_2 in the disintegration series from the point of view of Meitner's nuclear model. The position given by Hahn (A., 1921, ii, 498) in the series $U_{III} \xrightarrow{\alpha} UZ_1 \xrightarrow{\beta} UZ_2 \xrightarrow{\beta} U_{IV}$ is criticised, and it is shown, for several reasons, that only two elements of the uranium type, uranium I and uranium II, can possibly exist. The elements uranium II and uranium III are shown to be identical and the



put forward to represent the disintegration of uranium. A method for the detection of isotopes of the fourth order (this vol., ii, 107) is described. It consists in determining the number of particles emitted by the disintegrating substance; should this number be in keeping with the disintegration constant, then the substance does not consist of isotopes of the fourth order, but of a single element.

J. F. S.

A New Radioactive Substance. A. PICCARD and E. STAHEL (*Physikal. Z.*, 1922, 23, 1).—A quantity of uranium-X, separated from uranyl nitrate by the ether-water method, has been repeatedly measured with respect to its β -radiation for a prolonged period. It is shown that in addition to the hard β -radiation of uranium-X, there is a soft radiation which with increasing age of the preparation decreases more and more slowly; this indicates the presence of a substance of longer life than uranium-X. This substance has been provisionally named uranium-V. It has an approximate half life of forty-eight days, or about twice as long as uranium-X₁. The β -radiation due to this element is half absorbed by an aluminium sheet 0.003 mm. thick, that is, the absorption coefficient is $2300 \text{ cm}^{-1} \text{ Al}$. It is shown that this substance may be a member of the actinium series, but it has not been decided whether it or uranium-Y is the first thorium isotope in the disintegration series put forward by one of the authors.

J. F. S.

Some Oxidising Properties of Thorium-X. PIERRE LEMAY and LÉON JALOUSTRE (*Compt. rend.*, 1922, **174**, 171—172).—Thorium-X exerts a very marked catalytic action in the oxidation of adrenaline and morphine, the oxidation being much more rapid than in the presence of manganese salts. Oxidation could not, however, be proved in the case of the primary alcohols of the fatty series. W. G.

Ionisation Tension of the Halogen Hydrides. PAUL KNIPPING (*Z. Physik*, 1921, **7**, 328—340).—The ionisation tension of hydrogen cyanide, chloride, bromide and iodide has been determined by the method previously described by Franck and Knipping for helium (A., 1920, ii, 72). The following values are recorded: hydrogen cyanide, 15.5 volts, 357 Cal.; hydrogen chloride, 14.4 volts, 331 Cal.; hydrogen bromide, 13.8 volts, 317 Cal.; and hydrogen iodide, 13.4 volts, 308 Cal. The electron affinity, in Cal. and volts, the limiting wave-length, and frequency have been calculated for chlorine, bromine, and iodine, and the values compared with those of other investigators. The following values are recorded: chlorine, 98 Cal., 4.26 volts, $\lambda=2890$, $\nu=34600$; bromine, 68 Cal., 2.96 volts, $\lambda=4150$, $\nu=24100$, and iodine, 61 Cal., 2.65 volts, $\lambda=4600$, $\nu=21500$. J. F. S.

Ionisation and Excitation Tension of Nitrogen. ERICH BRANDT (*Z. Physik*, 1921, **8**, 32—44).—The ionisation tension of nitrogen has been found to be 17.75 ± 0.1 volt with reference to the resonance tension of helium, 20.5 volts. Higher ionisation stages have been found at 25.41 ± 0.1 volt and 30.72 ± 0.2 volt, both with reference to the value 17.75 volts. The limits of light excitation of the nitrogen molecule by electron collisions have been investigated, and an analogy between the light-electric curve and that of band emission is pointed out. J. F. S.

Electrical Conductivity of Zinc Sulphate Solutions in the Presence of Sulphuric Acid. HERMAN V. TARTAR and HARMON E. KEYES (*J. Ind. Eng. Chem.*, 1921, **13**, 1127—1129).—The conductivity of zinc sulphate solutions increases with the sulphuric acid concentration, but the conductivity of sulphuric acid is decreased by the addition of zinc sulphate; when magnesium sulphate is added to a strongly acid zinc sulphate solution, an additional decrease in conductivity occurs. The addition of small quantities of gelatin does not affect the conductivity. The temperature coefficients of conductivity vary, and are a function of the acid and zinc concentration. During the electrolysis of zinc sulphate solutions there is an increase in the volume of the solution, the increase amounting to 1.5% for each 100 grams of zinc deposited. W. P. S.

Anomalous Dissociation in Aqueous Solutions. A. J. RABINOWITSCH (*Z. physikal. Chem.*, 1921, **99**, 338—360).—By anomalous dissociation is understood the phenomenon which occasions a decrease in the molecular or equivalent conductivity

with increasing dilution, that is, the degree of dissociation, as expressed by $\alpha = \lambda/\lambda_\infty$, decreases with increasing dilution. With the object of finding a connexion between the viscosity and the electrical conductivity of solutions of salts in water, the author has determined the density, viscosity, and electrical conductivity of aqueous solutions of caesium chloride, cadmium chloride, cadmium bromide, cadmium iodide, zinc bromide, zinc iodide, and sodium iodide at 0°, 25°, and 50°. It is shown that in the case of caesium chloride the viscosity and the conductivity are very closely connected. A comparison of the corrected molecular conductivity curves and the relative viscosity curves at 25° and 50° for the halogen salts of cadmium with one another and with those of other salts shows that the form of the relative viscosity curve has a strong influence on the form of the $\lambda\eta_a$ curve. In those cases with a high value for η_a , the introduction of the usual viscosity correction of the $\lambda\eta_a$ curves can lead to an anomalous form of the curve because of over-correction. This anomaly is general in the case of highly concentrated aqueous solutions. The over-correction is explained as follows: In introducing the correction, it is assumed that the ionic mobility is inversely proportional to the viscosity of the medium. This assumption, however, does not hold because a reduction of the ionic diameter is brought about by increasing concentration, due largely to a dehydration of the ions. With increasing temperature, the anomaly extends over a considerable portion of the $\lambda\eta_a - V$ curve. This is in opposition to the view that the anomaly is due solely to the over-correction on account of a reduction of the ionic diameter. If the over-correction is due alone to the inapplicability of Stokes's law to all concentrations, then it is to be expected that the minimum, displaced on warming, should correspond with higher viscosity values; but since this is only observed in the case of caesium chloride, it follows that this cause of over-correction does not explain the anomaly in all cases. It is held that the anomalous form of the conductivity curve is not to be explained by the over-correction alone, but is due to several causes. It is suggested that the causes which bring about the "true anomalous dissociation" in non-aqueous solutions are operative in aqueous solutions also. This suggestion would explain the displacement of the minimum with increasing temperature, since with increasing temperature water in respect of its dielectric constant approaches in behaviour the other solvents. It is also shown that in concentrated aqueous solutions, in addition to the over-correction of the conductivity values, there is also a typical anomalous progression of the molecular and equivalent conductivity, which in all probability has its origin in the same causes as in non-aqueous solutions.

J. F. S.

Electrolytic Dissociation of Salts in Concentrated Solutions, and in the Fused and Solid States. A. J. RABINOWITSCH (*Z. physikal. Chem.*, 1921, 99, 417—433; cf. preceding abstract).—The conductivities, viscosities, and densities of aqueous solutions of caesium chloride, silver nitrate, ammonium nitrate, thallium

nitrate, and thallium silver nitrate were determined at high concentrations. In the case of thallium ammonium nitrate the results were extended to the fused salt. The molecular conductivities were extrapolated to the pure salts. After the application of the viscosity correction, all the molecular conductivity curves assumed an abnormal form, and on extrapolation to pure salt gave high values of $\mu\eta_a$, where μ is the molecular conductivity and η_a the relative viscosity. The values of $\mu\eta_a/\mu_\infty = \alpha$ were therefore abnormally high. The true values of α for the salts probably lie between the values calculated from the corrected and the uncorrected (μ/μ_∞) conductivities, and nearer the former. The course of the dissociation in very concentrated solutions is thus abnormal. The extrapolation was confirmed by the form of the curve for thallium silver nitrate, which continued smoothly up to the fused salt.

J. R. P.

Reversal of the Molecular Conductivity Curve and Abnormal Dissociation. A. J. RABINOWITSCH (*Z. physikal. Chem.*, 1921, 99, 434—453; cf. preceding abstract).—Abnormal dissociation occurs when the degree of dissociation (or the molecular conductivity) decreases with increasing dilution. It is most commonly observed with non-aqueous solutions, and is most marked when the dielectric constant of the solvent is small. The various hypotheses which have been advanced to account for the phenomenon are reviewed. In the ordinary method of representation of conductivities, the dilution V is taken as the variable volume of solution in which a constant weight of one gram equivalent of solute is dissolved. The author considers the results obtained when a constant weight of one gram equivalent of solvent is taken and the volume V_1 of solution containing it is taken as the dilution. If k is the specific conductivity, the product $kV_1 = \mu_1$ is the newly-defined molecular conductivity. The curves representing the values of μ_1 and V_1 are called "reversed conductivity curves." When only one constituent of the solution is capable of ionisation and the other is a strong ioniser (for example, acetic acid in water), the original molecular conductivity curve is normal but the reversed curve is abnormal, exhibiting a maximum but not a minimum, after correction for viscosity. When the ionising constituent is also a strong ioniser (for example, silver nitrate in aniline or water), the original curve is abnormal, without a maximum, or apparently abnormal (without correction). The reversed curve is normal (water in silver nitrate and thallium silver nitrate), or, in consequence of the uncorrected increase in viscosity is apparently abnormal (aniline in silver nitrate). When neither constituent is ionisable, but when its polymeride or solvate is ionisable, then in both cases abnormal curves result, in the latter case with a maximum, the position of which indicates approximately the maximum content of solvate in the solution. To the right and left of the maximum the conductivity decreases in consequence of the diminution of solvation due to insufficient quantity of solvent and to depolymerisation respectively. Examples of such curves are

furnished by acetic acid and aniline and by acetic acid and pyridine. A definition of abnormal dissociation is given. J. R. P.

Effective Potential Difference of Electro-osmosis and Allied Phenomena. H. FREUNDLICH (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 146—149).—A theoretical paper in which the author discusses the nature of the potential difference at work in electro-osmosis, cataphoresis, and allied phenomena. A great deal of experimental work is reviewed, and it is shown that the Nernst potential difference, ϵ , is in no sense identical with the electrokinetic potential difference, ζ ; the Nernst potential represents the total difference between the interior of the first phase and that of the second phase, the electrokinetic potential represents that portion of the difference which falls within the displaceable liquid layers. J. F. S.

Selenium [Cells]. WILHELM SPÄTH (*Z. Physik*, 1921, **8**, 165—183).—The influence of illumination on the dielectric constant of selenium has been investigated in connexion with the fatigue and inertia of the element. It is shown in all selenium cells that the change in conductivity on illumination runs parallel with a change in capacity. The final capacity value and the final conductivity are reached with similar inertia phenomena. The conductivity of the cells increases two- or three-fold on illumination, but the capacity increases only 5%. A cell which, with respect to its conductivity, exhibits fatigue, also exhibits the same phenomenon with respect to its capacity. The dependence of the change in capacity on the intensity of illumination is much the same as that of the conductivity. With increasing intensity of illumination, the sensitiveness of the capacity increases in a parabolic manner. The inertia on darkening the cell is greater than the inertia on illumination as far as the capacity effect is concerned, and, further, it is considerably smaller in soft cells. The fatigue effect in soft cells on intense illumination is more marked, both with regard to the capacity change and the conductivity. The author has put forward a hypothesis of the mode of action of the selenium cell and has calculated the equilibrium of the cell for illuminated and dark conditions. J. F. S.

Fatigue of Alkali Metal Cells in the Neighbourhood of the Discharge Potential and the Influence of this on the Results of Photometric Measurements. H. ROSENBERG (*Z. Physik*, 1921, **7**, 18—64).—Sodium, potassium, and rubidium photoelectric cells have been examined in connexion with the fatigue effects often noticed in these cells. It is shown that these cells, when filled as usual with an inactive gas, rapidly exhibit fatigue effects and also a rapid recovery. The effects are apparently not proportional to the intensity of the light or to the photoelectric current. In addition, slow changes of the sensitiveness of the cells are observed, which must be regarded as a type of fatigue effect. The cause of the fatigue is found to be due to the adsorption of a positively charged layer of gas by the alkali metal, but it is

not decided whether electron absorption or a reduction of the field is the ultimate cause of the fatigue effect. The process appears to be intimately connected with the appearance of a powerful collision ionisation. The pure photo-effect is shown to be strictly proportional to the amount of light which has entered the cell. Taking into account these phenomena, a photometric process has been tested which leads to intensity ratios which are accurate to 0.1%.

J. F. S.

Equilibrium Law of Electrolytes. K. JABLZYŃSKI and F. J. WIŚNIEWSKI (*Roczniki Chemji*, 1921, **1**, 116—134).—The authors have deduced a dilution law of the form $n^{4/3}/n_0 = k$ and have used this to calculate the value of k for potassium, sodium, and lithium chlorides, using data obtained from cryoscopic measurements. It is shown that only in the case of potassium chloride is the value of k constant, whilst in the case of the other two salts it may have even negative values. These facts are explained by hydration of the ions. Corrections which take into account the hydration have been introduced into van't Hoff's equation, and lead to a remarkably constant value for k in all three cases; thus for potassium chloride $k = 3.09$, for sodium chloride 3.10, and for lithium chloride 2.93. Furthermore, the number of molecules of water combined with the various ions has been calculated as follows: potassium, 0; sodium, 3; lithium, 11; chlorine, 0. Hydrochloric acid behaves in the same way as the salts mentioned, and when the hydrogen ion is taken as combined with nine molecules of water a very constant value, 4.74, is obtained for k . The equation has been applied to those weak electrolytes which apparently follow Ostwald's dilution law. The value of k has been calculated for acetic acid from cryoscopic measurements and a remarkably constant value 0.00504 obtained, whereas the value of k calculated from Ostwald's equation increases considerably with increasing concentration. On applying the equation to ebullioscopic data of solutions of the chlorides mentioned above, it is shown that the value of k increases even more strongly than when cryoscopic data are used. This is explained by assuming that the ions are more heavily hydrated at 100° than at 0°. This is shown to be in keeping with facts. The value of k at 100° is smaller than that at 0°, which shows that the degree of ionisation decreases with increase of temperature. This the authors attribute to a fall in the dielectric constant of water with increase of temperature. A rule has been deduced, in keeping with facts, which shows that the equilibrium constant of salts in aqueous solution is proportional to the dielectric constant of the solvent. J. F. S.

Velocity of Sound in Air and Hydrogen at 0° and 1 Atm. E. GRÜNEISEN and E. MERKEL (*Ann. Physik*, 1921, [iv], **66**, 344—364).—The velocity of sound in air is found to be 331.57 m./sec. and in hydrogen 1260.6 m./sec. The ratio of the specific heats for air is $C_p/C_v = 1.4034$ and for hydrogen 1.408, both at 0° and 760 mm.

J. F. S.

Specific Heats of Ammonia, Sulphur Dioxide, and Carbon Dioxide. J. R. PARTINGTON and H. J. CANT (*Phil. Mag.*, 1922, [vi], **43**, 369—380).—The ratio of the specific heats $k=c_p/c_v$ for ammonia, sulphur dioxide, and carbon dioxide has been determined by a method depending on the relative velocities of sound in the gases and in air. The specific heats have been calculated using Berthelot's equation of state in all calculations. The following results were obtained at one atmosphere pressure: ammonia at 14.5° , c_p/c_v , 1.308, C_p 8.77 cal., C_v 6.70 cal.; sulphur dioxide at 13.2° , c_p/c_v , 1.290, C_p 9.47 cal., C_v 7.34 cal.; carbon dioxide at 20° , c_p/c_v , 1.303, C_p 8.76 cal., C_v 6.72 cal. J. F. S.

Numerical Values of the Gas Constants. F. HENNING (*Z. Physik*, 1921, **6**, 69—72).—The data on which the gas constant is based have been critically discussed and, on the basis of the most trustworthy experimental data, the value of this constant, in different units, has been calculated. The following values are recommended for general use as the most accurate, $R=0.08204\pm0.00003$ litre-atm./degree mol.; $R=(8.313\pm0.003)10^7$ erg/degree mol.; and $R=1.986\pm0.001$ cal.₁₅/degree mol. J. F. S.

Theoretical Determination of the Chemical Constants of Monatomic Gases. E. BRODY (*Z. Physik*, 1921, **6**, 79—83).—The author have deduced a mathematical expression for calculating the chemical constants of ideal monatomic gases on the basis of the first quantum theory and from statistical considerations. The expression obtained is the same as that deduced by Stern (A., 1919, ii, 219) and Planck (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1916, 653). The expression has the form $C=\log_e (2\pi m)^{3/2} k^{5/2} / h^3$. J. F. S.

Chemical Constants of Sodium and Potassium. R. LADENBURG and R. MINKOWSKI (*Z. Physik*, 1921, **8**, 137—141).—The chemical constants of sodium and potassium have been calculated from existing data on the specific heat, vapour pressure, and latent heat of fusion of these elements. In the case of sodium, the value of the chemical constant C is found to be 0.846, and on inserting this value in the equation $C=C_0+1.5 \log M$, where M is the molecular weight, the value of the constant C_0 is found to be -1.20 instead of -1.59 , as in the case of mercury, argon, hydrogen, cadmium, and zinc. The data on which the calculation is based are analysed with the object of finding the cause for the discrepancy. In the case of potassium, the value of C is found to be 1.016, which gives the value of C_0 as -1.37 . J. F. S.

Absolute Entropy and Chemical Constants. MAX PLANCK (*Ann. Physik*, 1921, [iv], **66**, 365—372).—An answer to the criticism of Ehrenfest and Trkal (*ibid.*, 1921, **65**, 609) in which the difficulties in calculation of entropy experienced in the author's book ("Theorie der Wärmestrahlung," 1921) are pointed out. It is also doubted whether the equation $s=k \log W$, in which W is the thermodynamic probability, will give the value of the entropy. The author answers the objections and criticisms and points out that they arise from a confusion of terms. J. F. S.

Equation of Condition. RUDOLF WEGSCHIEDER (*Z. physikal. Chem.*, 1921, 99, 361—382.)—A theoretical paper in which the equation of condition put forward by Wohl (this vol., ii, 117) is discussed and criticised. It is shown that this equation of condition leads to results which can scarcely be accepted; for example, the decrease of pressure at constant volume with increasing temperature in liquid systems, consequently this equation can have no theoretical significance. The critical point is always given by equations of condition which yield isotherms of the van der Waals form, by the coincidence of the three roots of the equation $v=f(p, T)$. The equality of four roots involves the introduction of a relationship between the constants; the equality of two roots leads to conditions which include, in addition to the critical point, also the maxima and minima. J. F. S.

Physical Properties of Vapour-Liquid Systems. I. WOJCIECH SWIENTOSLAWSKI (*Roczniki Chemji*, 1921, 1, 276—296).—Starting from relationships based on van der Waals's hypothesis of corresponding conditions, $\tau=T/T_c$ and $d_c/d=K=f(\tau)$. Where T , d , T_c , and d_c are the temperature and corresponding density and T_c and d_c the same critical values, the author has deduced the following regularities from the experimental work of Young, Amagat, Mathias, Villard, Kamerlingh Onnes, and Crommelin. (1) The value of K or $\log K$ increases with increasing molecular weight of the liquid, and also when the liquid is associated. (2) Oxygen and argon have small values for K . In the case of associated liquids, it is shown that the concentration of non-associated molecules, y , is given by $y\%=100K/K_A$, where $K=d_c/d_p$ for a non-associated liquid and K_A is the same ratio for an associated liquid at the same relative temperature ($\tau=\text{const.}$). The concentration of non-associated molecules in methyl alcohol and propyl alcohol increases proportionally to the temperature, but this is not true for ethyl alcohol. Ramsay's results for water and ethyl alcohol are satisfactory if it is assumed that the associated molecule of water contains three simple molecules and that of ethyl alcohol two simple molecules. The value of K plays an important rôle in all cases where the physical state of a system liquid-vapour is characterised. The relationship between the surface tension γ and the reduction of pressure below the meniscus in a capillary tube of radius r is given by $(2\gamma/r\Delta f)_{\tau=\text{const.}}=K=\text{const.}$, and in the case of osmotic pressure $(P/\Delta f)_{\tau=\text{const.}}=K=\text{const.}$ The constant of Trouton's rule may be calculated by the equation $W_{\text{mol.}}=bR \log_e K=20.4$, in which $R=2 \text{ cal.}$ $\log_e K=2.303$, $\log_{10} K=2.203 \times 2.38$ or 2.38 , depending on the ratio $K=d_c/d_p$ for the liquid at the relative boiling point $\tau=0.65$ under a pressure of one atmosphere. J. F. S.

Physical Properties of Vapour-Liquid Systems. II. WOJCIECH SWIENTOSLAWSKI (*Roczniki Chemji*, 1921, 1, 297—304; cf. preceding abstract).—It is shown that over the range of relative temperatures $\tau=0.50$ to $\tau=0.95$ the expression $d_c^2/T \log_e K=B$ is constant, where d_c is the density of the liquid, and K the ratio d_c/d_p in

which d_p is the density of the vapour at the absolute temperature T . The deviations of B never exceed a mean amount of $\pm 2.3\%$. A minimum value of B is found between $\tau=0.85$ and 0.90 and a maximum about $\tau=0.60-0.65$. Associated liquids are exceptional; these show a continual increase in the value of B from $\tau=0.50$ to the critical temperature $\tau=1$. J. F. S.

Vaporisation Coefficients of Solid and Liquid Mercury. M. VOLMER and I. ESTERMANN (*Z. Physik*, 1921, 7, 1—12).—The authors have determined the velocity of vaporisation of mercury at temperatures from 59° to -180° . This demands the determination of the fraction, (α), of the vaporised mercury which is condensed on a cooled surface, whilst the rest ($1-\alpha$) is reflected. It has been previously shown by Knudsen (*Ann. Physik*, 1915, [iv], 47, 697; 1916, 50, 472) that at 19.45° $\alpha=0.95$, but at -140° $\alpha=1.00$. For the temperature range $59-0^\circ$ the rate of vaporisation and consequently the value of α has been determined by measuring the rate at which a small globule of mercury deposited on the interior of the outside wall of a highly evacuated Dewar vessel filled with liquid air decreases. The Dewar vessel is kept in a thermostat at the required temperature during the experiment and the temperature of the bath up to 40° is taken as the temperature of the mercury, but for higher temperatures a correction is applied to the bath temperature to get the temperature of the mercury. This method is inapplicable at temperatures below 0° and above 60° . For these temperatures, 0° to -64° , the rate of vaporisation is determined by measuring the rate of change of the electrical resistance of the condensed film of mercury. A third method is also described which depends on the difference of readings in a graduated capillary tube due to vaporised mercury. The results show that for pure liquid mercury, irrespective of the temperature, the value of α is unity, but for solid mercury it is less than unity and decreases with decreasing temperature. It is shown that with sulphur, phosphorus, and benzophenone the value of α lies between 0.2 and 0.5 . It is also shown that there is a close connexion between α and the extent to which a liquid may be supercooled. J. F. S.

Coefficients of Vaporisation and their Relationship to Ostwald's Step Rule. M. VOLMER and I. ESTERMANN (*Z. physikal. Chem.*, 1921, 99, 383—394).—The coefficient of vaporisation, α , has been determined for mercury over the temperature $+59^\circ$ to -64° , and found, for the liquid phase, to be equal to unity irrespective of the temperature. The known expression $G=1/\sqrt{2\pi R} \cdot \sqrt{M/T} \cdot p$ expresses actually the velocity of vaporisation for all temperatures: If this equation yields results for other substances similar to those obtained for mercury, then it becomes the first strictly true reaction velocity equation. In the case of solid mercury α is found to be approximately 0.9 . The ratio α (solid)/ α (liquid) has been determined for sulphur, phosphorus, and benzophenone and the values $0.3-0.4$, $0.4-0.5$, and 0.25 respectively have been obtained. The Ostwald step rule and the

limits of its applicability to the separation of the liquid and solid phases from the vapour condition are shown to be due to the different α -values of the solid and liquid phases. J. F. S.

The Separation of Miscible Liquids by Distillation. II. ARTHUR FELIX DUFTON (T., 1922, 121, 306—308).

Divergences of the Value of the Mechanical Equivalent of Heat. WOJCIECH SWIENTOSLAWSKI (*Roczniki Chemji*, 1921, 1, 171—177).—The author gives a short description of facts which show that the value of the mechanical equivalent of heat requires exact verification. It is shown to be probable that the values obtained by electrical and mechanical methods are not in agreement. The measurements of Jaeger and Steinwehr show that in bomb calorimetry conditions often exist which increase the amount of heat obtained by the introduction of electrical energy into a calorimeter. It is also pointed out that adiabatic calorimetry has not been employed in the measurement of this constant. J. F. S.

Heat of Vaporisation of Sodium and the Probability of the Transition of the Sodium Atom from the Resonance to the Normal Condition on the Basis of Optical Measurements. R. LADENBURG and R. MINKOWSKI (*Z. Physik*, 1921, 6, 153—164).—The authors have measured the magnetic rotation of the plane of polarisation in the immediate neighbourhood of the *D* line by the method described by Senftleben (*Ann. Physik*, 1915, [iv], 47, 949) at various temperatures of the emitting vapour. The sodium used was contained in an air-free glass tube in an electric furnace the temperature of which was constant to $\pm 0.1^\circ$. It is shown that the dependence of *N* (the number of electrons which vibrate with the atoms) on the temperature can be regarded as a relative vapour pressure curve, if the theory that *N* is proportional to the number of sodium atoms present is accepted. Calculation from the experimental results leads to the value for the heat of vaporisation of sodium $h_{T=0}=25.9$ Cal. This value is probably uncertain to about 2%. J. F. S.

Action of Forces between Separated Atoms in Diamond and Aliphatic Molecules. K. FAJANS (*Z. physikal. Chem.*, 1921, 99, 395—415).—A theoretical paper in which it is shown that if in analysing the results of heat of combustion experiments the assumption is made, as a first approximation, that only neighbouring atoms have a noticeable energetic action on one another, then it appears that the firmness of a C—C linking in the diamond is somewhat greater than that in aliphatic hydrocarbons. From this it follows that the heat of combustion of hydrocarbons with branched chains should be somewhat smaller than that of the straight chain isomerides, a conclusion which is in keeping with experimental data. To explain the above relationships it is assumed, (1) that the energy of the C—C linking in aliphatic substances and diamond is constant, irrespective of whether or no the carbon atom is bound to further carbon atoms or also with hydrogen. (2) That separated and distant atoms have a notice-

able energetic action on one another. As a second approximation in the quantitative analysis, only those linkings which lie on a common edge of the tetrahedron are considered. From a comparison of diamond with the hydrocarbons the relationship $y_m - 2x_m + h \sim 1 - 2 \text{ Cal.}$, between the energies of the three types of edge linkings (C-C, C-H, H-H), where y_m , x_m , and h are respectively the energies of formation of the three types of linking. This relationship indicates a method of explaining the difference in properties of the chain isomerides and also the exceptional position of the first member of homologous series. In the case of aliphatic hydrocarbons, alcohols, ketones, and esters of monobasic acids, the chain isomerides with low boiling point and heat of vaporisation possess a lower heat of combustion, a stronger saturation of the forces in the molecule corresponding with a weaker intermolecular force. The difference in the boiling points and the specific heats of the chain isomeride is therefore brought into relationship with the difference in the intramolecular energy, and the latter is attributed to the mutual action between separated and distant atoms.

J. F. S.

The Meaning of the Atomic Constants of Heat of Combustion and Molecular Refraction. WALTER HÜCKEL (*J. pr. Chem.*, 1921, [ii], 103, 241—248).—A theoretical paper, in which the author states the various relations that have been found by Steiger (A., 1921, ii, 473) and others between the various "atomic" and "linking" constants of organic compounds and of the elements forming them, and points out some relations that seem to follow.

W. O. K.

New Data in the Thermochemistry of Organic Substances. WOJCIECH SWIENTOSLAWSKI (*Roczniki Chemji*, 1921, 1, 305—315).—The heat of dissociation of hydrogen, chlorine, bromine, iodine, and solid carbon into individual atoms, determined during recent years, has been used to obtain the value of the constant ϵ of the equations $(\text{C}-\text{I}) = (\text{H}-\text{I}) + \epsilon - 3$; $(\text{C}-\text{Br}) = (\text{H}-\text{Br}) + \epsilon - 3$; $(\text{C}-\text{Cl}) = (\text{H}-\text{Cl}) + \epsilon$; $(\text{C}-\text{C}) = (\text{H}-\text{C}) + \epsilon$; $(\text{C}-\text{N}) = (\text{H}-\text{N}) + \epsilon$; $(\text{C}-\text{S}) = (\text{H}-\text{S}) + \epsilon + 2$; $(\text{C}-\text{O}) = (\text{H}-\text{O}) + \epsilon + 5$; $(\text{C}-\text{H}) = (\text{H}-\text{H}) + \epsilon + 15$. The symbols (C-I), (H-I) indicate the heat of formation of the single link between the atoms named. When the values 81.3 Cal., 106 Cal., 46 Cal., and 36 Cal. are taken as the heat of formation of the molecules of hydrogen, chlorine, bromine, and iodine, respectively, as represented by $2\text{X} - = \text{X}_2 + Q \text{ Cal.}$, and the heat of formation of solid diamond as $-\text{C} - = \text{C}_{\text{sol}} \times 287 \text{ Cal.}$, it is possible to calculate the heat of formation of the links (C-C) and (C-H). According to Fajans (A., 1920, ii, 354), $(\text{C}-\text{C}) = 137.5 \text{ Cal.}$ and $(\text{C}-\text{H}) = 117.0 \text{ Cal.}$ Using the above data in the equations, a mean value of 20.6 is obtained for ϵ . From the heat of formation of the linkings $(\text{H}-\text{Cl}) = 115.5 \text{ Cal.}$, $(\text{H}-\text{Br}) = 72.0 \text{ Cal.}$, $(\text{H}-\text{I}) = 52.7 \text{ Cal.}$, it is shown that $(\text{C}-\text{Cl}) = 136.3 \text{ Cal.}$, $(\text{C}-\text{Br}) = 89.7 \text{ Cal.}$, and $(\text{C}-\text{I}) = 70.3 \text{ Cal.}$ An analysis of the above results shows that the heat of formation of a link is an additive

quantity made up of parts due to the links of the atoms concerned. These parts have been calculated as follows: (C—)=68·8 Cal., (H—)=48·2 Cal., (Cl—)=67·4 Cal., (Br—)=23·8 Cal., (I—)=4·4 Cal. The heat of formation of a link between two atoms is the sum of the two atomic values. This regularity is probably existent in inorganic compounds also, for if the above atomic values of the halogens are subtracted respectively from the heat of formation of the corresponding haloids of potassium, the value of (K—) is found to be 91·2, 94·5, and 93·7 Cal., and by the same method the value for sodium (Na—) is 83·3, 84·0, and 82·7 Cal. J. F. S.

Heat of Coagulation of Ferric Oxide Hydrosol with Electrolytes. FREDERICK L. BROWNE and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1921, **43**, 2336—2352).—The heat of coagulation of ferric oxide hydrosol of various concentrations and purity by various concentrations of sodium oxalate, sulphate, chloride, and hydroxide, potassium ferricyanide, and sulphuric acid has been determined. It is shown that the dilution of ferric oxide hydrosols of varying purity is accompanied by measurable heat effects until the purity exceeds 21 or 22 (the ratio of gram equivalents of ferric oxide per litre to gram equivalents of chlorine per litre is termed the purity of the sol), beyond which point the heat of dilution is zero. If the heat of dilution per gram-equivalent of chlorine in the sol is plotted against the chlorine content, the curve is of the same nature as that for the heat of dilution of ferric chloride solutions of varying concentration. The thermal behaviour of ferric chloride solutions on dilution confirms the observations of Goodwin (*Physical Rev.*, 1896, **9**, 251; 1900, **11**, 193), to the effect that the hydrolysis of ferric chloride takes place in two steps, the first an instantaneous and the second a slow reaction. The mixing of ferric chloride solutions with common electrolytes involves very significant heat changes. The heats of coagulation have been reduced to curves showing the heat of coagulation as a function of the purity which vary widely in shape with the nature of the coagulant; the heat effect is usually positive, but with sodium sulphate and sodium chloride at low purities it is negative. As the purity increases, the heat of coagulation becomes smaller, and finally becomes negligible, except in the case of sulphuric acid. The peculiar behaviour of this last electrolyte is due to solution of the ferric oxide. When the heat of coagulation is plotted against the concentration of the coagulating electrolyte, smooth curves are obtained which show no break at the point of limiting concentration. The heat effects observed on coagulating ferric oxide sols with electrolytes are to be attributed to the action of the electrolytes in the coagulants on the electrolytes, particularly ferric chloride, present in the sol. The change in dispersity of the ferric oxide on coagulation does not involve a greater heat change than 1—2 cal./gram-equivalent of ferric oxide. In the case of ferric oxide hydrosols, there is no heat of peptisation analogous to the heat of solution of crystalloids. J. F. S.

Kation Volumes in Permutite. RICHARD LORENZ (*Z. Physik*, 1921, **6**, 269—270).—A criticism of the work of Günther-Schulze

on the determination of the kation volumes in permutite (A., 1921, ii, 624). It is pointed out that the value found for the alkali ion is practically the same as that of the alkali atom. It is suggested that the alkali ions in permutite fill only a small amount of the space and have a large space to vibrate in. This great mobility is characteristic of permutite. The kation radii calculated by Günther-Schulze are probably too large, for the new determinations of Fajans and Herzfeld and also those of Landé are much smaller and lie very close to those calculated from the ionic mobility by Lorenz and Born.

J. F. S.

The Velocity of Extension of Thin Layers of Oils on the Surface of a Sheet of Water. PAUL WOOG (*Compt. rend.*, 1922, 174, 162—165).—For fatty oils, where all the molecules intervene, the velocity of extension is practically proportional to the ratio (the carboxyl groups of the glycerides + the double linkings + the acidity)/viscosity. In mineral oils, however, the velocity of extension depends only on the unsaturated molecules, which are few in number, and hence the viscosity plays an insignificant part. In mixtures of the two types of oil, the results depend on the relative proportions in which the active fatty oil and the comparatively inactive mineral oil are mixed.

W. G.

High Pressure Due to Adsorption. WILLIAM D. HARKINS and D. T. EWING (*Chem. News*, 1922, 124, 23—24, 31—35).—Cf. this vol., ii, 123.

J. F. S.

Electro-adsorption as a Purely Chemical Process. I. M. KOLTHOFF (*Kolloid Z.*, 1922, 30, 35—44).—The author discusses electro-adsorption (adsorption of ions) and from the experimental results of Freundlich, Odén, and others shows that the process is strictly a chemical one. The adsorption of copper, lead, morphine, codeine, papaverine, atropine, ferricyanide, oxalate, chromate, and iodate ions by norit carbon confirms this view. It is shown that the adsorption isotherm can be deduced directly from the stoichiometric relationships, if it is assumed that the electro-adsorption is a process in which a sparingly soluble substance, contained in the adsorbent, is converted by the adsorbed ion into another sparingly soluble substance. The coefficient $1/n$ of the adsorption isotherm bears a direct relationship to the valency of the reacting substances. If $1/n$ is equal to a for a univalent ion, then it has the value $a/2$ for a bivalent ion and $a/3$ for a trivalent ion. This relationship is confirmed by the present experiments and by the earlier work of Freundlich and Odén. The significance of the quantity of the adsorbent is explained by the characteristic constitution of its surface layer of particles. The active ion, which determines the charge in the surface layer, and in adsorption forms the insoluble salt, is present in this layer in far larger concentration than in the liquid. When equilibrium has been set up on the surface of a particle, then the concentration of the active ion, in contact with the excess of reacting ions, is small. In such a case, if fresh adsorbent is placed in the liquid, then the reacting ions

are again in contact with large concentrations of active ions, and the reaction commences anew. The general chemical theory in its relationships to colloid chemistry is shortly discussed. J. F. S.

Origin of the Charge of a Colloidal Particle and its Neutralisation by Electrolytes. JNANENDRA NATH MUKHERJEE (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 103—115).—The charge of a number of suspensoids has been shown to be due to the adsorption of a common ion and the nature of the chemical forces which cause this adsorption has been defined. The effect of the electrical charge of a surface (due to the disorption of ions) on ions of opposite sign has been theoretically investigated for the case when chemical action does not take place between the surface and the ion. It has been shown that the electrical forces are sufficiently strong to account for adsorption. The stability of the adsorption of an ion of opposite sign by electrical forces has been given a quantitative form, assuming that the charge of the surface consists of ions which can be treated as point charges widely separated from each other. Actual calculations justify this assumption. The reversal of the charge by electrical adsorption has been discussed. The following series of the adsorbability of kations by a negatively charged surface has been deduced from the theory: $\text{Th}^{+++} > \text{Al}^{+++} > \text{Ba}^{++} > \text{Sr}^{++} > \text{Ca}^{++} > \text{Mg}^{++} > \text{H}^{+} > \text{Cs}^{+} > \text{Rb}^{+} > \text{K}^{+} > \text{Na}^{+} > \text{Li}^{+}$. This order is the same as that of the precipitating power of these ions for a number of suspensoids of widely differing chemical properties. Equations deduced from the theory agree satisfactorily with the experimental observations of Elissaffoff (A., 1912, ii, 419) on electro-endosmosis. The chemical affinity of the surface atoms is not always negligible, and for this reason the series given above cannot be expected to hold in all cases. J. F. S.

Electrical Theory of Adsorption. W. HARRISON (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 116—118).—A criticism of Mukherjee's theory of adsorption (cf. preceding abstract). The author is of the opinion that the double layer consists of a surface of rigidly fixed atoms under continuous bombardment of positively and negatively charged ions, any particular point on the rigid surface becoming in turn negative, neutral, and positive, these conditions arising in any order. The observed contact difference is the average effect of these conditions. When several kinds of atoms are present in the solution, the average number of any one of them at the surface will depend on their concentration, valency, and mobility. The variation of contact difference from negative to neutral and positive was observed with cotton and aluminium sulphate near the neutral point (*J. Soc. Dyers and Col.*, 1911, **27**, 279; 1918, **34**, 91). These variations occurred during the same experiment, the readings being direct measurements of *E.M.F.* developed by filtration under pressure. J. F. S.

Diffusion of Hydrogen through Iron and Platinum. GERHARD C. SCHMIDT and TH. LÜCKE (*Z. Physik*, 1921, **8**, 152—159).—The diffusion of hydrogen through iron and platinum has

been investigated. A sheet of the metal was fixed between two glass vessels, hydrogen was electrolytically generated on one side of the sheet and the potential on the other side measured over a period of time up to about twenty-four hours. The metal sheets were of various thicknesses. It is shown in the case of iron that the passage of the hydrogen through the metal is always indicated by a fall of potential. In the case of thin sheets, the fall of potential is observed as soon as the electrolysis commences; the fall of potential is rapid at first, and gradually becomes slower until, when the liberation of hydrogen has proceeded for some time, it becomes constant. With sheets of medium thickness (0.5—1.0 mm.) the fall of potential is gradual, and with sheets thicker than 1.0 mm. there is no fall of potential. On breaking the polarising current, the potential increases, the more quickly the thinner the metal. From this fact it is deduced that the hydrogen diffuses into the liquid. With thicker sheets, the increase of potential is slower, which is explained by the longer time required for the relatively large volume of hydrogen to diffuse into the liquid. Similar results are obtained in the case of platinum. The results show that the passage of hydrogen across platinum plates is a diffusion and not, as stated by Nernst and Lessing (*Göttinger Nachr.*, 1902, 146), due to small pores in the metal. The Nernst-Lessing rule was shown by them to hold for palladium and thin sheets of platinum, but not for thicker sheets of platinum. It is shown that the reason for the rule holding with palladium is that on account of the great power of palladium for absorbing hydrogen practically none is liberated from the other side, and consequently the condition of the rule is obtained.

J. F. S.

Dispersoid Analysis of Non-aqueous Systems. WOLFGANG OSTWALD (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 89—93).—The author describes the preparation of membranes and jellies suitable for dispersoid analysis of solutions in alcohol of 97%, for both dialysis and diffusion experiments. The mercury sulphide alcisol, the preparation of which is explained, is an especially stable sol suitable for these tests. Solutions of dyes, resins, neutral salts, fatty acids, and soaps, as far as at present examined, produced by the spontaneous solution of these substances in 97% alcohol, are all molecular-dispersed, or contain, at any rate, molecular-dispersed particles in considerable proportions. Zein, the protein of maize which is soluble in alcohol, is also found to be dialysable.

J. F. S.

Solubility. III. Solubility of Metal Ammonia Salts in Salt Solutions. J. N. BRÖNSTED and AGNES PETERSEN (*J. Amer. Chem. Soc.*, 1921, **43**, 2265—2292; cf. A., 1920, ii, 536).—A long list of the solubilities of eighty-six cobalt, chromium, and rhodium complex ammine salts in water at 0° and 20° is given in the paper. The solubilities of a large number of complex ammine salts of cobalt and chromium in solutions of potassium chloride, formate, chlorate, trichloroacetate, dichloroacetate, monochloroacetate, thio-

cyanate, hydroxide, nitrate, and phthalate; sodium chloride, sulphate, chlorate, nitrate, formate, oxalate, and benzenesulphonate; magnesium sulphate and chloride; calcium formate, acetic acid; and mono-, di-, and trichloro-acetic acids of various concentrations have been determined at 0°. In the preceding papers (*loc. cit.*) it was shown that the expression $\log S/\bar{S}_0 = a(C_i^{1/3} - \bar{S}_0^{1/3})$ represents approximately the solubility changes of salts in hetero-ionic solvents up to about 0.1*N*-solutions, when a is a constant which for uni-univalent salt systems has the value 1/3, C is the concentration of the solvent salt, \bar{S}_0 the solubility in water, and S that in the salt solution at the same temperature. The experimental data furnished for salts of the same type in the present paper agree approximately with the formula, and an equation of the same type is found for bivalent salts. The individual nature of the salts employed is more pronounced in the larger amount of material now presented and tends to obscure any numerical regularity in salt systems of promiscuous types. The experiments lead to the following rules. The influence of the solvent increases with increasing valency of the ion of the solvent salt, which, in the case of ter-bivalent salts, leads to an enormous increase of solubility, even on the addition of solvents of very low concentration. When both the dissolved and dissolving ions are of higher valency, the effect of the sign of the electric charge is very marked, producing the highest solubility values when the multivalent ions of solvent and solute are of different sign. The reason for the appearance of individuality in the solubility curves is to be sought partly in the hydration of the solvent and the solute, and partly in the fact that in these ions the mass is not to be regarded as a point, but as a particle of varying size bearing a number of electric charges of opposite signs, the algebraic sum of which gives the valency of the ion. It is probable that the size of the ion in the present cases will have an influence of considerable magnitude. J. F. S.

Probability of Spontaneous Crystallisation of Supercooled Liquids. C. N. HINSHELWOOD and HAROLD HARTLEY (*Phil. Mag.*, 1922, [vi], 43, 78—94).—The statistical investigation of the spontaneous crystallisation of supercooled salol, phenol, *p*-toluidine, and *o*-nitrophenol leads to the following conclusions: In all these cases crystallisation is provoked by colloidal organic dust particles, the activity of which diminishes in general as the result of heating or ageing. The effectiveness of the dust particles depends on their radius. If this is equal to the radius of a small particle of the solid which should thermodynamically be in equilibrium with the supercooled liquid, then crystallisation occurs at once. If the radius is less than this, the supercooled liquid has an average life depending on the discrepancy between the equilibrium radius and the radius of the particles present. The magnitudes of these quantities are discussed. The results of crystallisation experiments are given: 16 sets of 70 tubes of salol were kept at 32.3° in a thermostat and the number which had crystallised at various times noted; similar results are recorded for 12 sets of 41 tubes of phenol at 18—25°;

8 sets of 122 tubes of *p*-toluidine at 33.36—17.48° and 5 sets of 130 tubes of *o*-nitrophenol at 38.72—31.1°. J. F. S.

Structure of [Hanging] Drops of Mixed Liquid Crystals. O. LEHMANN (*Ann. Physik*, 1921, [iv], 66, 323—343).—The structure of hanging drops of liquid crystals of *p*-hydroxyphenetole and cholesteryl benzoate has been examined between parallel Nicols by means of the dichroic effects produced. A number of diagrams and descriptions of the structure observed are included in the paper. J. F. S.

Submicrons Visible in the Tyndall Cone to the Naked Eye. J. TRAUBE and P. KLEIN (*Kolloid Z.*, 1922, 30, 19—20).—When 30 c.c. of 1/30000 *N*-lead nitrate solution are treated with 2 drops of *N*/2-sodium carbonate solution in a rectangular vessel, stirred, and illuminated by a Tyndall cone, it is found that in forty to sixty seconds an extremely large number of small particles are visible by means of a hand lens. The particles are in violent and irregular motion. As the time of the existence of these particles increases more and more light is reflected from them, so that in about two minutes they are visible to the naked eye at a distance of 2 metres. It is held that the particles are crystals and are visible on account of their rotation, which causes an intermittent reflexion of light from the crystal faces. The phenomenon is not produced by all concentrations of lead nitrate, *N*/10000 is too concentrated and *N*/70000 is too dilute; the best concentration is that given above. The same phenomenon may be observed with very dilute solutions of calcium sulphate, calcium ammonium phosphate, barium sulphate, mercurous chloride, and lead chloride. J. F. S.

Fibrous Structure of Hard Drawn Metal Wires. M. ETTISCH, M. POLANYI, and K. WEISSENBERG (*Z. physikal. Chem.*, 1921, 99, 332—337).—From the *X*-ray examination of hard and soft wires of copper, tungsten, iron, molybdenum, palladium, aluminium, silver, and zinc, it is shown that the crystallite in soft wires is arranged irregularly, whilst in hard wires it is arranged regularly. In the case of the metals with a space centred cubic lattice (tungsten, iron, molybdenum), it is found that only a single lattice plane lies in the section of the wire, namely, the plane (110), whilst in the case of the metals with a face centred cubic lattice (copper, palladium, and aluminium) two lattice planes lie in the section of the wire, namely, the planes (111) and (100). The crystallite arrangement in hard wires is termed a fibrous structure because this arrangement was first observed in natural fibres such as ramie and silk. J. F. S.

Molecular Structure of Amorphous Solids. C. V. RAMAN (*Nature*, 1922, 109, 138—139).—In view of the fact that glass exhibits a very strong scattering of light, its magnitude being of the order that might be expected if the arrangement of the molecules

was irregular, it is assumed that such is the case. If the arrangement of the molecules approximated to the crystalline state, the scattering of light would be merely that due to the thermal movements of the molecules, and would be much smaller. Careful microscopic examination failed to disclose any inclusions, to which the effect has previously been ascribed (Strutt, *Proc. Roy. Soc.*, 1919, [A], 95, 476). A. A. E.

Action of Penetrating Radium Radiation on Inorganic and Bio-colloids. III. A. FERNAU and WO. PAULI (*Kolloid Z.*, 1922, 30, 6—13; cf. A., 1915, ii, 722; 1917, ii, 189).—A continuation of previously published work (*loc. cit.*). In the present paper the influence of the radiation from a radium preparation equivalent to 78.6 mg. of radium on gelatin, albumin, casein, acid albumin, and lecithin has been investigated. Of the radiation emitted by the radium preparation, only 25% of the hardest β -radiation and 99% of the γ -radiation came in contact with the colloids. It is shown that the viscosity of a 0.99% solution of glutin from bone glue at 35° falls rapidly at first under the influence of the radiation and then successively less rapidly, but in the presence of 0.1N-sodium chloride the fall in viscosity is much slower. The addition of 0.01N-hydrochloric acid to 0.5% glutin solution causes at first a rapid fall in the viscosity, which becomes less rapid as the time increases. Under the action of the radiation, the rate of fall of the viscosity is still more rapid. The action of the radiation is analogous to the action of heat on glutin. Glutin jellies when exposed to the radiation liquefy, but the portion nearest the tube containing the radium sets to a solid, opaque mass which sticks to the tube and is insoluble in water, although soluble in alkali hydroxide. The coagulation of serum-albumin, which had been freed from globulin, by the radiation is found less rapid in the presence of sodium chloride, the retardation being greater the greater the concentration of the salt. The time required for coagulation of albumin depends on the concentration of the albumin; it decreases at first with increasing concentration, passes through a minimum at 0.5—1.0% of albumin, and then increases. The action of the radiation on solutions of the sodium salts of acid albumin and casein is to displace the equilibrium toward the acid side, that is, to decrease the concentration of the hydroxyl ion. Thus an acid albuminate, prepared from serum-albumin, had a hydroxyl-ion concentration $1.66 \times 10^{-5}N$; after subjection to the radiation for a week the value was $1.57 \times 10^{-6}N$, and after three weeks $3.62 \times 10^{-8}N$, whilst sodium caseinate solution had the value 8.64×10^{-5} , which became 1.19×10^{-6} after treatment with the radiation for a week. A solution of 3 grams of lecithin in 200 grams of water exhibited at 25°, under the action of the radiation, a gradual fall in viscosity, but scarcely any change in the hydrogen-ion concentration or in the specific conductivity. Similar results are also found with a 0.2% emulsion of cholesterol. The results show that whilst albumins undergo considerable change under the action of radium radiation, this is not the case with lipoid emulsions. J. F. S.

Protective Colloids. XI. Carragheen as a Protective Colloid. I. General Colloid-chemical Investigation of the Extract of Irish Moss. A. GUTBIER and J. HUBER (*Kolloid Z.*, 1922, **30**, 20—31; cf. A., 1921, ii, 537).—The method of preparation and properties of colloidal solutions prepared from Irish moss are described. Purified carragheen (30 grams) is placed in a litre of water at the ordinary temperature and kept until the swelling process is complete, then it is vigorously shaken for five hours. The mucilage is separated by pressing through linen. Several other preparations are described; the amount of dry colloid varies between 0.4400 gram and 0.2100 gram per 100 c.c. of mucilage, and the ash between 0.0246 and 0.0600. Dialysis reduces the amount of ash and removes the turbidity and the foul odour and raises the degree of dispersion. Carragheen solutions do not produce fungoid growths when kept, and it is therefore unnecessary to add stabilising agents. On keeping, the viscosity of a 0.55% mucilage fell from 15.29 to an approximately constant value of 7.19 in thirty-three days. The rate of decrease in viscosity is rapid at first and subsequently much slower. The change in viscosity with ageing indicates the change of the mucilage to a more stable system. Boiling the mucilage reduces the viscosity by an amount which increases with the length of time of boiling. This indicates a change in the chemical constitution of the mucilage, but after filtration no further change occurs on prolonged keeping. Heating therefore may be regarded as a hastened ageing and gives rise to stable colloidal solutions. The viscosity increases with increasing concentration, but the amount of increase is greater the higher the temperature employed in the preparation. Electrolytes have no unfavourable action on the mucilage, no coagulation or visible change being brought about except in the case of sodium hydroxide, where it becomes light brown in colour. Increasing concentration of hydrochloric acid, sodium hydroxide, and sodium chloride decreases the viscosity to values which approach a constant value as the concentration of the electrolyte increases.

J. F. S.

Protective Colloids. XI. Carragheen as Protective Colloid. II. Colloidal Silver. A. GUTBIER, A. WOLF, and A. KIESS (*Kolloid Z.*, 1922, **30**, 31—35; cf. preceding abstract).—Extract of Irish moss prepared as indicated previously (*loc. cit.*) has been investigated as to its efficacy as a protecting colloid in the case of colloidal silver. Before use, the mucilage is aged for a considerable time and thereby stabilised. Colloidal silver prepared in the presence of carragheen by hydrazine hydrate has colours varying from dark reddish-brown to brownish-yellow in transmitted light, depending on the concentration of the silver nitrate used. It is exceedingly stable and remains unchanged for two months, and may be evaporated to dryness on a water-bath to an almost black residue which is completely reversible. On the other hand, evaporation in a vacuum over sulphuric acid yields a viscous paste which is not completely reversible, but yields a secondary system with water which is only stable in dilute solutions. Colloidal

solutions of silver have been prepared in the presence of carragheen with a concentration of 17% of silver, but they were not very stable. Carragheen itself has a reducing action on silver nitrate and produces colloidal silver. This action is not complete, but the percentage of reduced silver increases with the dilution of the silver nitrate; thus $N/10$ -silver nitrate gives 8.98% of reduced silver, whilst $N/640$ -silver nitrate gives 58.54% of reduced silver, the amount of carragheen being the same in all cases. J. F. S.

Ultra-violet Spectroscopical Studies on the Antagonistic Action of Salts in Organic Colloidal Solution. TETSUTARO TADOKORO (*J. Coll. Agric. Hokkaido Imp. Univ.*, 1921, **10**, 37—49; cf. A., 1918, ii, 432).—The effect of different salts on the degree of dispersion of organic colloidal solutions (egg-albumin, taka-diastrase, blood-serum, and lettuce juice) was studied by observing the changes induced in their absorption spectra in the ultra-violet. Certain pairs of salts were shown to have antagonistic effects on dispersion. Ultramicroscopic observations confirmed the conclusions drawn from the spectroscopical observations. G. W. R.

The Importance of Imbibition for some Biochemical Problems. M. RICHTER-QUITNER (*Biochem. Z.*, 1921, **121**, 273—292).—By means of the Zsigmondy-Haen ultra-filtration apparatus, the author has examined the influence of electrolytes and non-electrolytes on the velocity of ultra-filtration of various dispersoid systems, for example, sera, for substances which inhibit imbibition will accelerate filtration. All potassium salts, heavy metal salts, urea, and sugar inhibit, whilst other kations favour imbibition. For anions the Hofmeister series holds good. H. K.

Reversal of Phases in Emulsions and Precipitation of Suspensoids by Electrolytes. SHANTI SWARUPA BHATNAGAR (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 27—31).—A study of the reversal of phase in oil-water emulsions in the presence of pure soaps by electrolytes (cf. T., 1920, **117**, 542), and the precipitation of arsenic sulphide sols by lithium chloride (Mukherjee, *J. Amer. Chem. Soc.*, 1915, **37**, 2030). It is shown that the power of ions in reversing the phases in oil-water emulsions in the presence of soap follows the order: $Al^{+++} > Cr^{+++} > Ni^{++} > Pb^{++} > Ba^{++} > Sr^{++} > Ca^{++}$. The amount of electrolyte required varies with different soaps but the order of the different electrolytes remains the same. The greater the dilution, that is, the distance between the oil particles in an emulsion, the larger the amount of a multivalent ion required to bring about reversal of the phases. Some measurements are given of the effect of diluting milk on the rate of coagulation by dilute sulphuric acid. It is shown that the greater the dilution the larger is the concentration of acid required to bring about an immediate coagulation. Soaps are regarded as exerting a protective action on oil-water emulsions, and it is shown that the protective action follows the order: potassium stearate > sodium stearate > sodium and potassium oleate > potassium oleate > sodium oleate.

J. F. S.

Peptisation and Precipitation. N. G. CHATTERJI and N. R. DHAR (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 122—127).—Silver chloride, silver chromate, calcium silicate, cupric fluoride, and barium sulphate when precipitated in the presence of glycerol or concentrated sucrose solutions are not peptised. The hydroxides of iron, nickel, cobalt, thorium, and mercury may be peptised by adding an alkaline hydroxide to the solutions of salts of these metals in the presence of glycerol or concentrated sucrose solution. In the case of gold or uranium salts, ammonium hydroxide should be used instead of sodium hydroxide. In these cases, peptisation can only be brought about if the alkali is added to the mixture of the salt and glycerol, but precipitation takes place if the solution of the salt is added to the mixture of glycerol and alkali. These results are supported by conductivity measurements. The major portion of the hydroxides of aluminium, chromium, lead, mercury, and copper, when dissolved in sodium or potassium hydroxide, exists as a colloid, whilst zinc hydroxide mainly forms a zinc oxide, as shown by conductivity experiments. Similarly, the hydroxides of aluminium, iron, and chromium form colloidal solutions in acetic acid, whilst zinc hydroxide forms zinc acetate. The transformation of the blue hydroxide of copper to the black variety and that of the blue hydroxide of cobalt to the pink form are changes of the same type, and are almost equally effected by different catalysts. The hydroxides of aluminium, chromium, and zinc respectively are adsorbed by ferric hydroxide when the latter is precipitated in the presence of solutions of the hydroxides of these metals in potassium hydroxide.

J. F. S.

A Kinetic Precipitation Measurer. WO. OSTWALD and F.-V. VON HAHN (*Kolloid Z.*, 1922, **30**, 62—70).—Two new precipitation measures are described, which permit of the precipitation process and the peptisation of colloidal solutions being studied kinetically. The one instrument, the two-limbed measurer, is based on the principle of level difference in communicating tubes, and the change of this difference due to decrease of density of one liquid by the sedimentation of the disperse phase contained in it. The second apparatus, the single-limbed measurer, depends on the rise of the seal liquid column of an enclosed gaseous volume, through change in the density of the seal liquid in consequence of the precipitation of the disperse phase which it contains. A number of examples of the use of these instruments in the kinetic measurement of the precipitation processes of typical sols are given.

J. F. S.

Distribution of certain Drugs between Immiscible Solvents. W. O. EMERY and C. D. WRIGHT (*J. Amer. Chem. Soc.*, 1921, **43**, 2323—2335).—Distribution experiments between water and chloroform have been carried out with caffeine, antipyrine and *p*-acetoxyacetanilide. It is shown that the most suitable temperature for the extraction of caffeine from water by chloroform is the ordinary temperature, although a change of temperature from 12° to 40° only reduces the amount recovered from water by a single extraction from 96.3% to 93.2%. The distribution is the more favourable to

the chloroform the more dilute the aqueous solution. The effect of small concentrations of sodium hydroxide, sodium acetate, sulphuric acid, sodium salicylate, sucrose, alcohol, and citric acid on the distribution of caffeine between water and chloroform has been examined at 25°. The presence of sulphuric acid leads to a less efficient extraction of the caffeine, whilst sodium salicylate reduces the amount extracted from 96% to 20.7%, due in all probability to the formation of a molecular compound between caffeine and sodium salicylate. The solubility of caffeine in water, and aqueous solutions of sulphuric acid (*N*), citric acid (*N*), potassium bromide (*N*) and (2.5*N*), sodium salicylate (*N*) and (0.1*N*), sodium benzoate (*N*) and (0.1*N*) has been determined at 25°. The solubility in grams per 100 c.c. of solvent is 2.071 in water, 3.355 in sulphuric acid, 6.411 in citric acid, 2.136 and 2.035 respectively in potassium bromide, 22.22 and 4.921 respectively in sodium salicylate, and 15.27 and 3.422 respectively in sodium benzoate. The solubility determinations and cryoscopic measurements of mixtures of caffeine with sodium salicylate and sodium benzoate respectively confirm the complex salt formation with these salts. Distribution experiments of caffeine between absolute chloroform and water, *N*-sulphuric acid, *N*-potassium bromide, 0.1*N*-sodium salicylate, and 0.1*N*-sodium benzoate have been made at 25°. It is shown that potassium bromide has but little effect on the partition, whilst sodium salicylate reduces the amount of caffeine recovered from the water solutions by the greatest amount. The distribution of antipyrine shows that there is no tendency to the formation of double salts with sodium salicylate, but, on the other hand, there is a far greater depression in the percentage of antipyrine extracted from *N*-sulphuric acid, when compared with that from pure water solution, due presumably to difference in basicity. In the case of *p*-acetoxyacetanilide, somewhat lower distribution ratios are obtained than for either caffeine or antipyrine. The solubility of *p*-acetoxyacetanilide in water at 25° is found to be 0.239 gram per 100 c.c. of water, and in chloroform at the same temperature 3.250 grams in 100 c.c. of chloroform. J. F. S.

Theory of the Liesegang Rings. MARTIN H. FISCHER and GEORG D. McLAUGHLIN (*Kolloid Z.*, 1922, **30**, 13—16).—It is shown that Liesegang rings are only observed when a liquid phase is present; they may be formed when two dissolved substances, which react with one another, are brought together in the presence of a third insoluble substance; the formation of the rings occurs on the side of the solution of lower concentration, the rings tend to increase in thickness from the commencement of their formation and during the growth tend to pass from the originally liquid and amorphous condition to the solid and crystalline form. All substances which give satisfactory Liesegang rings are impermeable toward molecularly dissolved substances, and consequently it would seem unlikely that after the formation of the first ring a second and third ring could be formed. The view is put forward that true semi-permeable media are solvated and when these become less solvated

holes appear through which the dissolved substance can diffuse and so go to form a second ring. J. F. S.

Thermodynamical Theory of Explosions. I and II. SIR J. B. HENDERSON and H. R. HASSÉ (*Proc. Roy. Soc.*, 1922, [A], **100**, 461—482).—A theoretical paper in which calculations are made of the maximum temperature and pressure of an explosion in a closed vessel, also the calculation of the curve of reversible adiabatic expansion of the products, and incidentally the ideal indicator diagram. The calculations are applied to a gun, in which the variation with time of the volume of the chamber, of the composition of the products, and the temperature and pressure of explosion are worked out and the value of the maximum pressure determined. The maximum temperature obtained with Mark I cordite is 3210° , and with *MD* cordite 2870° , whilst the maximum pressure of Mark I cordite is 8370 atmospheres or 55.1 tons/sq. in. J. F. S.

Equation for the Velocity of Reaction of Hydrogen Peroxide and Potassium Permanganate. JAN ZAWIDZKI (*Roczniki Chemji*, 1921, **1**, 135—139).—From the measurements of Baeyer and Villiger (A., 1900, ii, 719) on the course of the reaction between hydrogen peroxide and potassium permanganate, the author calculates that the time law of this reaction is expressed by the differential equation $dx'/dt = k_2(1-x')/\sqrt{a}\sqrt{x'}$. The velocity coefficient $k' = k_2/\sqrt{a}$ is calculated for -16° and $+15^{\circ}$ and the values 0.119 and 0.379 respectively are obtained. From these, the temperature coefficient of the velocity constant is found to be 1.452. J. F. S.

The Velocity of Reaction in Mixed Solvents. II. The Velocity of Saponification of the Ethyl Esters of some Mono-substituted Benzoic Acids. ALBERT ERIC CASHMORE, HAMILTON McCOMBIE, and HAROLD ARCHIBALD SCARBOROUGH (T., 1922, **121**, 243—253).

Influence of Temperature on the Velocity of Interpenetration of Solids. H. WEISS and P. HENRY (*Compt. rend.*, 1922, **174**, 292—294; cf. A., 1920, ii, 545; 1921, ii, 551).—From a study of the velocity of solution of silver antimonide, Ag_3Sb , in solid silver at different temperatures in the case of a silver-antimony alloy containing 14% of antimony, it is shown that the velocity is proportional to the temperature, being expressed by the equation $v = Ka^T$, where T is the absolute temperature and, in this case, $K = 4.17 \times 10^{-12}$, and $a = 1.0324$. W. G.

The Mechanism of Catalytic Hydrogenation. A. SKITA (*Ber.*, 1922, **55**, [B], 139—143).—In a recent communication, Willstätter and Waldschmidt-Leitz (A., 1921, ii, 185) have pointed out the necessity of priming the platinum catalyst with oxygen during the course of hydrogenations and have advanced the hypothesis that a platinum peroxide or oxide is intermediately formed. This suggestion is quite consonant with the author's repeated observation that the activity of the catalyst produced in situ is

superior to that of the pre-formed agent, since the experimental conditions do not guarantee the complete absence of oxygen. Comparative experiments with a platinum catalyst produced *in situ* do not show any difference in the rate of hydrogenation of pulegone or *as-p*-xylidine when every trace of oxygen is excluded and when special precautions to this end are not observed; the formation of a peroxide as catalyst cannot therefore be assumed in these cases. Further, if the platinum catalyst is in reality a peroxide, its oxygen must liberate iodine from potassium iodide, and hydrogenation must be impossible in the presence of the salt. It is found, however, that phenol is reduced smoothly to *cyclohexanol* at 40° in the presence of potassium iodide. On the other hand, the addition of potassium iodide completely inhibits the reduction of phenol or *as-p*-xylenol at the atmospheric temperature, whereas in its absence they are transformed readily into *cyclohexanol* and 1 : 4-*dimethylcyclohexan-2-ol*, b. p. 179°, respectively. Reduction occurs quantitatively but slowly if the mixtures are heated at 50°. At the higher temperature, it appears, therefore, impossible that hydrogenation should depend on the formation of a platinum peroxide. It has not yet been elucidated whether the failure of the action at the atmospheric temperature is due to the inactivation of a platinum peroxide or to poisoning of the catalyst.

H. W.

The Mechanism of Catalytic Action in the Hydrolysis of Fats. E. BRINER and (Mlle) A. TRAMPLER (*Helv. Chim. Acta*, 1922, 5, 18—20).—The product obtained by the sulphonation of phenylacetic acid is inferior to hydrochloric or sulphuric acid as a catalyst in the hydrolysis of ethyl acetate in homogeneous solution. It thus appears that the presence of a common group in catalyst and substrate does not confer any supplementary chemical activity on the former. In Twitchell's and similar catalysts, the activity of the sulphonic group is diminished by the presence of the aliphatic radicle, but this effect is more than compensated by the greater mutual solubility caused by the two similar groups.

H. W.

Conclusions from the Spherical Form of the Simplest Atom. L. ZEHNDER (*Physikal. Z.*, 1922, 23, 53—55).—A theoretical paper of a highly speculative character, in which, on the basis of a spherical primordial atom, an atomic ether, the atoms of which have a mass of about one-millionth that of hydrogen, elasticity, and gravitational forces, the author draws a number of conclusions respecting the atomic weight of helium, the structure of the carbon atom, and the subdivision of organic compounds into three classes, aliphatic, aromatic, and carbohydrates.

J. F. S.

A New Model of the Nucleus. MAXIMILIAN CAMILLO NEUBURGER (*Z. physikal. Chem.*, 1921, 99, 454—473).—Previous speculations (cf. A., 1921, ii, 479) are extended by the consideration of *isohydrogen* particles, of mass 1. The disintegration series of thorium, uranium, and actinium are considered on the basis of this hypothesis.

J. R. P.

Structure of the Atomic Nucleus. O. CHWOLSON (*Z. Physik*, 1921, 7, 268—284).—A theoretical paper in which an attempt is made to deduce the structure of the atomic nucleus. It is maintained that any hypothesis of the structure of the atomic nucleus must conform to the following: (1) the mass of the atomic nucleus is practically the same as that of the atom, (2) the positive charge, E , of the nucleus is eN , where $-e$ is the charge of the electron, and N the atomic number of the corresponding element, (3) the atomic weight is roughly $M=2N$, (4) in the case of hydrogen $M=2N$ is not true, and (5) the hypothesis must not be in conflict with Bohr's hypothesis. As the basis of the present hypothesis, the author assumes that the volume density, δ , of electricity of both signs is a constant and that a given charge, E , irrespective of its sign, has the same volume, $v=\delta/E$. From this it is shown that the atomic nucleus cannot easily be represented as a sphere built up of spherical particles, and the assumption is made that it is cylindrical and is built up of disks. This conception is strictly in keeping with the relatively large volume of the nucleus in comparison with that of the electron. It is further assumed that the positive elementary disk is identical with the helium nucleus and the α -particle. The elementary positive disk is termed the "pentalon." Negative electricity consists of spherical electrons and positive electricity of disk-shaped pentalons. If $-e$ is the charge of an electron, e' , the charge of the pentalon is $e'=2e$; the mass of the pentalon is $m'=4$. The order number of the pentalon N' is $N'=N+1$, where N is the atomic number of the element. The atomic nucleus is a disk or cylinder made up of pentalons, between each pair of which is a disk of negative electricity, of charge $-e$, equal to that of an electron. The disk of negative electricity is termed a "piezo-electron" and its order number is $N''=N-2$. The atomic nucleus of an element of atomic number N consists of $N-1$ pentalons and $N-2$ piezo-electrons; these $2N-3$ disks form a cylinder which has no interstices. The charge of the nucleus is $E=(N-1)2e-(N-2)e=Ne$. Calculating from the above, it is shown that the radius of the pentalon is $69.9s$, where s is the radius of the electron, and the thickness, D , is $0.0005450s$; the radius of the piezo-electron is also $69.9s$, and the thickness is half that of the pentalon. The pentalon has a mass which is 7340 times that of the electron. The thickness $D(N)$ of the nucleus of an element of atomic number N is $D(N)=(N-1)D+(N-2)D/2=(3N-4)D/2$ and the mass, $M_1=4(N-1)+2(N-2)=2N$. The hypothesis is compared with the Bohr hypothesis, and found not to conflict with it. The hydrogen nucleus on the basis of the hypothesis is shown to be built up of one pentalon and one piezo-electron, both of double thickness and of reduced radii in the ratio $1:\sqrt{2}$. That is, the hydrogen nucleus is three times as thick as the helium nucleus, and has a radius $49.5s$ and a thickness $0.001635s$.

J. F. S.

Attempt [to Find] a Physical Basis for Atomic Radiation. E. GEHRCKE (*Z. Physik*, 1921, 6, 400—402).—The author imagines

the electrons surrounding an atomic nucleus as rings round the nucleus and not as spheres rotating in an orbit round the nucleus. The ring form of the electron has the same mass, volume, and surface as the spherical electron, and is to be regarded as a spacial isotope of the spherical electron. If for any reason the ring electron changes its diameter, a change in the ether must also occur, and this change in the ether gives rise to emission or adsorption; emission when the ring reduces its diameter and absorption when the diameter increases. The change in the diameter of the ring consists in the displacement of the ether over the space between the initial and final positions of the ring. The mechanism of this process is visualised as follows. An atomic ether, E , the atoms of which are arranged in a space lattice, is assumed. The space lattice has spherical symmetry in the neighbourhood of a positive atomic nucleus. Between the atoms of E , a magnetic ether, M , is assumed, which in comparison with E can be regarded as a continuum. The atomic ether, E , is the carrier of electric forces and is named the electric ether. The magnetic ether can spread out in stream lines (magnetic field lines), whilst the electric ether cannot spread out in the same way, but may change the shape of its space lattice. The sudden change of the space lattice, due to a change in diameter of the ring electron, occasions vibrations in the ether atoms which are transmitted to neighbouring ether atoms, and when the transmission of the vibration extends outside the ring emission of radiation results. Absorption results when incoming vibrations increase the kinetic energy of the ring electron, that is, increase its velocity and so increase its diameter. It is therefore not the ring electron which makes the spring at each energy step, but the E ether which is displaced by the thickness of a ring electron. The generator of light and Röntgen radiation in the material atom is, therefore, not a vibrating electron, but the whole system of ether atoms between two radii, R and r , swinging in a pendulum-like manner. The frequency, ν , of the vibrations of the ether atoms is given by the ether between the radii R and r , and is proportional to the thickness and inversely proportional to the square of the length, that is, $\nu \sim R - r/Rr = 1/r - 1/R$. J. F. S.

Condition of Motion of Molecules in Space. J. BÖESEKEN, CHR. VAN LOON, DERY, and P. HERMANS (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **24**, 198—204).—A theoretical paper in which it is shown that atoms which are not directly bound to one another exercise a mutual action on other atoms in the same molecule. Saturated non-cyclic molecules execute, among others, movements in which the parts of the molecule revolve in opposite directions, or with different velocities round the single bonds as axes. In the case of non-uniformly loaded molecules, that is, practically all molecules except those of hydrogen, nitrogen, oxygen, ethane, hexachloroethane, and similar molecules, the movements are irregular, because the most stable position of the atoms will be passed most frequently. In the saturated cyclic molecules with six or seven atoms, the ring-forming atoms are not fixed in one

plane, but lie in a curved surface which travels through space in undulatory movements; the atoms in this surface are under no tension. J. F. S.

Transition Elements and the Octet Theory: A New Arrangement of the Rare Earth Elements in the Periodic Classification. R. G. W. NORRISH (*Chem. News*, 1922, 124, 16—22).—A theoretical paper in which the author considers the fourth postulate of Langmuir's octet hypothesis from the point of view of valency and colour of the ions produced in solutions of salts of the metals. A new arrangement of the periodic system is drawn up, which has as its basis that the transition elements and the rare earth metals have a variable electronic structure as far as the outermost shell of electrons is concerned. It is shown that the elements which yield coloured kations can all be grouped together in a rectangle which extends from groups 4A to 1B and from series IV to VI. These elements are assumed to possess the variable electronic structure. The rare earth metals which give coloured kations are sharply cut off from those which give colourless kations by this rectangle. The existing data concerning the characteristic infra-red frequency, the latent heat of vaporisation, the compressibility, and the magnetic susceptibility are tabulated with the periodic arrangement, and it is shown that these properties maintain a more or less high value inside the rectangle but fall off sharply on either side of it. The elements inside the rectangle (excluding copper, silver, gold, and zirconium) are paramagnetic, whilst to the right of the rectangle all the elements except tin, which is feebly paramagnetic, are diamagnetic and those to the left of the rectangle are either feebly paramagnetic or diamagnetic. It appears that the magnetic susceptibility and colour are dependent on the presence of an incomplete subsidiary ring in the atom. J. F. S.

Radii of the Alkali Metals and the Alkali Metal Ions. RICHARD LORENZ (*Z. Physik*, 1921, 6, 271—275).—A theoretical paper in which the author has discussed the values previously obtained for the atomic radii (A., 1921, ii, 191) and the space filling of the atoms concerned. A new table of the atomic radii, ionic radii, and the space filling of the alkali metals and alkali metal ions has been drawn up which is based on the present discussion and recent work of other investigators. J. F. S.

A Lecture Experiment for Demonstrating the Dependence of the Antiseptic Action of Mercury Compounds on the Degree of Ionisation. G. JOACHIMOGLU (*Biochem. Z.*, 1921, 121, 259—261).—The fermentation of dextrose by yeast with the visible production of carbon dioxide in fermentation tubes affords a means of demonstrating the antiseptic influence of mercuric ions. Addition of mercuric chloride inhibits fermentation completely, but repression of the ionisation by addition of sodium chloride gives a moderate evolution of carbon dioxide. Mercuric cyanide has practically no inhibiting influence. H. K.

Inorganic Chemistry.

The Steric Formula of the Molecule of Water. JEAN PICCARD (*Helv. Chim. Acta*, 1922, 5, 72—74).—It is only possible to explain certain physical properties of water if it is assumed that the centre of gravity of the positive charges of the molecule does not coincide with that of the negative charges. This asymmetry of the charges might result from the inequality in the distances of the two hydrogen atoms from the oxygen atom or by such a disposition of the hydrogen atoms that the valencies uniting them to the oxygen atom are disposed at an angle other than 180° . There is, however, no evidence in favour of the first supposition. A consideration of oxonium salts, on the other hand, shows that in them the co-ordinative valency of oxygen is three, and that the oxygen atom may be regarded as placed in the centre of an equilateral triangle with its valencies directed towards the apexes and therefore inclined to one another at an angle of 120° . An explanation is thus given for the observation that only those carbon-oxygen heterocyclic rings are stable in which the total number of atoms is five or six. Thus, for example, if the valencies of carbon form an angle of $109^\circ 28'$ with one another and those of oxygen an angle of 120° , the mean deviation in a cyclic system composed of three carbon and three oxygen atoms is only $2^\circ 38'$ whereas in *cyclohexane* the mean deviation is $5^\circ 16'$. H. W.

Electrolytic Concentration of Aqueous Solutions of Nitric Acid. I. HENRY JERMAIN MAUDE CREIGHTON (*J. Franklin Inst.*, 1922, 193, 89—95).—When a solution of nitric acid is electrolysed in a cell in which the anode and cathode are separated by a porous diaphragm, concentration of the acid occurs through electrolytic decomposition of water and at the same time the concentration of the acid in the anolyte is increased at the expense of that in the catholyte on account of the different migration velocities of the hydrogen and nitrate ions. The acid in the catholyte is further reduced by reduction to nitrogen oxides, hydroxylamine, or ammonia according to the nature of the cathode metal. Experiments were made in which 70—71% nitric acid was electrolysed in a diaphragm cell using platinum electrodes, and provision was made for returning the gaseous nitrogen oxides formed in the anolyte chamber back to the catholyte chamber. The current used was 6—8 amperes and the *E.M.F.* 3.0—6.5 volts. It was found possible thus to increase the concentration of acid in the anolyte chamber to 99.65% HNO_3 . The porous cylinder used underwent considerable disintegration in the process. [See further *J. Soc. Chem. Ind.*, 1922, 172A.]

E. H. R.

Preparation of Silicic Acid and Tungsten Hydroxide Sols by means of Hildebrand Cells. M. KRÖGER (*Kolloid Z.*, 1922, 30, 16—18).—By the electrolysis of a 1.5% solution of sodium silicate

between a mercury cathode and a platinum anode in a Hildebrand cell sols of silicic acid are obtained which do not gelatinise until they have been kept for four weeks. A 6% solution gelatinises as soon as the solution becomes neutral. The electrolysis is started with a current of 0.55 ampere, but this steadily falls as the process proceeds, and in ninety minutes has reached the value 0.12 ampere. After one hundred and ten minutes' electrolysis, the solution has a neutral reaction toward litmus. In the case of the 6% solution, the gelatinisation proceeds so rapidly that the waves occasioned by stirring are often reproduced in the gel, which is usually as clear as glass. Electrolysis of a 30% solution of water glass causes silica to separate on the anode. Electrolysis of a 2% solution of sodium tungstate, using the apparatus named above with a silver anode, rapidly produces the hydrosol of tungsten hydroxide. The removal of alkali may be hastened by the cautious addition from time to time of a little hydrochloric acid, but in no circumstances may the neutral point be passed. Should the solution become acid, blue tungsten compounds are produced. The tungsten hydroxide hydrosols are clear and transparent, but of a deep brown colour, which in dilute solutions is yellowish-brown. They are coagulated by potassium chloride to form a black powder which resembles the lower oxides of tungsten.

J. F. S.

Influence of Tungstic Acid on the Gelatinisation of Silicic Acid in Concentrated Hydrochloric Acid Solutions. M. KRÖGER (*Kolloid Z.*, 1922, **30**, 18—19).—The time required for the gelatinisation of silicic acid in the presence of tungstic acid by hydrochloric acid has been investigated. The solution consisted in each case of 7 c.c. of a solution of sodium silicate containing 33.7% of silica, to which had been added volumes of a 10% solution of sodium tungstate varying from 0.5 c.c. to 15 c.c., the total volume in each case being made up to 22 c.c. Nine c.c. of 9.77*N*-hydrochloric acid were added in each case and the time required for complete gelatinisation was noted. The time-tungstic acid concentration curve passes through a minimum at 1 c.c. of tungstic acid and a maximum at 2.5 c.c. of tungstic acid and then falls continuously.

J. F. S.

Frequency of the Electrons in the Neon Atom. LAURENCE ST. C. BROUGHALL (*Phil. Mag.*, 1922, [vi], **43**, 339—344).—A mathematical paper in which the frequency, angular velocity, and linear velocity of the electrons in the neon atom have been calculated on the assumption that the electrons do not radiate energy under normal conditions. The following numerical results are recorded: Frequency of the electrons about the axis XX' , $n_3 = 0.73 \times 10^{16}$; frequency about YY' and ZZ' , $n' = 1.00 \times 10^{16}$; angular velocity about XX' , $\omega_3 = 4.58 \times 10^{16}$ rad./sec.; angular velocity about YY' and ZZ' , $\omega' = 6.28 \times 10^{16}$ rad./sec.; instantaneous linear velocity of the outer electrons about XX' , $v_3 = 2.98 \times 10^8$ cm./sec.; instantaneous linear velocity of the outer electrons about YY' and ZZ' , $v' = 4.08 \times 10^8$ cm./sec.; instantaneous linear velocity of the inner electrons about YY' and $ZZ' = 3.83 \times 10^8$ cm./sec.

The value of v is small when compared with the velocity of light, in consequence of which it follows that no appreciable error is committed in not correcting for the variation of mass with velocity according to the equation $m_v = m_0(1 - v^2/c^2)^{1/2}$, where c is the velocity of light.

J. F. S.

Crystal Structures of the Alkali Haloids. I. RALPH W. G. WYCKOFF (*J. Washington Acad. Sci.*, 1921, **11**, 429—434).—From data as to the crystalline structure of the alkali haloids obtained from powder photographs and on the assumption that the unit cell consists of four molecules, it is held by the author that there are only two possible arrangements of the molecules within the unit cell, namely, the sodium chloride arrangement and the zinc sulphide arrangement. The geometrical considerations involved and the method of calculating the nature of the diffraction effects to be expected are given elsewhere (Wyckoff and Posnjak, following abstract). A closer accord of the normal decline of intensity of reflection with the spacing of the reflecting planes as observed in experiments on sodium chloride and similar crystals is obtained by assuming the intensity to be proportional to the 2.35 power of the spacing instead of the simple square. Experimental determinations of the intensity for a few of the principal lines of the spectrum were compared with the intensities calculated with alternative assumption of the two groupings above mentioned. The results agreed with the assumption of the sodium chloride grouping in the case of sodium bromide, sodium iodide, potassium bromide, potassium iodide, and rubidium chloride. Cæsium bromide and cæsium iodide have a similar structure to cæsium chloride, which has been shown to be body-centred (Davey and Wick, *Physical Rev.*, 1921, **17**, 403).

G. W. R.

Crystal Structure of Ammonium Platinichloride. RALPH W. G. WYCKOFF and EUGEN POSNJAK (*J. Amer. Chem. Soc.*, 1921, **30**, 2292—2309).—The crystal structure of ammonium platinichloride has been determined by a general method which is based on the theory of space groups. It is shown that crystals of ammonium platinichloride have a structure which is analogous to that commonly assumed for fluorspar, in which the PtCl_6 groups occupy the positions of the calcium in fluorspar or crystals and the NH_4 groups the positions of the fluorine. The unit crystal cell has a side 9.843×10^{-8} cm. The only assumption made which is not required in the ordinary determination of the wave-length of X-rays from a reflection spectrum is that the four hydrogen atoms of the ammonium radicle are exactly alike, with this exception, that in attempting to place the chlorine atoms with accuracy, it was assumed that atoms scatter X-rays in an amount which is roughly proportional to their atomic numbers and that in a lattice arrangement of atoms the intensities of reflection follow quantitatively the order of $1/(h^2 + k^2 + l^2)$.

J. F. S.

Revision of the Atomic Weight of Glucinum. Analysis of Glucinum Chloride. O. HÖNIGSCHMID and L. BIRCKENBACH (*Ber.*, 1922, **55**, [B], 4—12).—The ratios $\text{BeCl}_2 : 2\text{Ag}$ and

$\text{BeCl}_2 : 2\text{AgCl}$ have been determined in the same manner as used previously in the determination of the atomic weight of bismuth (Hönigschmid and Birckenbach, A., 1921, ii, 646). As mean result of all analyses, the value $G1=9.018$ is adopted, this figure being about 1% lower than that assigned by the International Commission.

Technical glucinum carbonate is converted into the basic acetate and purified from iron compounds by repeated crystallisation from glacial acetic acid. The purified acetate is sublimed and converted into the nitrate. The solution of the latter in water is treated with an excess of ammonium carbonate and filtered from any undissolved aluminium compounds; the glucinum carbonate is subsequently precipitated by boiling the filtrate, and is finally converted into the oxide by calcination in a platinum dish in an electrically heated furnace. The pure oxide is transformed into the chloride by ignition with carbon in a current of chlorine. The apparatus used is identical with that described previously (*loc. cit.*). Great caution is needed in the quantitative decomposition of glucinum chloride by water.

Glucinum chloride has d_4^{25} 1.8995.

H. W.

Inorganic Luminescence Phenomena. IV. Preparation of Pure Magnesium Sulphide and its Phosphorescence.

II. Phosphorescent Magnesium Sulphides. ERICH TIEDE and FRIEDRICH RICHTER (*Ber.*, 1922, 55, [B], 69—74).—The specimens of magnesium sulphide described previously (A., 1916, ii, 619) were not sufficiently pure to allow definite conclusions to be drawn with respect to the capacity of the substance to phosphoresce. Pure magnesium sulphide has now been prepared by the ignition of magnesium oxide or, preferably, of anhydrous magnesium sulphate in a current of nitrogen laden with carbon disulphide vapour. The compound is not phosphorescent, but becomes so by suitable additions of manganese, bismuth, or antimony, the optimal amount of metal for 1 gram of sulphide being 0.001—0.002 gram of manganese as sulphate or chloride, 0.0024 gram of bismuth as the basic nitrate, and 0.0013 gram of antimony as potassium antimonyl tartrate. The main band of emission of phosphorescent light in the case of magnesium sulphide containing manganese lies in the red, approximately between 615 and 765 $\mu\mu$ with a maximum at 720 $\mu\mu$. The intensity at the atmospheric temperature for metal content from 0.00023—0.004 gram is almost constant and not markedly dependent on wide variations of temperature and duration of ignition. The duration of the phosphorescence is small. Magnesium sulphide containing bismuth exhibits an intensely blue phosphorescence which is excited by daylight or arc or mercury-vapour light. The band lies between 430 and 550 $\mu\mu$ with a maximum at 465 $\mu\mu$. Specimens of magnesium sulphide containing antimony have a delicate, yellow colour and a persistent, intensely yellowish-green phosphorescence after excitation by daylight or arc or mercury-vapour light, or, particularly, by exposure to cathode rays. The band lies between 570 and 610 $\mu\mu$ with a maximum at 545 $\mu\mu$.

H. W.

8**

Lead in the Uranium Minerals of Madagascar. MUGUET (*Compt. rend.*, 1922, **174**, 172—173).—The industrial treatment of several tons of betafite from Madagascar resulted in the isolation of lead to the extent of 0.6% of the mineral treated. The mineral being perfectly crystalline and practically free from impurities, the lead apparently occurs in the same chemical form as the uranium and is a disintegration product of uranium. The radioactivity of this lead has increased regularly for six months. W. G.

Abnormal Crystallisation of Lead Azide by Protective Colloids. A. G. LOWNDES (*Trans. Faraday Soc.*, 1921, **16**, Appendix, 128—129).—Lead azide when formed in large crystals is liable to explode and is therefore not entirely suitable for detonators. It is generally held that the explosions are caused by the fracture of large crystals. It is shown in preparing lead azide that if instead of running sodium azide and lead acetate solutions into water the solutions are run into a 0.5% solution of gelatin or dextrin small crystals which are not liable to fracture are produced. The presence of ferric chloride also causes the formation of small crystals, but these are useless for the filling of detonators. A number of photomicrographs of lead azide prepared by the various methods are included in the paper. J. F. S.

Preparation of Catalytic Copper. JEAN PICCARD (*Helv. Chim. Acta*, 1922, **5**, 147—148).—The following modified method (cf. Piccard and Larsen, A., 1917, i, 644) yields catalytic copper which is superior in its activity to Kahlbaum's "copper-bronze" or "naturkupfer C."

Granulated zinc (600 grams) is mixed with finely-powdered potassium dichromate (190 grams) or, preferably, with an equal weight of hydrated sodium dichromate, in a three-litre flask and concentrated hydrochloric acid (1300 c.c.) is added within five to ten minutes. A vigorous action ensues which leads to the formation of a clear, blue solution. The latter is filtered through glass wool into a flask filled with carbon dioxide, a current of the gas being passed over the filter during the process. The solution is treated with brisk agitation with copper sulphate (120 grams) dissolved in ice-cold water (700 c.c.). Reduction is instantaneous. The precipitated copper is washed five times by decantation with water, then filtered, and washed successively with ordinary and absolute alcohol and benzene. If the product is to be dried, the final washing should be effected with benzene containing a little vaselin. After desiccation in a vacuum, the copper is relatively stable towards air, but is preferably preserved in evacuated sealed tubes. It may also be stored as a paste beneath alcohol. H. W.

Colloidal Copper Hydroxide. C. PAAL and HERMANN STEYER (*Kolloid Z.*, 1922, **30**, 1—5).—The preparation of solid colloidal copper hydroxide is described. To 50 c.c. of 2% sodium prot-albinate solution, which acts as protective colloid, 20 c.c. of *N*-sodium hydroxide and 20 c.c. of 1% copper sulphate solution are added alternately in small quantities at a time. A light blue

turbid sol is produced which is dialysed for four days, treated with 3 drops of *N*-sodium hydroxide, and evaporated to dryness at 60° in a vacuum. A blackish-blue, brittle substance is obtained in the form of lamellæ which dissolve in water to form the original sol. The solid colloid contains 14.02% of copper and 1.34% of sodium. By using sodium lysalbinat as protective colloid and varying the quantities of the other reagents, solid colloids, similar in appearance and properties to the above but varying in composition, may be obtained. The colloid richest in copper contains 35.47% of copper and 5.31% of sodium. If solutions of the sols are heated for some time on a water-bath black lamellæ are deposited which dissolve in water to give a dark brown, turbid hydrosol. This does not change in colour when treated with 4*N*-ammonia solution, even after keeping for four days. The product is regarded as colloidal cupric oxide, and has been obtained containing 28.58% of copper and 4.37% of sodium.

J. F. S.

The Peroxidic Compounds of Copper. (MISS) JOAN ALDRIDGE and MALCOLM PERCIVAL APPLEBEY (T., 1922, 121, 238—243).

Reduction of Solutions of Ferric Salts with Mercury. LEROY W. MCCAY and WILLIAM T. ANDERSON, jun. (*J. Amer. Chem. Soc.*, 1921, 43, 2372—2378).—Neutral and acid solutions of ferric chloride are completely and rapidly reduced when shaken with a little mercury. In the case of ferric sulphate, the reduction proceeds to an equilibrium which at 20° lies at about 53% of ferrous iron, but if a little free hydrochloric acid or sodium chloride is added the reduction becomes complete. Under similar conditions, solutions of titanous acid are not reduced. If the mercurous salt is filtered off, the ferrous iron in the solution may be estimated by titration with either potassium permanganate or dichromate. Experiments on the estimation of iron in ferric alum and other ferric compounds show that this constitutes a rapid, accurate, and convenient method. Solutions of potassium ferricyanide, potassium chromate, ammonium molybdate, sodium vanadate, and potassium antimonate when acidified with hydrochloric acid are all reduced when shaken with mercury.

J. F. S.

Strengths of Cobaltammine Bases and Werner's Theory of Bases. ARTHUR B. LAMB and VICTOR YNGVE (*J. Amer. Chem. Soc.*, 1921, 43, 2352—2366).—The relative strengths of the following cobaltammine bases: hexamminecobaltic dibromide dihydroxide, hexamminecobaltic hydroxide, aquopentamminecobaltic hydroxide, diaquotetramminecobaltic hydroxide, triethylenediaminecobaltic hydroxide, diaquodiethylenediaminecobaltic hydroxide, carbonatotetramminecobaltic hydroxide, 1 : 2-dinitrotetramminecobaltic hydroxide, 1 : 6-dinitrotetramminecobaltic hydroxide, and dinitroaquotriamminecobaltic hydroxide have been determined by measuring the electrical conductivity over a range of concentrations at 25° and comparing these with the conductivities at zero concentration, as calculated from conductivity measurements of salts derived

from these bases. The determinations show that these bases are very strong, some of them being as highly ionised as potassium hydroxide; the replacement of ammonia by ethylenediamine has no effect on the strength of the base. The replacement of ammonia by water molecules produces a marked and progressive decrease in the strength; the substitution of acid-groups has no marked effect on the strength, the electrostatic effect of a decrease in valency probably counteracting the chemical effect of the acid radicle; the stronger acid radicle produces the weaker base. There is no marked difference in the ionisation of the successive hydroxyl groups in hexamminecobalt hydroxide. The improbability of the distinctive features of Werner's theory of bases is pointed out, and a more probable interpretation suggested. Equations have been derived, giving an important correction of the conductivity of solutions of bases for the conductivity of the carbon dioxide dissolved in the water. These equations have been applied in the present work.

J. F. S.

Sub-salts of Bismuth. HENRY GEORGE DENHAM (*J. Amer. Chem. Soc.*, 1921, **43**, 2367—2371).—Making use of the method and apparatus formerly employed in the preparation of the sub-salts of lead (T., 1917, **111**, 29; 1918, **113**, 249; 1919, **115**, 109), the author has prepared sub-salts of bismuth from bismuth sub-oxide. The products obtained are a sub-oxiodide, $2\text{BiI}_2 \cdot 3\text{BiO}$, the sub-iodide, BiI_3 , and bismuth dimethyl. The *sub-oxiodide* is a non-volatile, brick-red substance which is stable in dry air; it commences to decompose at 350° . A saturated solution gives a faint darkening with hydrogen sulphide and a faint turbidity with silver nitrate. It is decomposed into the metal and a soluble trivalent bismuth salt by sulphuric, hydrochloric, and acetic acids. It is insoluble in alcohol and in aqueous potassium iodide solutions, and reduces acid solutions of potassium permanganate. *Bismuth sub-iodide* is a volatile substance which crystallises in red, orthorhombic needles. In aqueous solution, it gives stronger reactions for bismuth and iodine than the oxiodide; it dissolves freely in potassium iodide solution, giving solutions of the colour of dichromate solutions. It speedily reduces aqueous solutions of iodine and acid permanganate, and is decomposed at 400° into bismuth tri-iodide and metallic bismuth. The distillate of excess methyl iodide from the preparation of the above compounds was yellow in colour, but on exposure to air it became colourless, and a white solid which turned yellow on keeping separated. This white compound is probably *bismuth dimethyl*, and is insoluble in alcohol; it is a strong reducing agent, and on oxidation is converted into *bismuth dimethoxide*, $\text{Bi}(\text{OCH}_3)_2$.

J. F. S.

Mineralogical Chemistry.

Chemical Aspects of Volcanism with a Collection of the Analyses of Volcanic Gases. E. T. ALLEN (*J. Franklin Inst.*, 1922, **193**, 29—80).—The author has collected and tabulated all published analyses of volcanic gases of any importance for the purpose primarily of determining whether any relation exists between the composition of the gases and the temperature at which they issue from the ground. The analyses are made the basis of a critical inquiry into the nature of the original gases and into the extent to which they have become contaminated with atmospheric gases and water. Consideration of the gases contained in igneous rocks leads to the conclusion that these are the source of the original volcanic gases, of which the most important is water. The original gases are probably changed in composition by the time they reach the point of collection; in some cases they probably lose a portion of the strong acid gases by interaction of these with metallic oxides; in most cases they become diluted with steam from surface waters and by atmospheric gases. In some volcanic gases the relations between the inert gases, argon and nitrogen, point to an atmospheric origin for these constituents; in others, they must either be of deep-seated origin or their original atmospheric relation has been changed by selective solubility in the magma. The composition of the original gases may also be changed by interaction with mineral substances, by surface oxidation, or by the shifting of chemical equilibrium due to change of temperature. Such equilibria as the following may be affected: $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{H}_2\text{O} + \text{CO}$; $3\text{S}_2 + 4\text{H}_2\text{O} \rightleftharpoons 4\text{H}_2\text{S} + 2\text{SO}_2$; $\text{H}_2\text{S} + 2\text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{SO}_2$; $2\text{H}_2\text{S} \rightleftharpoons 2\text{H}_2 + \text{S}$. These and other reactions are discussed from the thermal point of view. A more or less abrupt evolution of gas from the magma may occur during crystallisation. Energy derived from shifting chemical equilibria may have a considerable influence in prolonging the life of an eruption, but not in initiating volcanic activity. Surface combustion is sometimes an important factor in keeping up the temperature. Secondary explosions of great violence are undoubtedly produced by the access of surface water to hot volcanic ejecta. Primary explosions are probably the result of pressure from magmatic gases, not the result of chemical action. E. H. R.

Absence of Cobalt in Cornetite. ALFRED SCHOEP (*Min. Mag.*, 1922, **19**, 301—302).—Cornetite from the original locality, Star of the Congo mine in Katanga, Belgian Congo (A., 1920, ii, 441), is intimately mixed with minute black specks of heterogenite (A., 1921, ii, 649). When freed from these, the mineral shows no cobalt when tested microchemically with mercury thiocyanate. It thus agrees completely with the cornetite from Bwana Mkubwa in Northern Rhodesia (A., 1921, ii, 701). L. J. S.

Chemical Investigation of Japanese Minerals containing Rarer Elements. II. Analysis of Columbite and Monazite of Ishikawa, Iwaki Province. YŪJI SHIBATA and KENJIRŌ KIMURA (*J. Chem. Soc. Japan*, 1921, **42**, 957—964; cf. A., 1921, ii, 269).—Columbite (d 5.59) from Ishikawa, Iwaki Province, gave on analysis:

Nb ₂ O ₅ , Ta ₂ O ₅ .	SnO ₂ .	Al ₂ O ₃ .	MnO.	FeO.	H ₂ O.	Total.
78.94	0.38	0.36	3.56	15.99	0.90	100.13

with traces of SiO₂, TiO₂, WO₃, and CaO. The amount of Ta₂O₅ was about 10%. The ratio (Fe,Mn)O : (Nb,Ta)₂O₅ = 1 : 1.03.

Monazite (d 5.17) from the same locality gave on analysis :

P ₂ O ₅ .	SiO ₂ .	UO ₃ .	ThO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Ce ₂ O ₃ .	(La,Nd) ₂ O ₃ , etc.	Y ₂ O ₃ , etc.	CaO.	MgO.	H ₂ O.	Total.
27.52	2.98	0.42	11.08	0.80	0.66	21.08	31.27	3.53	0.52	0.27	0.56	100.69

Various samples differed; some contained traces of ZrO₂, TiO₂, and SnO₂, whilst others did not contain UO₃, and the quantities of ThO₂ and SiO₂ were very irregular. On spectroscopic examination, lines of praseodymium, gadolinium, dysprosium, erbium, ytterbium, holmium, and terbium were observed. K. K.

Density, Refractivity, and Composition Relations of some Natural Glasses. C. E. TILLEY (*Min. Mag.*, 1922, **19**, 275—294).—The natural glasses fall into two groups: (a) tektites, including moldavites and australites, which are perhaps of meteoric origin, and (b) volcanic glasses, including rhyolitic, trachytic, and basaltic obsidians. The refractive index and density were determined for a number of these, and their specific refractivity ($r_g = (n-1)/d$) compared with that of artificial glasses of definite composition (silica, feldspars, and CaSiO₃—MgSiO₃). When plotted on graphs, the different glasses fall in well-defined areas according to their composition. Values for the specific refractivity of various rock-constituents in a state of glass are calculated. An analysis is given of tachylite forming the selvage of a basic andesite at Kildonan, Eigg, Western Isles of Scotland. An estimation of water in the pitchstone of Newry, Ireland, gave 7.04%. The presence of water has a marked influence on the specific refractivity, as shown in the case of analysed rhyolite-obsidians from the Island of Lipari. L. J. S.

Augite from Hawaii. HENRY S. WASHINGTON and H. E. MERWIN (*Amer. J. Sci.*, 1922, [v], **3**, 117—122).—Loose, jet-black crystals of augite from the volcano of Haleakala on the island of Maui, were powdered and pure material separated by heavy solutions and the electromagnet, d 3.358. In thin sections the material is pale grey with a darker surface film; extinction-angle 47° (red) to 49° (blue), α 1.700, β 1.706, γ 1.724. An analysis of the powder dried at 110° gave :

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O.	Total.
47.70	1.89	6.82	0.23	3.36	4.43	0.16	21.35	13.34	0.65	0.03	0.15	100.11

Tschermak's (A., 1921, ii, 121), Boeke's (A., 1914, ii, 283), and Zambonini's (1914) views as to the constitution of aluminous augites are criticised; and the alumina and excess of ferric oxide are regarded as being in solid solution in the pyroxene constituents (diopside-hedenbergite, acmite-jadeite, and clinoenstatite). The present analysis is interpreted as $\text{CaMgSi}_2\text{O}_6$, 69.12; $\text{CaFeSi}_2\text{O}_6$, 15.13; $\text{NaFeSi}_2\text{O}_6$, 5.08; MgSiO_3 , 1.90; FeSiO_3 , 0.40; $(\text{Al,Fe})_2\text{O}_3$, 8.65%. Assuming, with Zambonini, that the alumina is present as spinel (12.23%), there remains a residue of silica (4.20%) and CaSiO_3 (6.61%).

L. J. S.

Analytical Chemistry.

A Microvolumenometer. A. BOLLAND (*Roczniki Chemji*, 1921, 1, 147—156).—A volumenometer is described which consists of a thick-walled capillary tube which is closed at its lower end; the tube is 50 mm. long and has a capacity of 0.02 c.c., it is accurately graduated into forty divisions each corresponding with 0.0005 c.c. and widens at the top into the shape of a test-tube 40 mm. long. The method of weighing, filling, and emptying the apparatus is described. It is shown that it may be used for quantitative micro-analysis by measuring the volume of precipitates after centrifuging.
J. F. S.

Standard Dropping Pipette. HEDE HALPHEN (*Pharm. Zentr.-h.*, 1921, 62, 767—768).—A pipette which will deliver 20 drops of water per gram should have an orifice 3 mm. in diameter (external measurement); such a pipette can be made by drawing out a glass tube at one end and passing this narrow portion as far as it will go through a 3 mm. hole drilled in a brass plate. The tube is then cut exactly at the surface of the plate.
W. P. S.

Rapid Extraction Funnel. H. WOLFFRAM (*Chem. Ztg.*, 1922, 46, 93).—A very simple apparatus to replace a Soxhlet extractor consists of a cylindrical part somewhat wider than the extraction thimble to be employed, narrowing below to an outlet tube in the usual way. A small glass triangle prevents the thimble from closing up the way into the outlet tube, and three or four indentations in the sides of the glass cylinder prevent the thimble from leaning over against the side of the glass.
G. F. M.

Proposed Standard Method of Colorimetry. HERBERT E. IVES (*J. Opt. Soc. Amer.*, 1921, 5, 469—478).—For the purpose of simplifying spectrometric measurements for colour specification, the author has designed a method of colour measurement, which consists essentially of the spectrophotometry of adjacent patches of the spectrum, each patch of a width fixed by the hue scale, and

narrow enough so that there is no colour difference in the spectrophotometer field at each setting. The number of patches is determined by the kind of colour and the degree of accuracy required. An instrument is described by which the measurements can be made and in which any colour may be reproduced for comparison.

J. F. S.

The Salt Error of Coloured Indicators. I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, **41**, 54—67; cf. Sørensen, A., 1909, i, 861; 1910, i, 147).—The corrections that should be made for the presence of solutions of sodium chloride and potassium chloride of concentrations ranging from decinormal to normal have been determined for a large number of indicators. The results are discussed in detail for each indicator and a table summarising the chief results is appended, together with notes as to the suitability of the different indicators for various conditions.

H. J. E.

The Colorimetric Estimation of Hydrogen-ion Concentration without Buffer Solutions. I. M. KOLTHOFF (*Pharm. Weekblad*, 1922, **59**, 104—118).—Hydrogen-ion concentration may be estimated by comparing the colour given with standard indicators with the colours given by mixtures of coloured salts in specified proportions. For many indicators, suitable comparison solutions may be made by mixing a solution of 11.262 grams $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 250 c.c. of 1% hydrochloric acid solution with a solution of 18.2 grams of crystallised cobalt nitrate in 250 c.c. of 1% hydrochloric acid solution; both these solutions may be employed after long keeping. Mixtures of these salt solutions in various proportions given in the tables show the same tints as the following: Neutral-red in solutions with range p_{H} from 7.0 to 8.0; methyl-orange, range 3.05—4.60; tropæolin-OO, range 1.80—3.00; methyl-red 5.2—6.0. For solutions having p_{H} between 4.2 and 6.0, where methyl-red is used as indicator, suitable comparison solutions may be made up with permanganate solution (0.004*N*) and dichromate solution (0.01*N*—potassium dichromate in 0.4*N*— H_2SO_4), but these solutions are not stable in colour, and must be prepared afresh as required. For the range 4.4—6.0 with this indicator, the ferric chloride solution may be mixed with one obtained by mixing 10 c.c. of 0.025% pure methyl-red solution with 10 c.c. of 4*N*-acetic acid solution, and diluting to 250 c.c.; the latter solution is stable for about a week.

For the range of p_{H} between 8.2 and 10.0, with phenolphthalein as indicator, the comparison solutions are best prepared by adding to 10 c.c. of 0.5*N*-sodium carbonate solution given volumes of a 0.004% phenolphthalein solution. From the figures prepared for this table, the dissociation constants of phenolphthalein have been calculated; the values agree approximately with the figures deduced from theory (assuming the indicator is a bibasic acid) by Rosenstein (A., 1912, ii, 893).

For the range of p_{H} between 6.0 and 7.0, *p*-nitrophenol is a suitable indicator, the colour comparison solutions being prepared in this case also from an alkaline solution of the indicator. With this

range completed, it is possible to use the method for all values of p_H between 2.0 and 10.0. S. I. L.

The Titration of Moderately Strong Acids or Bases in the Presence of Very Weak Ones. I. M. KOLTHOFF (*Pharm. Weekblad*, 1922, 59, 129—142).—The observation of Tizard and Boeree (T., 1921, 119, 132) that the hydrogen-ion concentration is equal to $\sqrt{K_1 K_2}$ in the case of two acids having the same concentration, in the presence of sufficient alkali to neutralise the stronger one, and where K_1 and K_2 are the dissociation constants of the two acids, is confirmed theoretically and by experiment. To obtain accurate results by titration, it is necessary that the ratio $K_1 : K_2$ should be not less than 1×10^4 , and the approximate concentrations must be determined before the final titration is made. For this purpose, the approximate concentration of both acids is first determined by titration with *N*-sodium hydroxide solution in presence of tropæolin-*O*, and the concentration of the stronger acid by titration in presence of neutral-red or phenol-red. The value of p_H can then be calculated from the above, and a comparison solution made up from the sodium salt of the strong acid and the necessary proportion of the weak acid, or a buffer solution of the same p_H can be selected. With this comparison solution to give the colour required for the particular indicator employed, the accurate titration may be made. Generally, neutral-red or an indicator of the same transition range is most suitable. S. I. L.

Formation of Nitrogen Oxides in the Slow Combustion and Explosion Methods in Gas Analysis. G. W. JONES and W. L. PARKER (*J. Ind. Eng. Chem.*, 1921, 13, 1154—1155).—When the time of burning is not more than three minutes and the platinum wire is not heated above bright yellow, the formation of nitrogen oxides in the slow combustion method does not exceed 0.003 c.c., and nitrogen oxides are not produced in the explosion method when air is used as the oxygen supply. If a mixture of air and oxygen is employed in the explosion method, appreciable quantities of nitrogen oxides are formed and the error thus introduced may amount to 2%; their formation is due to increase in the flame temperature produced by the addition of oxygen.

W. P. S.

Estimation of Water in Fuels. ANDRÉ MARINOT (*Ann. Chim. Analyt.*, 1922, [ii], 4, 7—8).—In the estimation of water in fuels or fuel oils, errors may be introduced by the absorption of oxygen or the distillation of anthracene concurrently with the evaporation of the water, even at temperatures below 100°. These errors are avoided by carrying out the operation in a current of dry hydrogen, and an apparatus is described for the purpose consisting of two 100 c.c. flasks connected together and heated in a constant level water-bath. From 10—15 grams of the material are placed in each flask and a slow current of hydrogen dried in a calcium chloride-sulphuric acid tower is passed through for one and a half hours. The vapours from the flasks pass through a

horizontal elongated bulb where any anthracene is deposited into a weighed U-tube containing calcium chloride, the exit of which is protected from atmospheric moisture by a guard tube.

G. F. M.

Potassium Ferricyanide as a Reagent in Iodometry. I. M. KOLTHOFF (*Pharm. Weekblad*, 1922, 59, 66—68).—The accuracy of the author's method of standardising thiosulphate solutions by the use of potassium ferricyanide (*ibid.*, 1919, 56, 1618) having been questioned, a further examination has been made. The method is found extremely accurate and very rapid. The ferricyanide must be pure and dry, and if the zinc sulphate and hydrochloric acid used are free from iron, a perfectly white precipitate of zinc ferrocyanide is obtained, and the end-point with starch is very sharp.

S. I. L.

High Percentage Hydrogen Peroxide (Perhydrol) for the Estimation of the Total Sulphur in Illuminating Gas. ALOYS KLEMMER (*Chem. Ztg.*, 1922, 46, 79).—The sulphur compounds, including hydrogen sulphide, carbon oxysulphide, carbon disulphide, and mercaptan, are oxidised to sulphuric acid by passing the gas through a strongly alkaline solution of hydrogen peroxide. Ten c.c. of perhydrol are mixed with 80 c.c. of fairly concentrated sodium hydroxide, and the gas is led through the thick, crystalline paste consisting of sodium peroxide, $\text{Na}_2\text{O}_2 \cdot 8\text{H}_2\text{O}$, which is formed, at a rate not exceeding 100 litres per hour. At the end of the operation the liquid is acidified with hydrochloric acid, boiled to expel the excess of hydrogen peroxide, and the sulphuric acid precipitated as barium sulphate.

G. F. M.

Estimation of Sulphur in Cast Irons and Steels. ANDRÉ MARINOT (*Ann. Chim. Analyt.*, 1922, [ii], 4, 5—6).—Five grams of the metal are treated with a reagent consisting of 30 c.c. of 50% sulphuric acid and 60 c.c. of hydrochloric acid in an apparatus consisting of a conical reaction flask of 375 c.c. capacity surmounted by a vertical condenser into the top of which is ground a small pear-shaped gas washer from which a delivery tube leads into a flask containing 200 c.c. of a 2.5% solution of zinc acetate acidified with acetic acid. The gas washer consists of a vertical narrow tube surmounting the condenser and extending almost to touch the apex of a conical muff which surrounds it and is sealed to the tube at the base, where, however, it is perforated with five or six small holes which allow of the escape of the gas into the outer envelope of the pear and thence through the delivery tube into the zinc acetate flask. All the sulphur in the metal is evolved as hydrogen sulphide, and a slow stream of carbon dioxide is passed through the whole apparatus to displace the gas and prevent the formation of colloidal sulphur or organic sulphur compounds. The sulphur is finally estimated by oxidising the zinc sulphide formed in the flask by standard iodine solution and titrating back the excess.

G. F. M.

Estimation of Available Sulphur in Golden Sulphide of Antimony. B. D. W. LUFF and B. D. PORRITT (*J. Soc. Chem. Ind.*, 1921, **40**, 275—278r).—It is suggested that the "available sulphur" be estimated by extraction with carbon disulphide after the pigment has been heated at 150° for five hours in an atmosphere rendered slightly alkaline with ammonia; this heating converts any amorphous sulphur which may be present into a form which is soluble in the solvent. The carbon disulphide used should be purified previously by distillation over sulphur. W. P. S.

Sulphates in Blood. W. DENIS (*J. Biol. Chem.*, 1921, **49**, 311—317).—A nephelometric method for the estimation of inorganic sulphates in blood or plasma is described. Proteins are removed by means of mercuric chloride and the precipitate produced by the addition of acidified barium chloride solution is compared with a standard in a nephelometer. No evidence was obtained of the existence in deproteinised blood of other compounds of sulphur. E. S.

A Micro-method for Estimation of Nitrogen. D. ACÉL (*Biochem. Z.*, 1921, **121**, 120—124).—After destruction of the organic matter with sulphuric acid in the usual manner, the ammonia formed is not distilled off, but is determined colorimetrically by Nessler's reagent. The control is treated with standard ammonium chloride solution until the colours match. The method is suitable for the estimation of nitrogen in as little as 0.001—0.003 c.c. of serum or urine if diluted for measurement. H. K.

A Rapid Method for the Estimation of Ammoniacal Nitrogen. R. MEURICE (*Ann. Chim. Analyt.*, 1922, [ii], **4**, 9—10).—In the estimation of ammonium salts by converting them into hexamethylenetetramine and titrating the free acid thus produced, errors are likely to occur if phenolphthalein is used as indicator in the preliminary exact neutralisation of the ammonium salt owing to the uncertainty of this indicator in presence of ammonia. This error is eliminated if rosolic acid is used as indicator for the preliminary neutralisation, but as under ordinary conditions it is also sensitive to hexamethylenetetramine a special device is adopted to render it insensitive. After the mixture of ammonium salt and formaldehyde has been kept about thirty minutes, an equal volume of ether is added, and the whole is well shaken, whereby the rosolic acid passes into the ether and becomes insensitive to the amine, although still sensitive to a strong base such as sodium hydroxide. Titration of the free acid with standard alkali can now therefore be proceeded with until the appearance of a pale rose colour which persists on agitating the liquid with the ether. G. F. M.

Precipitation of Arsenic Sulphide from Arsenates. J. H. REEDY (*J. Amer. Chem. Soc.*, 1921, **43**, 2419).—The time required for precipitation of arsenic sulphide from solutions of arsenates may be greatly reduced by the addition of a small quantity of a soluble iodide, such as ammonium iodide. The hastening of the

precipitation is due to the reduction of the arsenic acid to arsenious acid, according to the equations $\text{H}_3\text{AsO}_4 + 2\text{HI} \rightarrow \text{H}_3\text{AsO}_3 + \text{H}_2\text{O} + \text{I}_2$; $\text{H}_2\text{S} + \text{I}_2 \rightleftharpoons 2\text{HI} + \text{S}$. The reaction is applied by adding 1–2 c.c. of *N*-ammonium iodide solution to the hot solution which contains 4 c.c. of 6*N*-hydrochloric acid in 40 c.c. of solution, just before the hydrogen sulphide is passed in. Precipitation begins immediately and is usually complete in four to five minutes. Complications arise in the precipitation of mercury and copper as iodides and in the partial reduction of mercury to the mercurous condition. This difficulty is, however, removed during the digestion with yellow ammonium sulphide which oxidises both metals to the higher valency, precipitating them as mercuric and cupric sulphides. J. F. S.

Method for the Estimation of Free and Combined Carbon Dioxide. J. A. SHAW (*J. Ind. Eng. Chem.*, 1921, **13**, 1151–1152).—A definite quantity of the solution under examination (for example, mine water) is drawn into a cylindrical bulb which is fitted at the top and bottom with three-way taps; the tap at the top connects with a small funnel for the introduction of the sample and with a measuring burette, whilst the tap at the bottom connects with a smaller cylindrical bulb and with a mercury reservoir. At the commencement of the operation the whole apparatus is filled with mercury. Any gas liberated from the sample is passed over into the burette, the upper tap is then closed and the mercury reservoir lowered so that the whole of the liquid is drawn into the lower cylinder, a low pressure being thus produced in the upper cylinder and above the surface of the liquid. The gas collecting in the upper cylinder is then forced over into the burette by raising the mercury reservoir, the tap between the two cylinders being meanwhile closed, and, by repeating these operations several times, the whole of the carbon dioxide may be collected and its volume measured in the burette. Concentrated sulphuric acid is added after the sample has been introduced into the cylinder when it is desired to estimate the total (free and combined) carbon dioxide. W. P. S.

Laboratory Notes. [Estimation of Silica, Phosphorus in Iron, etc.]. ERNST MURMANN (*Österr. Chem. Zeit.*, 1921, **24**, 142).—In the estimation of silica, two evaporations with an intervening filtration are necessary in order to render the whole of the silica insoluble, care being taken that the evaporation is carried to complete dryness of the residue. To estimate phosphorus in iron, soil extracts, etc., the sample is evaporated with hydrochloric and nitric acid, and the residue heated in order to destroy any organic matter; by extracting the residue with nitric acid, the phosphoric acid is obtained in solution and it is not necessary to dissolve the ferric oxide resulting from the decomposition of the ferric nitrate during the heating. The grinding of ores is facilitated if the powder is moistened with ether, and graphitic carbon burns readily if it has been moistened previously with a small quantity of magnesium acetate solution. The use of chalk, mineral phos-

phate, or bone-ash is recommended in place of sand in sand-baths, since sand is liable to scratch glass vessels and cause them to break when heated. W. P. S.

Volumetric Estimation of Potassium. MACHELEIDT (*Woch. Brau.*, 1922, **39**, 23—24).—A standard solution of sodium hydrogen tartrate is prepared by dissolving 60 grams of tartaric acid and 16 grams of sodium hydroxide in water and diluting to 1 litre. Six grams of potassium hydrogen tartrate are added and the solution is shaken for several hours. Thirty c.c. are filtered off and titrated with *N*/10-barium hydroxide solution. A second 30 c.c. are shaken for one to two hours with 0.5—0.75 gram of the salt mixture to be tested, the solution is filtered into a tared basin and, without washing the filter, titrated with the barium hydroxide solution. The solution is weighed before and after filtering, and allowance is made for the loss. The difference between the two titrations is calculated to potassium oxide. [See further *J. Soc. Chem. Ind.*, 1922, 200.] A. R. P.

Estimation of the Calcium Content of Blood. R. WEISS (*Deut. med. Woch.*, 1921, **47**, 1298; from *Physiol. Abstr.*, 1922, **6**, 568).—A small measured quantity of serum is placed in a specially graduated tube, ammonium oxalate is added, and the precipitate washed on the centrifuge with water. It is dissolved in sulphuric acid and titrated with permanganate. The figures given are: Normal 12, in tetany as low as 4, in rickets as high as 18 mg. per 100 c.c. E. S.

Micro-estimation of Calcium in Whole Blood, Plasma, and Serum by Direct Precipitation. GUY W. CLARK (*J. Biol. Chem.*, 1921, **49**, 487—517).—The method described is practically identical with that of Halverson and Bergeim (*A.*, 1916, ii, 270). E. S.

Sensitiveness and Applicability of Qualitative Reactions.
III. Strontium Ions. O. LUTZ (*Z. anal. Chem.*, 1921, **60**, 433—441; cf. *A.*, 1921, ii, 596).—The minimum quantities of strontium which can be detected by various reagents are as follows: in each case, 5 c.c. of the strontium salt solution were treated with 0.5 c.c. of the reagent in the cold and the observation made after five minutes. Sodium phosphate, 1:9400; sodium sulphite, 1:12000; ammonium oxalate, 1:50000; ammonium carbonate and ammonia (at 100°), 1:210000; sulphuric acid, 1:125000. The addition of 5 c.c. of alcohol increases the sensitiveness of the sulphuric acid test to 1:140000. W. P. S.

Estimation of Magnesium in Technical Nickel. K. CHALUPNY and K. BREISCH (*Chem. Ztg.*, 1922, **46**, 91).—For the estimation of small quantities of magnesium in technical nickel 10—15 grams of the metal must be used, and the filtration and washing of the voluminous precipitate of nickel sulphide are very laborious and a frequent source of error. The advantage of a

method whereby the magnesium could be precipitated whilst the nickel remained in solution is apparent, and the non-precipitation of nickel phosphate from potassium nickelocyanide by sodium phosphate affords a means of attaining this object. The analysis is carried out as follows: 15–20 grams of the metal are dissolved in nitric acid, and the solution is twice evaporated to dryness with hydrochloric acid to precipitate silicic acid. To the filtered solution is then added 5–10 grams of ammonium chloride, followed by bromine water and ammonia to precipitate iron, manganese, etc. The filtrate is approximately neutralised with hydrochloric acid, and a concentrated solution of potassium cyanide is added until the precipitate of nickel cyanide is just redissolved, followed by 20 c.c. of 10% disodium hydrogen phosphate solution and a third of the volume of concentrated ammonia. After keeping overnight, the crystalline precipitate of magnesium ammonium phosphate is separated, and washed free from nickel. It is dissolved in dilute hydrochloric acid and reprecipitated with sodium phosphate and ammonia (this step is necessary on account of the large excess of alkali cyanide, present during the first precipitation, which causes somewhat too high results). The precipitate is collected in a Gooch crucible, ignited, and weighed as magnesium pyrophosphate in the usual way. G. F. M.

Estimation of Zinc as Zinc Pyrophosphate. D. BALAREFF (*Z. anal. Chem.*, 1921, 60, 442–448).—The precipitation of the zinc phosphate should be made under the following conditions. The slightly acid solution, containing ammonium chloride and ammonium phosphate is treated with ammonia until it is slightly alkaline in reaction towards litmus; the mixture is kept at the ordinary temperature for eighteen hours, then heated on a water-bath for fifteen minutes, and the precipitate is collected, ignited, and weighed. The amorphous precipitate which first forms when zinc is precipitated as phosphate from a solution containing ammonium salts is not zinc phosphate but ammonium zinc phosphate; if the zinc is precipitated by treating the hot solution with ammonia, ammonium zinc phosphate and zinc phosphate are precipitated together, and the results obtained are too low (cf. Austin, A., 1900, ii, 49, and Dakin, A., 1900, ii, 624). W. P. S.

The Separation of Aluminium from Glucinum. III. HUBERT T. S. BRITTON (*Analyst*, 1922, 47, 50–60; cf. A., 1921, ii, 657, 712).—Berzelius's method, consisting in boiling the precipitated hydroxides with ammonium chloride solution whereby the glucinum hydroxide is dissolved, is unsatisfactory, as no means could be found by which the occlusion of glucinum hydroxide by aluminium hydroxide could be eliminated, the results being accordingly low for glucinum and correspondingly high for aluminium. Wünder and Wenger's sodium carbonate fusion method (A., 1912, ii, 687) is satisfactory, but the time required for an analysis is long, as two fusions are necessary for a complete separation. The thiosulphate method in which the neutral salt solutions are boiled

with an excess of sodium thiosulphate until evolution of sulphur dioxide has ceased does not give quantitative separations owing to adsorption of glucina by the aluminium hydroxide which is precipitated. Haven's ether-hydrochloric acid method (A., 1898, ii, 142) is quantitative and is one of the most satisfactory and easily manipulated of all the methods investigated. Of the remaining methods, none were investigated, but it is probable that only Kling and Gelin's basic acetate distillation method (A., 1914, ii, 867) and Renz's ethylamine method (A., 1903, ii, 729) are quantitative, and as the former requires considerable manipulation and time, and the latter involves the use of a large quantity of an expensive reagent, they have no particular feature to recommend them. G. F. M.

Detection of Manganese with Benzidine and of Cobalt by means of the Thiocyanate Reaction. HUGO DITZ (*Chem. Ztg.*, 1922, 46, 121—122).—The author claims priority for the method described by Feigl and Stern (A., 1921, ii, 278) of detecting traces of manganese by the blue coloration produced on adding an acetic acid solution of benzidine to the peroxidised manganese compound formed by autoxidation in an alkaline medium. As little as 0.000008 gram of manganese can be detected by this method. No interference with the reaction by iron salts occurs provided a considerable excess of acetic acid is present, and it can therefore be used for the detection of manganese in iron ores and slags. Vogel's thiocyanate reaction for cobalt (*Ber.*, 1879, 12, 2314) is rendered more sensitive by using acetone instead of either amyl or ethyl alcohols, and quantities of the order of 0.003 mg. of the metal can be detected by this means. G. F. M.

Separation of Molybdenum and Tungsten by means of Selenium Oxychloride. HENRY BALDWIN MERRILL (*J. Amer. Chem. Soc.*, 1921, 43, 2383—2387).—Mixtures of molybdenum trioxide and tungsten trioxide may be quantitatively separated by boiling 1 gram of the mixture with 30 c.c. of a 1 : 1 mixture of selenium oxychloride and concentrated sulphuric acid for sixty minutes. The solution is decanted through a weighed Gooch crucible and the residue washed several times with small quantities of selenium oxychloride and finally brought on to the filter with a hot 10% solution of ammonium nitrate. The crucible is ignited and weighed, and gives the weight of tungsten trioxide, the molybdenum trioxide being obtained by difference. The above method, which is effective for mixtures made by mixing the two oxides by hand, does not work with mixtures of the two oxides precipitated together, if the amount of tungsten trioxide is greater than 10%. In such cases, it is impossible to dissolve all the molybdenum trioxide owing to the formation of solid solutions. This difficulty is overcome by dissolving the oxides in ammonia, adding sufficient nitric acid to precipitate most of the tungsten, evaporating to dryness, and proceeding as described above. The method gives good results. J. F. S.

Technical Estimation of the Colloidal Part of Tungsten Powder. A. LOTTERMOSER (*Kolloid Z.*, 1922, **30**, 53—61).—Two methods are described for the estimation of the percentage of colloidal tungsten in commercial tungsten powders. The methods are (1) a sedimentation method, and (2) an optical method, both of which lead to approximately the same results. Sedimentation method: the sample (20 grams) is shaken thoroughly with 100 c.c. of water in a tube and allowed to sediment for two days, 75 c.c. of the supernatant liquid are removed, and 75 c.c. of water added to the sediment. The mixture is shaken and allowed to sediment for a further two days. The process is repeated as long as a measurable quantity of tungsten remains in the supernatant liquid. The sediment is then dried and weighed and gives the non-colloidal portion. The addition of ammonia to the water shows that whilst most specimens of tungsten powder are very finely divided and give suspensions, some only are truly colloidal, inasmuch as they are peptised by ammonia. Optical method: this consists in estimating the quantity of tungsten in the solutions from which the powder has sedimented by means of its absorption of light. The light from a quartz mercury lamp is allowed to pass through the solution on to a potassium photo-electric cell and the absorption determined from the galvanometer deflection. In this connexion, it is shown that the de Beer-Fick law is applicable. Five specimens of tungsten powder have been examined and found to contain respectively 7.5%, 5.5%, 11.25%, 39.75%, and 7.0% of colloidal tungsten. The fourth and fifth samples are peptised by ammonia. J. F. S.

Separation of Columbium and Tantalum by means of Selenium Oxychloride. HARRY BALDWIN MERRILL (*J. Amer. Chem. Soc.*, 1921, **43**, 2378—2383).—A method of analysis of mixtures of tantalum and columbium oxides, and for the preparation of the pure oxides is described. The mixed oxides together with titanium oxide if such be present are separated together from the mineral, ignited, and weighed. A sample (0.2—0.3 gram) of the mixed ignited oxides is boiled in an Erlenmeyer flask with 50 c.c. of a 1 : 1 mixture of selenium oxychloride and concentrated sulphuric acid for thirty minutes on a sand-bath, care being taken that clouds of vapour are not evolved. The solution after cooling is decanted on to an asbestos pad in a Gooch crucible and filtered by suction. The filtrate is poured into a large volume of water and boiled, when hydrated columbium pentoxide is precipitated. The residue is boiled with 20 c.c. of the 1 : 1 mixture for fifteen minutes, decanted, and treated as before and the process repeated until the filtrate on hydrolysis gives only a faint cloudiness due to traces of tantalum pentoxide. The residue from the flask is now washed into the Gooch crucible and without much washing the crucible is ignited and weighed; the gain in weight gives the amount of tantalum pentoxide, whilst the loss of weight gives the columbium pentoxide, with titanium if this is present. The method gives results which have a maximum error of 3% and

is therefore better than the Marignac method whilst at the same time being more rapid.

To prepare pure columbium oxide, the mixed oxides are extracted with sufficient solvent to dissolve all the columbium, but it should not be boiled until all the columbium is dissolved, since this would mean the solution of much tantalum oxide. The dissolved oxide is precipitated with water and ammonia, filtered, and ignited. It still contains some tantalum oxide which by repeating the treatment can be removed and very pure columbium oxide obtained. Pure tantalum oxide is prepared by boiling the mixed oxides with the reagent until all the columbium oxide is dissolved; thus whilst sacrificing a little tantalum oxide, a very pure product is obtained. The complete removal of the columbium oxide is hastened by adding a little more sulphuric acid to the 1 : 1 mixture of selenium oxychloride and sulphuric acid.

J. F. S.

The Estimation of Small Quantities of Antimony in Copper and Brass. B. S. EVANS (*Analyst*, 1922, 47, 1—9).—Five grams of the sample are dissolved in 60 c.c. of nitric acid (*d* 1.2) and 10 c.c. of sulphuric acid and the solution evaporated until it fumes strongly. When cold, the mass is dissolved in 100 c.c. of water, 14 grams of sodium hypophosphite are added, and the solution is heated nearly to boiling whereby the copper is precipitated. The solution is filtered and the precipitate washed with hot water. A further 2 grams of sodium hypophosphite and 100 c.c. of hydrochloric acid are added to the filtrate and the liquid is boiled for fifteen minutes to precipitate any arsenic present. After cooling slightly, 10 c.c. of benzene are added to the filtrate and the liquid is well shaken so that the colloidal arsenic becomes suspended in the benzene layer. The liquid is filtered through a wet filter (to retain the benzene and arsenic) and the latter is washed twice with warm water. The filtrate is heated to boiling and a spiral roll of clean copper foil is dropped in and the boiling continued for one and a half to two hours; the liquid is then poured off, the copper washed rapidly with cold water, covered with water, and treated with 1 gram of sodium peroxide. The liquid is warmed until the deposited antimony has dissolved, then decanted off and the strip washed with cold water. The solution is treated with 0.5 gram of zinc sulphide and, after one and a half to two hours, filtered. The filtrate is acidified with hydrochloric acid, treated with sulphur dioxide, and evaporated to 10 c.c. Five c.c. of standard antimony solution (1 c.c.=0.0001 gram Sb), 80 c.c. of water, and a few drops of hydrochloric acid are treated with sulphur dioxide, and the solution is evaporated to 10 c.c. Both assay and standard solutions are treated with 5 c.c. of 1% gum arabic solution, diluted to 100 c.c., treated with hydrogen sulphide for a few seconds, and transferred to Nessler tubes. The liquid having the greater depth of colour is poured from the glass until the colours match; the depth of the two liquids is measured and the result calculated from these figures. The standard antimony solution is made by dissolving 0.2764 gram

of potassium antimonyl tartrate in 100 c.c. of hydrochloric acid and diluting to 1 litre. A. R. P.

I. Estimation of Methyl Alcohol in Remains for Forensic Purposes. II. Occurrence of Methyl Alcohol in the Human Body. H. JANSCH (*Vrtiljschr. ger. Med. öffentl. Sanitätsw.*, 1921, 62, 1—18; from *Chem. Zentr.*, 1921, iv, 983—984).—A weighed portion of the finely divided remains is acidified with tartaric acid and distilled in a current of steam. The distillate (500—1500 c.c.) is repeatedly redistilled, recovering about 60% each time, until a distillate of 5 to 10 c.c. is obtained. Fatty acids are removed by filtration. The later distillations are carried out with alkaline reaction. Acetaldehyde and glycerol which may be present are suitably oxidised. The density and refractive index of the end distillate are determined; from these the amount of methyl alcohol present is calculated, using appropriate tables. For the detection of methyl alcohol, the iodoform, benzoyl chloride, and morphine-sulphuric acid tests are used. Methyl alcohol is a normal constituent of human fæces and urine with mixed diets. It originates probably from pectins in the food. G. W. R.

Apparatus for the Estimation of Methoxyl Groups. WILLIAM M. CUMMING (*J. Soc. Chem. Ind.*, 1922, 41, 20r).—An improved form of apparatus for the estimation of methoxyl groups by Hewitt and Jones's modification of the Zeisel method in which the methyl iodide is absorbed in pyridine, consists of a round-bottomed flask of 250 c.c. capacity with a neck 10 inches long to which a delivery tube is attached by a ground glass joint. A thermometer is provided with its bulb opposite the delivery exit, and a carbon dioxide inlet tube. The delivery tube leads to a narrow bored U-tube, one arm of which contains four convolutions, and each convolution a bulb. This absorber holds about 10—15 c.c. of pyridine, and by passing a very slow current of carbon dioxide the whole of the methyl iodide is carried out of the flask and completely absorbed. The thermometer should not register more than 40° (cf. T., 1919, 115, 1030). G. F. M.

A Method for the Estimation of Trimethylene Glycol in Crude Glycerol. L. V. COCKS and A. H. SALWAY (*J. Soc. Chem. Ind.*, 1922, 41, 17—20r).—The method previously described (*ibid.*, 1918, i, 123, 158r) consisting in the distillation of the crude glycerol and the determination of the specific gravity and acetin value of the distillate, from which figures the trimethylene glycol content was calculated from the known specific gravity and acetin values of the pure substances, gives only approximate results, as no allowance is made for alterations in volume when glycerol, water, and trimethylene glycol are mixed. The specific gravity of a series of mixtures containing known proportions of these three substances has now been systematically determined, and tables and curves have been constructed by means of which the trimethylene glycol content of any glycerol distillate of known gravity and apparent

glycerol content can be deduced. The pure trimethylene glycol prepared for the purpose boiled at 210—211°/760 mm., or 171°/174 mm.; $d_{20}^{20}=1.0554$. The reduction in specific gravity with increasing trimethylene glycol content was fairly regular, and as a simple method for calculating the amount present, apart from reference to the curves, all that is necessary is to divide by the given factor the difference between the observed sp. gr. and the sp. gr. of pure glycerol of the strength indicated by the acetin figure of the mixture. The factor in question increases regularly with the acetin value from 0.00134 per 1% trimethylene glycol for 50% acetin to 0.00179 for 95% acetin value. An accuracy of ± 0.2 is claimed.

G. F. M.

Test for Sucrose in the Presence of Dextrose. LEON A. CONGDON and CHARLES R. STEWART (*J. Ind. Eng. Chem.*, 1921, **13**, 1143—1144).—When a dry mixture of sucrose and dextrose is extracted with hot ethyl acetate, the dextrose dissolves and the sucrose remains insoluble; on cooling the ethyl acetate solution, crystals of dextrose are obtained.

W. P. S.

Clarification of Urines by Zinc Ferrocyanide. C. CARREZ (*Ann. Chim. Analyt.*, 1922, [vi], **4**, 11—12).—Polemical. The author points out that his method involving the use of potassium ferrocyanide and an excess of zinc acetate (A., 1908, ii, 329) was never intended as a preliminary step for any estimation other than that of glucose in the urine, and Thiéry's criticism (A., 1921, ii, 527) therefore has no point.

G. F. M.

Colour Reaction of Sucrose. FERDINAND KRYZ (*Österr. Chem. Ztg.*, 1921, **24**, 141—142).—When a mixture of 1 c.c. of saturated ammonium nickel sulphate solution, 1 c.c. of sucrose solution, and a few drops of sulphuric acid or hydrochloric acid is boiled, the green colour of the mixture changes to yellow and then to red; this red coloration persists even when the mixture is cooled. The reaction cannot be obtained with less than 0.005 gram of sucrose, but other sugars do not interfere. The coloration is not obtained when nitric acid is used in place of the sulphuric acid or hydrochloric acid.

W. P. S.

Re-testing the 100°-point of the Saccharimeter. II. Preparation of Chemically Pure Sucrose. ANTON KRAISY (*Z. Ver. deut. Zuckerind.*, 1921, 785—797).—A method of procedure for recrystallising refined sugar from alcohol for the preparation of pure sucrose for purposes of standardisation is described. The product obtained after several successive crystallisations is considered to be free from invert-sugar. Such a product yielded 0.002—0.005% of ash, and reduced 36—38 mg. of copper under the well-known Herzfeld conditions for estimating invert-sugar in sucrose, and 1.5—1.8 mg. under the conditions of the method recently proposed by the author (*ibid.*, 123). [See also *J. Soc. Chem. Ind.*, 1922, 151A.]

J. H. L.

Detection of Formic Acid in Wine. W. FRESSENIUS and L. GRÜNHUT (*Z. anal. Chem.*, 1921, 60, 457—463).—The wine is acidified with sulphuric acid and extracted with ether; the ethereal extract is then shaken with dilute sodium hydroxide solution, the alkaline aqueous solution is separated, evaporated to dryness, and the residue heated at 130° for one hour to remove any traces of formaldehyde. The residue is dissolved in 10 c.c. of water and the solution treated with 5 c.c. of hydrochloric acid (d 1.12) and 0.4 gram of magnesium turnings. After two hours, the mixture is distilled, 5 c.c. of distillate being collected; this distillate is boiled for one minute with the addition of 2 c.c. of milk and 7 c.c. of hydrochloric acid (d 1.12) containing a trace of ferric chloride. If the wine contained formic acid or its salts, a violet coloration develops in the mixture. W. P. S.

Apparatus for Measuring the Hydrogen-ion Concentration of a Solution. Application to the Detection of Mineral Acids in Vinegar. ANDRÉ KLING, A. LASSIEUR, and (MME) A. LASSIEUR (*Compt. rend.*, 1922, 174, 165—168).—A compensation electro-metric method for measuring hydrogen-ion concentration is described in which a millivoltmeter capable of measuring 1200 millivolts with an accuracy of 1 millivolt is used. The hydrogen-ion concentration of vinegar measured with this apparatus or by the colorimetric method, using thymolsulphonphthalein as indicator, serves as a ready means of detecting the presence of mineral acids. The presence of 0.24% of sulphuric acid in vinegar alters the p_H value at 18° from 2.67 to 1.96. W. G.

Estimation of β -Hydroxybutyric Acid. Estimation of Acetone Substances in the Urine. Estimation of Acetone Substances in the Blood. ROGER S. HUBBARD (*J. Biol. Chem.*, 1921, 49, 351—357, 357—374, 375—384).—A modification of Shaffer's method (A., 1914, ii, 77; 1916, ii, 352) for the estimation of β -hydroxybutyric acid is described, in which the time required for the oxidation is reduced to half an hour. The method is applied to urine after removal of interfering substances by precipitation with basic lead acetate, copper sulphate, and sodium hydroxide. The estimation of acetone plus acetoacetic acid in urine is made more accurate by adding to the technique of Shaffer a distillation from acid potassium permanganate solution. The same method is applied to blood after treatment of the latter with colloidal iron, basic lead acetate, and sodium hydroxide.

It is found that in normal urine the total acetone averages about 2 mg. per 100 c.c., the greater part representing β -hydroxybutyric acid; in blood, the total acetone varies normally between 0.1 and 1.0 mg. per 100 c.c. C. R. H.

Effect of the Presence of Filter-paper on Permanganate-Oxalate Titrations. STEPHEN G. SIMPSON (*J. Ind. Eng. Chem.*, 1921, 13, 1152—1154).—Filter-paper reduces permanganate rapidly, especially when the paper is highly disintegrated. In the titration of calcium oxalate precipitates with permanganate solution, the

precipitate should be washed off the filter-paper with hot water and the paper added only when the titration is nearly complete.

W. P. S.

The Estimation of *H*-Acid. HENRY R. LEE (*J. Ind. Eng. Chem.*, 1921, **13**, 1049—1051).—The choice of a diazonium salt for use as a standard solution for the estimation of the hydroxyl group should depend on the stability of the salt in the solution in which it is prepared and in which it is to be used, the completeness of the coupling with the intermediate product in question, and the rate of coupling. Comparative experiments in which *H*-acid was titrated with benzenediazonium chloride and with *p*-toluenediazonium chloride respectively show that the rate of decomposition of diazobenzene is approximately eight times as rapid in acid solution, and one and a half times as rapid in alkaline solution, as that of *p*-diazotoluene. Moreover, the rate of coupling of *p*-diazotoluene is slightly more rapid than that of diazobenzene, whilst the secondary coupling, which is marked in the case of commercial samples of *H*-acid titrated with diazobenzene, is very slight when coupled with diazotoluene, and consequently, in the latter case, the end-point is more definite. The use of *p*-diazotoluene in the estimation of *H*-acid, γ -acid, *J*-acid, *S*-acid, and other naphthol- and aminonaphthol-sulphonic acids is recommended. A stock solution of *p*-toluidine hydrochloride is prepared by dissolving 10.7082 grams of pure *p*-toluidine in 40 c.c. of pure concentrated hydrochloric acid, and diluting with water to 1 litre. One hundred c.c. of this solution are placed in a 250 c.c. graduated flask, cooled in ice and salt until frozen, and diazotised with 102 c.c. of *N*/10-sodium nitrite solution. After thirty to forty minutes, this is made up to 250 c.c. with water, and shaken well. This solution should be kept at 0° and protected from light. In carrying out the estimation, 5 grams of dry *H*-acid or 10 grams of press-cake are dissolved in 400 c.c. of water and sufficient sodium hydrogen carbonate to produce a clear solution, and made up to 500 c.c. with water. Twenty-five c.c. of this solution are placed in a 600 c.c. beaker, 200 c.c. of ice-water added, and 2 grams of sodium hydrogen carbonate. This solution is cooled in ice and the diazonium solution is added from a burette, jacketed with ice-water, with good agitation. When the titration is almost finished, about 2 grams of sodium carbonate are added to increase the rate of coupling, and 10—15 grams of salt are added near the end-point. The titration is continued to the point when a spot on filter-paper gives a faint purple ring when spotted with *H*-acid solution. The titration is complete if this purple colour develops again when tested after the solution has been left for five minutes. F. M. R.

Chlorohydrocarbons and Carbon Chlorides. II. The Knowledge of the Saturation Character of the Di-, Tri-, and Tetra-chloroethylenes. B. M. MARGOSCHES and RICHARD BARU (*J. pr. Chem.*, 1921, [ii], **103**, 216—226).—The iodine numbers of $\alpha\alpha$ - and $\alpha\beta$ -dichloroethylene, trichloroethylene, and tetrachloroethylene are practically zero as determined by the Hübl, Wijs, or other "iodine solution" in which the active agent is iodine

monochloride, and therefore these solvents can be used safely as solvents for fats in the determination of their iodine number. This is in accordance with previous work on the influence of chlorine on the degree of unsaturation of a double bond.

W. O. K.

Detection of Coconut Oil in Butter. C. F. MUTTELET (*Compt. rend.*, 1922, **174**, 220—223).—The method is based on the fact that pure butter contains cholesterol but not phytosterol, whilst the vegetable fat contains phytosterol, and the melting points of the acetates of these two sterols differ. The sterols in the butter are precipitated by the addition of 20 c.c. of a 1% alcoholic solution of digitonin to the fatty acids from 50 grams of the butter. The precipitate is collected and washed free from fatty acids by chloroform and ether, and then boiled with 2—4 c.c. of acetic anhydride. The acetate is twice crystallised from alcohol and its melting point determined. The acetate from pure butter has m. p. 113.6—114.2°. With 10% of coconut oil present in the butter the resulting acetate has m. p. 114.5° and the m. p. increases as the percentage of coconut oil in the butter increases.

W. G.

A Simple and Exact Method for the Direct Estimation of Acetaldehyde in the Presence of Acetone. WILHELM STEPP and ROBERT FRICKE (*Z. physiol. Chem.*, 1921, **116**, 293—301).—To estimate the acetaldehyde, the solution is treated with an excess of alkaline-ammoniacal silver of known strength, the reduced silver is filtered off, and the unreduced silver is titrated in the acidified filtrate with *N*/10-ammonium thiocyanate, using ammonium iron alum as indicator. An accuracy of 0.1 mg. can be obtained. In order to estimate the acetone, the acetaldehyde is removed by boiling with silver oxide or with Fehling's solution, the residual liquid is distilled, and the acetone estimated in the distillate by the Messinger-Huppert method. If acetaldehyde has to be estimated at the same time, a known suspension of silver oxide is used and the residual silver oxide is dissolved in ammonia and estimated volumetrically.

S. S. Z.

Spectrochemical Reaction of Methylfurfuraldehyde and Hydroxymethylfurfuraldehyde Phloroglucides. TETSUTARO TADOKORO (*J. Coll. Agric. Hokkaido Imp. Univ.*, 1921, **10**, 52—56; cf. Oshima and Tadokoro, *A.*, 1918, ii, 255).—The difference in the colour reactions of methylfurfuraldehyde and hydroxymethylfurfuraldehyde as phloroglucides was observed by means of the ultra-violet spectroscope. The colour reaction when the two aldehydes are allowed to react with phloroglucin and hydrochloric acid changes with the time and is complete in five minutes. At a half to two minutes after the beginning of the reaction, the two phloroglucides give almost the same absorption band in the visible spectrum ($\lambda\lambda$ 4200—5000 and $\lambda\lambda$ 4100—5000), but the methylfurfuraldehyde phloroglucide shows an absorption band in the ultra-violet at $\lambda\lambda$ 2400—3800. Five minutes after the beginning of the reaction, methylfurfuraldehyde phloroglucide gives an

absorption at $\lambda\lambda$ 4300—4800, whilst hydroxyfurfuraldehyde phloroglucide shows an absorption band at $\lambda\lambda$ 5000—5500. G. W. R.

A Supposed Method for the Quantitative Separation of "Saccharin" from *p*-Sulphaminobenzoic Acid. WALTHER HERZOG and J. KREIDL (*Österr. Chem. Ztg.*, 1921, **24**, 165—166).—A method for the estimation of *p*-sulphaminobenzoic acid in commercial "saccharin" has been described by O. Beyer ("Kontrolle und Herstellung von Saccharin," p. 97), which consists in dissolving the material in a slight excess of ammonia, adding a 50% excess of acetic acid, and keeping for twelve hours. The para-acid is said to be completely precipitated under these conditions, whilst the more strongly acidic "saccharin" remains in solution as undecomposed ammonium salt. Experimental investigation of the method with known mixtures of the two pure substances showed, however, that the results were inaccurate to the extent of 2—3%. For example, in mixtures containing 5 and 25% respectively of para-acid, only 3.33 and 23.11% were found. G. F. M.

Apparatus for Use in Titrating Intermediates with Unstable Diazo-solutions. C. P. ATKINSON (*J. Soc. Dyers and Col.*, 1922, **38**, 15—16).—The apparatus is intended for the estimation of intermediates for azo-dyestuff manufacture by titration with standard diazonium solutions.

An iron tripod about thirty inches high supports a circular tin trough containing a supply of ice-water, and inside the trough is a circular glass vessel, with an outlet through the centre of the trough, to contain the supply of diazonium solution. The burette, jacketed with the outer tube of a condenser through which the ice-water flows, is supported by a triangle attached to the three legs of the tripod. In one of the three legs of this support a funnel holder is fitted to receive the waste water as it flows from the jacket and conduct it to the sink. F. M. R.

Mercury or Water Ureometer for the Estimation of Urea in Urine or in Blood. RENÉ CLOGNE (*J. Pharm. Chim.*, 1922, vii, **25**, 99—100).—The method of graduation in the usual form of ureometer is modified so that the graduated tube immediately below the inlet tap is very narrow and is marked in twentieths of a c.c. as far as the 2 c.c. graduation, and then in fifths as far as the 25 c.c. graduation. This has the advantage of enabling the same apparatus to be utilised for estimating the small amount of urea usually present in blood, as, if the same quantity is taken as of urine for an estimation, namely, 2 c.c., the reading of the volume of liberated gas will fall within the range of the 0.05 c.c. graduations, and an amount as small as 2.5 grams per litre can be accurately estimated. G. F. M.

Silicotungstic Acid Applied to the Estimation of Caffeine. A. AZADIAN (*Bull. Soc. chim. Belg.*, 1922, **31**, 15—18).—Silicotungstic acid gives with caffeine, in the presence of 5% hydrochloric acid, a precipitate having the composition

$$12\text{WO}_3, \text{SiO}_2, 2\text{H}_2\text{O}, 3\text{C}_8\text{H}_{10}\text{O}_2\text{N}_4, 6\text{H}_2\text{O}.$$

On ignition, it leaves a residue having the composition $12\text{WO}_3 \cdot \text{SiO}_2$ and the factor for converting the weight of this residue into weight of caffeine is 0.2646. For the estimation, a known volume of an extract containing caffeine is evaporated to a syrup, which is extracted with hot water, the extract being made up to 50 c.c. Sufficient hydrochloric acid is added to bring the acid concentration up to 5% and then a solution of silicotungstic acid is added. The mixture is boiled and then left for twenty-four hours; the precipitate is collected, dried, ignited, and weighed. W. G.

New Method for the Detection of Thymine. OSKAR BAUDISCH and TREAT B. JOHNSON (*Ber.*, 1922, **55**, [B], 18—21).—The method depends on the conversion of thymine into carbamide, acetylcarbinol, and pyruvic acid, the latter being identified as indigotin. Preliminary experiments show that the action is not influenced by the presence of uracil, cytosine, or sugar.

A solution of sodium hydrogen carbonate in water is treated successively with aqueous solutions of thymine and ferrous sulphate; the mixture is well-shaken with air, which causes the gradual conversion of the white, ferrous hydrogen carbonate into ferric hydroxide. The latter is removed and the filtrate concentrated on the water-bath, when the original odourless solution which does not reduce Fehling's solution acquires a characteristic odour and strong reducing properties, probably owing to a Cannizzarro reaction resulting in the formation of acetylcarbinol and pyruvic acid. The presence of the former is conveniently established by distillation of the liquid and treatment of the distillate with *o*-aminobenzaldehyde; the solution is boiled until the odour of the latter disappears, cooled, acidified with hydrochloric acid, and made alkaline again with sodium hydrogen carbonate. The presence of 3-hydroxy-2-methylquinoline is shown by the blue fluorescence of the solution; the reaction is unusually sensitive. The residue from the distillation contains pyruvic acid, the presence of which is detected by the formation of indigotin after addition of *o*-nitrobenzaldehyde and sodium hydroxide. The dye is extracted with chloroform. The presence of 2—5 mg. of thymine is established readily by the formation of the blue chloroform solution.

H. W.

Application of Folin and Denis's Phosphotungstic Reaction to the Estimation of Uric Acid in Urine. THIÉRY (*J. Pharm. Chim.*, 1922, [vii], **25**, 87—92).—All the methods for the estimation of uric acid in urine hitherto proposed have the disadvantage of requiring at least 100 c.c. of urine for each estimation. The author considers that the direct application of Folin's phosphotungstic reagent to urine without any preliminary treatment gives results sufficiently accurate for all ordinary purposes, at least in such cases where the volume of urine at disposal is small. The reagents required are Folin's reagent, a solution containing 120 grams of anhydrous sodium carbonate per litre, and a standard solution of uric acid containing 0.2 part per 1000, prepared by means of mono- and di-sodium phosphate. Into a 100 c.c. graduated tube 1 c.c.

of urine and 2 c.c. of the phosphotungstic reagent are introduced, and into a further series of tubes 1, 2, 3, 4, etc., c.c. of standard uric acid solution are placed, each with 2 c.c. of the reagent. The contents of all the tubes are made up to 40 c.c. with the sodium carbonate solution and, after keeping fifteen minutes, when the blue colour has reached its maximum intensity, the volume is made up to 100 c.c. with distilled water, and the uric acid is estimated colorimetrically by comparison with the standard colours in a Duboscq colorimeter. The results furnished by this method are very close to those given by the present author's volumetric silver method after treatment of the urine with potassium zinc ferrocyanide (A., 1921, ii, 527).
G. F. M.

The Estimation of Purine Bases in Urine. H. STEUDEL and SUNG-SHENG CHOU (*Z. physiol. Chem.*, 1921, **116**, 223—225).—It is suggested that the filtrate from the second copper sulphate precipitation obtained in Krüger's method for the estimation of the purine bases in urine should after its decomposition with hydrogen sulphide be boiled with magnesium oxide in order to eliminate all traces of ammonia the nitrogen of which might otherwise be ascribed to the purine bases.
S. S. Z.

Electrometric Titration of Azo-dyestuffs. D. O. JONES and H. R. LEE (*J. Ind. Eng. Chem.*, 1922, **14**, 46—48).—The difficulties encountered in the analysis of azo-dyestuffs with titanous chloride by previous methods are enumerated, and an analytical procedure is described whereby the electrometric method of following oxidimetric reactions (cf. A., 1919, ii, 471, 480) is used in conjunction with titanous chloride for the analysis of azo-dyestuffs and nitro-compounds.

A sample of the finely powdered dye (0.5—1.0 gram), sufficient to require 30—45 c.c. of $N/4$ -titanous chloride for reduction, is placed in a reaction flask with 25 c.c. of distilled water, and heated on a steam-bath for ten minutes to dissolve or soften the particles. Twenty-five c.c. of 40% sulphuric acid are added, the flask is stoppered, and a current of carbon dioxide is passed through for five minutes; 35—50 c.c. of titanous chloride, being at least 5 c.c. of $N/4$ -titanous chloride in excess of that required for reduction, are added, the mixture is boiled for five minutes, and cooled to 30°. In the back titration, the potentiometer is adjusted, and the voltages read for each addition of $N/20$ -ferric alum solution. The latter is added in 5 c.c. portions at first, gradually decreasing to 0.1 c.c. or less. When passing over the end-point, the poles are reversed in the usual manner, and the voltages read as the additions of ferric alum become larger. Volts are plotted as ordinates and c.c. of ferric alum solution as abscissæ, and the end-point is determined from the curve. For routine analysis, almost all azo-dyestuffs can be analysed with sufficient accuracy without reading the voltmeter or plotting a curve. The potentiometer is adjusted at the beginning of the back titration, until, on closing the circuit, the galvanometer shows no deflection. A permanent large swing of the galvanometer is obtained at the end-point.
F. M. R.

Estimation of the Percentage of Fibrin in Blood and Plasma.

H. C. GRAM (*J. Biol. Chem.*, 1921, **49**, 279—295).—Citratd plasma is recalcified and heated at 35° for one and a half hours; the clot is then washed and dried, treated with alcohol and ether to remove lipoids, and weighed. The whole estimation, including the platelet count and the cell volume, is performed on 4.5 c.c. of blood.

E. S.

Chemical Blood Analysis. III. The Importance of the Ultra-filtration Method for the Analysis of Blood. M. RICHTER-QUITTNER (*Biochem. Z.*, 1921, **124**, 106—113).—Examples are given of the use of the Zsigmondy-Haen ultra-filtration apparatus for the estimation in blood of residual nitrogen, uric acid, chloride, sodium, free potassium, and calcium. The residual nitrogen, the uric acid, the chloride, and sodium are completely dialysable, but only a portion of the potassium, calcium, or dextrose is free and dialysable.

H. K.

Colorimetric Estimation of the Concentration of Hydrogen Ions in Very Small Quantities of Blood by Dialysis. J. LINDHARD (*Compt. rend. Trav. Lab. Carlsberg*, 1921, **14**, No. 13, pp. 13).—A modification of the method of Dale and Evans (*A.*, 1921, i, 142), in which the required quantity of blood is reduced to three drops, so that the process can be applied repeatedly by finger pricks. Hirudin is used, and phenolsulphonephthalein as indicator. The dialysate is not titrated but compared with a colour scale of phosphate-indicator mixtures. The error for the dialysis of phosphate mixtures compared with a separate scale is about P_H 0.02, but compared with the original mixture the P_H agrees in the second place of decimals. Bicarbonate solutions gave by the electrometric method a P_H 0.2 to 0.3 higher than by the colorimetric, but this discrepancy the author attributes to loss of carbon dioxide in dialysis and inapplicability of the electrometric control (cf., however, Evans, *A.*, 1921, i, 904).

G. B.

Preparation of Colloidal Gold Solution for Testing Spinal Fluid. A. O. GETTLER and J. W. JACKSON (*Arch. Neurol. Psychiatry*, 1921, **6**, 70—71).—To one litre of water (distilled in copper vessels from potassium permanganate) are added in turn 10 c.c. of 1% auric chloride solution, 7 c.c. of 2% potassium carbonate solution, and 0.5 c.c. of 1% oxalic acid solution. The liquid is heated until it boils, then removed from the flame and vigorously shaken, 0.2 to 0.3 c.c. of concentrated formaldehyde solution being simultaneously added, and the shaking continued for one minute; after three or four minutes, the colour usually commences to develop. If it does not do so, an additional 0.1 to 0.2 c.c. of formaldehyde solution is added, with agitation during and after the addition. A deep red colour should rapidly develop. CHEMICAL ABSTRACTS.

General and Physical Chemistry.

Relation between Atomic Volumes [of Elements in Combination] and Optical Refractivities. GERVAISE LE BAS (*Nature*, 1921, **108**, 272—274).—A periodic relationship is known to exist between the atomic volumes of elements in combination, the differences between the atomic volumes of successive members of the same series being of the order of that of hydrogen. Similar serial and group relations are observed with the atomic refractivities, the serial differences again being of the order of the atomic refractivity of hydrogen. When the atomic volumes of carbon, nitrogen, oxygen, fluorine, silicon, phosphorus, sulphur, chlorine, arsenic, selenium, bromine, and iodine are plotted against their atomic refractivities, the points obtained lie approximately on a straight line. A. A. E.

Molecular Refraction of some Molten Salts and their Degree of Dissociation. G. MEYER and HECK (*Z. Elektrochem.*, 1922, **28**, 21—23).—The molecular refraction of molten sodium hydroxide and nitrate and potassium hydroxide and nitrate has been measured at a series of temperatures between 320° and 440°. The method adopted was to allow a ray of light (sodium) to fall into a prism of the molten substance and be reflected from a metallic mirror inside the prism. The densities of the molten salts were determined for all the temperatures used. The mean molecular refraction over the whole temperature range is found to be : sodium nitrate 11·54, potassium nitrate 14·09, sodium hydroxide 5·37, and potassium hydroxide 7·71. These values, which are accurate to one unit in the second decimal place, the refractive index being accurate to one unit in the third decimal place, are in good agreement with the values calculated from the atomic refractions. Using the values 2·80 and 2·59, respectively, for the atomic refractions of the sodium atom and the sodium ion, it is calculated that molten sodium nitrate is dissociated to 61·7%. The influence of temperature on the molecular refraction of all the substances examined is very small. J. F. S.

Some Problems of the Mass Spectrograph. F. W. ASTON and R. H. FOWLER (*Phil. Mag.*, 1922, [vi], **43**, 514—528).—A mathematical discussion of some points raised by the performance and further design of the mass spectrograph. J. R. P.

The Broadening of Spectral Lines. J. FRANCK (*Festschrift Kaiser Wilh. Ges. Ford. Wiss. Zehnjährigen Jubiläum*, 1921, 77—81).—A summary of the manner in which the broadening of spectral lines has been explained, or is capable of explanation, both by classical methods and in terms of the quantum theory. Radiation damping has been fairly adequately explained on the quantum
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theory by Stern and Volmer; the Döppler effect may be explained by the influence of radiation pressure, whilst collision damping is considered to be due to the electron transitions produced by a collision, together with a sudden warping of the electron orbits.

CHEMICAL ABSTRACTS.

Intensity and Broadening of Spectrum Lines. CHR. FÜCHTBAUER and G. JOOS (*Physikal. Z.*, 1922, **23**, 73—80).—The form of a spectrum line broadened by another gas depends on the latter, not on the absorbing gas. The constant representing the broadening is, with hydrogen and nitrogen, proportional to the density. In the first pair of the principal series of cæsium, the number representing the dispersing electrons on the classical theory is equal to the number of cæsium atoms. For the mercury line 2537, the number of resonators is one forty-fifth of the number of atoms. The maximum of 2537 is less displaced towards the red by hydrogen than by carbon dioxide and nitrogen.

J. R. P.

Excitation Stages in Open Arc-light Spectra. I. Sodium, Potassium, Calcium, Strontium, Barium, and Magnesium. II. Silver, Bismuth, Cadmium, Zinc, Air, and Copper. B. E. MOORE (*Astrophys. J.*, 1921, **54**, 191—216, 246—272).—An investigation of the variation of the spectrum with current, using a potential of 2000 volts and currents of 0.02 to 1 ampere, distinguishes between five stages of excitation; the features of each are described, and a number of intensity-current curves are given. The relation of the results to previous work, including the Bohr theory, is briefly discussed.

A. A. E.

Influence of the Pressure of Foreign Gases on the D-Lines in Saturated Sodium Vapour. R. MINKOWSKI (*Physikal. Z.*, 1922, **23**, 69—73).—Measurements of the magnetic rotation of the D-lines of sodium vapour in presence of nitrogen under various pressures showed that the constant representing, on the classical theory, the number of dispersion electrons in unit volume is affected by pressure. The difference in the values of this constant determined by absorption measurements and extrapolated from the magnetic rotations is largely, perhaps entirely, to be ascribed to the influence of pressure. The broadening of the lines under the influence of pressure is largely confined to the side near the red. The method may be used in the determination of small partial pressures of monatomic vapours in mixtures.

J. R. P.

The Production of Enhanced Line Spectra. R. A. SAWYER and A. L. BECKER (*Science*, 1921, **54**, 305—306).—When calcium wires are exploded by the Anderson method (*Astrophys. J.*, 1920, **51**, 37), it is found that, as the size of the wires employed is decreased, the energy of the stimulus remaining the same, the intensity of the enhanced lines is increased, indicating a more complete ionisation of the calcium atoms. A fine asbestos fibre about 3 cm. in length was therefore saturated with an aqueous

solution of a calcium salt, and the charge of the high-tension condensers thrown across it. The fibre remained uninjured, and the calcium spectrum thus produced showed a striking enhancement of the spark lines of calcium over the arc lines, indicating that a large proportion of the emitting atoms were ionised. A table giving the relative intensities, under various conditions, of prominent spark- and arc-lines of calcium shows that the new source of light, provisionally called the "super-spark," yields a degree of ionisation comparable with, or perhaps in excess of, that existing in the high chromosphere of the sun and in the early (or hot) type *B* stars. Very minute amounts of material suffice for the production of intense spectra by this method, and practically only metallic lines are produced; the spectra of hydrogen, oxygen, or of the acid radicle of the salt used do not appear, and only the strongest air lines could be observed.

A. A. E.

The Evolution of the Spectrum of Magnesium under the Influence of Increasing Electric Fields. Applications to Astrophysics. A. DE GRAMONT and G. A. HEMSALECH (*Compt. rend.*, 1922, 174, 356—361).—In a discussion of previous work (A., 1921, ii, 611), it is shown that the spectral effects of intense electric fields are particularly marked in the initial stage of a luminous phenomenon (arc or spark) when the temperature and the electrical conductivity of the vapours are not very high. As the temperature increases, the emission, which depends on rapid falls in potential, diminishes or disappears. In consequence, the authors consider it dangerous to conclude that a star has a high temperature because the spark rays predominate in its spectrum.

W. G.

The Lines K_α of the Light Elements. V. DOLEJSEK (*Compt. rend.*, 1922, 174, 441—443).—The author has again measured the K_α lines of the elements from zinc to chlorine. He has found for these elements the lines α_3 and α_4 which Hjalmar had measured for the elements sulphur to sodium. They are inseparable above scandium. The line α_7 , according to Siegbahn's notation, was also found for the elements calcium to chlorine. In addition, a new satellite of α_1 of shorter wave-length has been found. It appears to be an emission band, and is denoted by α_1' . The line α_3 found by Duane and Stenström for tungsten could not be observed.

W. G.

The Complexity of the *K* Series of the Light Elements and its Theoretical Interpretation. A. DAUVILLIER (*Compt. rend.*, 1922, 174, 443—445).—Ten components of the *K* series for copper have previously been reported. Their wave-lengths are now recorded. Working under the same conditions (cf. A., 1921, ii, 669), the *K* series of molybdenum has been studied without observing any rays other than those found by Duane. The line α_3 found by Duane for tungsten does not exist either for copper or molybdenum. An attempt is made to show the relationship

between the author's measurements of the rays α_7 , α_3 , and α_4 of copper and those of Hjalmar for the elements calcium to sodium.

W. G.

Wave-lengths Longer than 5500 Å. in the Arc Spectra of Yttrium, Lanthanum, and Cerium, and the Preparation of Pure Rare Earth Elements. C. C. KIESS, B. S. HOPKINS, and H. C. KREMERS (*U.S. Bureau of Standards, Sci. Papers*, 1921, No. 421, 318—351).—Photographic determinations were made in the yellow, red, and infra-red regions of the arc spectra, as follows: yttrium, 170 lines to 7881.868 Å., lanthanum, 410 lines to 9078.99 Å., cerium, 1700 lines to 9024.68 Å. A description is given of the methods used in the purification of the substances employed, compounds of cerium, samarium, lanthanum, neodymium, and gadolinium being obtained from a sample of "Welsbach" sodium rare-earth sulphate, and those of yttrium, dysprosium, and erbium from gadolinite and xenotime. The cerium was removed from the "Welsbach" residues by precipitation with potassium bromate as basic ceric bromate; the other elements were then separated by way of the fractional crystallisation of the double magnesium nitrate. The yttrium-group material was freed from the elements of the cerium group, and then fractionally crystallised as bromate.

CHEMICAL ABSTRACTS.

The L Series of the X-Ray Spectrum. D. COSTER (*Compt. rend.*, 1922, 174, 378—379).—The author has again measured the spectra of a large number of elements (tantalum to rubidium), and in general the new results confirm the conclusions of previous work and in addition lend support to Bohr's theory of the structure of the atom (cf. this vol., ii, 277). Certain of the author's results are more or less opposed to the results and conclusions of Dauvillier (cf. A., 1921, ii, 421, 475, 699) and these divergences are summarised.

W. G.

The Infra-red Absorption Spectra of Alkali Hydroxides. G. E. GRANTHAM (*Physical Rev.*, 1921, 18, 340; cf. Howe and Gibson, *ibid.*, 1917, 10, 767).—When the absorption of solutions of sodium, potassium, and lithium hydroxides (of various concentrations) and of ammonium and caesium hydroxides (one solution each) was determined with reference to that of water, all the curves showed a broad, intense absorption band with a maximum at about 2.29μ , except in the case of the ammonium hydroxide solution, for which the maximum was found to be at 2.20μ . The absorption was found to be proportional to the concentration, but not to vary systematically with the atomic weight of the metal used. It is suggested that the band is due to dissociated hydroxide ions, although in the case of other hydroxide solutions such a band has not previously been observed. Maximum absorption of water was observed at 1.48 and 1.98μ . The effect of dissolving an alkali hydroxide is to decrease the absorption of the water in the band at 1.48μ by an amount proportional to the concentration of the solution and to the atomic weight of the metal of the base.

A. A. E.

The Ultra-violet Absorption Spectra and the Optical Rotation of the Proteins of Blood Sera. S. JUDD LEWIS (*Proc. Roy. Soc.*, 1922, [B], 93, 178—194; cf. A., 1917, ii, 62).—Eleven sera, six from the horse and five from man, were used for the separation and purification by modifications of well-known methods of the albumin, euglobulin, and ψ -globulin. The optical rotation and the ultra-violet absorption spectra of the individual proteins were examined in detail. ψ -Globulin, euglobulin, and albumin from horse sera had specific rotations of -52° , -43° , and -57.4° , respectively, the corresponding values for human being -46° and -48° for the globulins and varying values for the albumin. The absorption curves are similar in form and character to that of serum, well-developed bands being best found at concentrations of 0.08% for albumin and 0.04% for the globulins. The absorption curve of ψ -globulin is the same for the horse and man and differs from euglobulin in the extinction coefficients but not in general form. For horse and human albumin, the curves are the same except for a constant ratio in their magnitudes, due possibly to physical or chemical association of an aggregate of little or no absorptive power. H. K.

The Fluorescence of Mercury Vapour. J. S. VAN DER LINGEN and R. W. WOOD (*Astrophys. J.*, 1921, 54, 149—160).—Since the fluorescent spectrum of mercury vapour cannot be excited in quiescent vapour, but only in vapour which is being distilled from the metal at a temperature not less than 150° , the active molecules are presumably not neutral monatomic molecules, but others, possibly diatomic, present only during distillation. The spectrum consists of lines at 2536, 2539, and 2346 Å., and four structureless bands with maxima at 2346, 2540, 3300, and 4850 Å. The complete spectrum is excited by light from a zinc spark, but single lines excite only a part. The relation of the spectrum to the exciting light is examined in some detail. A. A. E.

Hydrates of Boron Trioxide as a Constituent of Systems Capable of Strong Phosphorescence and containing Organic Compounds. ERICH TIEDE and PETER WULF (*Ber.*, 1922, 55, [B], 588—597).—The phosphorescence of partly dehydrated boric acid (A., 1921, ii, 75) originates from traces of organic compounds, is removable, not by recrystallisation, ignition in a stream of oxygen, boiling with nitric acid, or fusion with potassium nitrate, but by boiling with fuming nitric acid for twenty-four hours, subsequently recrystallising three times from water specially purified, and finally igniting the upper portion of the filtered mass (which had not been in contact with filter-paper) in a platinum crucible. Phosphorescence could not be induced in such a product by any means other than by introduction of organic impurities. For this purpose, even those present in ordinary distilled water suffice. A number of fluorescent boric acid compounds were prepared by the respective additions to purified boric acid of fluorescein, its sodium salt (uranin), phenolphthalein, benzoic acid, quinone,

aniline, dimethylaniline, diphenylamine, phenol, quinol, naphthol, terephthalic acid, pyridine, and quinoline—in short, aromatic or heterocyclic compounds, but not aliphatic compounds, unless these (for example, ethylene glycol or sugar) undergo some decomposition—followed by fusion of the mixtures to transparent glasses, or by heating for two hours in the vacuum of a water-pump until a partly sintered mass is produced. Inorganic compounds, even those of uranium or the platinocyanides, with the exception of boron nitride (Tiede and Büscher, A., 1921, ii, 74) do not produce phosphorescent materials, nor can the boric acid be replaced by silicic or phosphoric acids. Hydration to orthoboric acid consequent on exposure of the products to air largely destroys the phosphorescence, as does also too intense dehydration. Phosphorescence is excited by daylight, but usually best by the ultra-violet light of the quartz lamp, and does not usually persist for more than two minutes. The intensity, however, is frequently much greater than that from the phosphorescent alkaline earths and sufficient momentarily to illuminate comparatively large spaces. Blue tones predominate, but reddish-yellow and green effects have been observed. Röntgen, cathode, and radium rays have no effect. The new products show only slight tendency towards thermoluminescence, down to the temperature of liquid air. In common with analogous cases, they are produced when the medium (boric acid) suffers contraction. They offer no support for the view that luminescence of organic compounds is dependent on their slow decomposition (Perrin, A., 1918, ii, 418; 1919, ii, 177). Pure anthracene, in spite of its fluorescence, causes no fluorescence in boric acid, but compounds like ethyl dihydrocollidinedicarboxylate, which are excited by radium rays, give a product in which fluorescence is produced by ultra-violet illumination, but is indifferent to radium. It is presumed that the phosphorescence emanates from definite organic derivatives of boric acid (cf. Dimroth and Faust, A., 1922, i, 155; Pictet, A., 1903, i, 601). Thus orange crystals result from evaporation of a solution of boric acid containing uranin (1 : 3000), but these, on fusion, become light green and simultaneously acquire capacity for phosphorescence.

J. K.

Action of Red and Infra-red Rays on the Phosphorescent Sulphides. MAURICE CURIE (*Compt. rend.*, 1922, **174**, 550—553).—As an explanation of the extinguishing action of the less refrangible part of the spectrum on certain phosphorescent substances, it is suggested that the action of the extinguishing rays will consist in rendering the medium a conductor by the detachment of electrons from the atoms of sulphur, in the case of the sulphides. In support of this theory, experiments are described in which an increase of conductivity was found for finely-powdered sulphur and certain sulphides when they were exposed to the action of red rays. This hypothesis also gives an explanation of the fact that the extinguishing action is not limited to the red and infra-red portions of the spectrum.

W. G.

Preparation of Phosphorescent Magnesium Sulphide.

ERICH TIEDE and FRIEDRICH RICHTER (*Z. Elektrochem.*, 1922, **28**, 20—21).—Strongly phosphorescent preparations of magnesium sulphide containing small quantities of bismuth, antimony, or manganese may be prepared. These substances exhibit a violet, golden-yellow, or dark red phosphorescence and an afterglow which in every way corresponds with that of the well-known preparations of the alkaline earth sulphide. Details of the method of preparation of phosphorescent magnesium sulphide are not given in the paper.

J. F. S.

Experimental Proof of some Theories of Natural Rotatory Power of Optically Active Solutions.

PAUL WETTERFORS (*Z. Physik*, 1922, **8**, 229—242).—With the object of testing the hypotheses of optical rotation put forward by Lorentz and Livens ("Theorie elektr. opt. Erscheinungen," 1906; A., 1913, ii, 543; 1914, ii, 830), the author has measured the specific rotation, $[\alpha]$, the refractive index, n , and the rotatory dispersion of solutions of camphor in ethyl alcohol, propyl alcohol, acetone, benzene, and toluene, and of α -bromocamphor in the three last-named solvents. The measurements were made with solutions of various concentrations from 10.02 to 49.98 grams per 100 c.c. of solution at temperatures from 11.1° to 18.0°. Four series of measurements were made in each case with light of wave-lengths $589\mu\mu$, $546\mu\mu$, $436\mu\mu$, and $710\mu\mu$, the first being obtained from a sodium lamp and the three latter from a quartz mercury lamp by the use of suitable light filters. The specific rotation of α -bromocamphor in acetone solution in various concentrations, c , is given by the equations $[\alpha]_{\lambda=710}=86.87+0.0625c$; $[\alpha]_{\lambda=589}=140.08+0.1043c$; $[\alpha]_{\lambda=546}=172.01+0.1389c$; $[\alpha]_{\lambda=436}=350.25+0.3561c$. It is shown in general the rotation increases with increase of temperature, since the concentration of a solution decreases with increasing temperature the specific rotation is also greater. An exception is found in the case of acetone solutions of α -bromocamphor; here the rotation decreases with increasing temperature, but the specific rotation is independent of temperature. The rotatory dispersion, defined as the ratio $[\alpha]_{\lambda} : [\alpha]_{589}$ where $[\alpha]_{\lambda}$ is the specific rotation for the wave-length λ and $[\alpha]_{589}$ the same quantity for $\lambda=589$, changes in general with the concentration. Bromocamphor shows an increase, camphor a decrease for the wave-lengths $\lambda=546\mu\mu$ and $436\mu\mu$ ($\lambda>589\mu\mu$), but for $\lambda=710\mu\mu$ ($\lambda<589$) an increase when the concentrations are greater. Solutions of camphor in acetone are exceptional, for here the rotatory dispersion is constant. According to Livens's theory, the expression $[\alpha]=rv^2/2 \cdot (n^2-1)[a(n^2-1)+1]$ must hold; this has been rewritten in the form $[\alpha]=ay_0(n^2-1)^2+y_0(n^2-1)$, where $y_0=rv^2/2$. On plotting the values of $[\alpha]/(n^2-1)$ against (n^2-1) , a straight line should be obtained. Treating the present experimental values in this way actually leads to straight lines for solutions of camphor in benzene and toluene, and for bromocamphor in benzene; in all other cases a straight line passes only approximately through the points. The values of a and y_0

have been evaluated by the method of least squares, and it is shown that the value of a is always negative as shown by Peacock (T., 1914, **105**, 2782; 1915, **107**, 1547). The numerical values of a are largest for bromocamphor in toluene and benzene and smallest for camphor in ethyl alcohol. The a value for camphor in toluene is the same for $\lambda=546\mu\mu$ and $\lambda=436\mu\mu$. It is shown, therefore, that the Lorentz-Livens hypothesis can only claim to give qualitative representation of the present material. According to Oseen's hypothesis, the expression $k=[\alpha]:(n^2+2)^2$ must be constant. The experimental data show that this is not the case, for in the case of solutions of camphor in benzene, toluene, and the alcohols, the k value increases with increasing concentration, but decreases with acetone solutions. Further, except in the case of solutions of camphor in propyl alcohol, the value of k is a linear function of the concentration.

J. F. S.

Photochemical Studies. XIV. Fundamental Photochemical Laws. J. PLOTNIKOW (*Z. wiss. Photochem.*, 1922, **21**, 134—140).—A theoretical paper in which Einstein's photochemical equivalent law and the Grotthus-van't Hoff photochemical absorption law are critically examined. It is shown that Einstein's law leads to the following improbabilities. On calculating the energy absorbed, by one gram molecule, from light of various wave-lengths, it is found that the extreme ultra-violet, $100\mu\mu$, gives up 300,000 cal. and Röntgen rays 3×10^9 cal., which indicates that with decreasing wave-length light becomes much more active, until, with Röntgen rays, all molecules will be simply destroyed. Further, all atoms in all reactions in all solvents must react with the same velocity at all temperatures and must take up the same quantity of energy. It is shown that the Grotthus-van't Hoff law is diametrically opposed to the Einstein law. Nine classes of photolytic reactions are quoted in which the Einstein law in no way represents the facts, and two further classes are noted in which deviations from the law of -8% to 22% are observed. The photolysis of hydrogen iodide and hydrogen bromide alone give an approximate agreement, but here there is a divergence varying between -3.3% and $+4\%$. Weigert's recent paper (*Z. Physik*, 1921, **5**, 421), which shows the applicability of the Einstein law and characterises the Grotthus-van't Hoff law as untenable, is criticised. It is shown that the reactions studied and the method of operation is much too complicated to make it possible to draw conclusions of the type drawn by Weigert from the results. In the present author's opinion, the Einstein law in its present form cannot be maintained.

J. F. S.

Photosynthesis and the Electronic Theory. II. HENRY H. DIXON and NIGEL G. BALL (*Sci. Proc. Roy. Dubl. Soc.*, 1922, **16**, 435—441; cf. Dixon and Poole, A., 1920, ii, 343).—In continuation of previous work, the photo-electric properties of chlorophyll were investigated. The electronic theory of sensitisation is supported by experiments in which sensitised photographic plates were affected by light at a temperature of -185° , chemical

action being thereby precluded. Using collodion films, it was shown that sensitisation by chlorophyll is also effective even at the temperature of liquid air. Since only light of visible wave-lengths is absorbed by chlorophyll, and since earlier experiments have shown that electrons are not expelled from chlorophyll, it follows that the light absorbed is wholly used in the displacement of electrons within the molecule, thereby making some atomic group or groups reactive. In photosynthesis, these groups may react with carbon dioxide and water, according to the scheme $\text{chlorophyll-}a + \text{CO}_2 = \text{chlorophyll-}b + \text{CH}_2\text{O}$ and $\text{chlorophyll-}b + \text{H}_2\text{O} = \text{chlorophyll-}a + \text{O}_2$. It is assumed that these reactions only take place during illumination and depend on its intensity. The velocity of the first reaction would only increase with intensity of illumination so long as carbon dioxide is in excess, whilst the velocity of the second reaction would only be indirectly influenced by this factor.

G. W. R.

Absorption of Röntgen Rays. K. A. WINGÅRDH (*Z. Physik*, 1922, 8, 363—376).—A method for the determination of the absorption coefficients of substances in solution for the homogeneous Röntgen rays of the K_α line of molybdenum is described. The atomic absorption coefficients are calculated, and it is shown that the logarithms of these when plotted against the logarithms of the ordinal numbers of the elements give two straight lines. Oxygen showed a marked deviation.

J. R. P.

Spark Lines in the Röntgen Spectrum. GREGOR WENTZEL (*Ann. Physik*, 1921, [iv], 66, 437—461).—It is assumed that the inner shells of the atom may under certain conditions undergo repeated ionisation. By the spontaneous transition of an atom from such a state to a state of equal level, Röntgen lines will be emitted which correspond with spark lines in the optical spectrum. It is shown that the emission can have only one fine-structure of known Röntgen lines, which is extended usually towards the region of short wave-lengths. All the lines which previously caused difficulty in the systematic arrangement of Röntgen spectra can be regarded as spark lines; in particular the hard $K\alpha$ satellites, from $K\alpha_3$ to α_6 can be derived from two combination relations, and the complex structure of the K -absorption edges observed by Fricke is also elucidated. The magnitudes of the frequency differences and their linear change with ordinal number are satisfactorily explained.

J. R. P.

X-Rays and Thermodynamic Equilibrium. L. DE BROGLIE (*J. Phys. Radium*, 1922, [vi], 3, 33—45).—The conditions of thermodynamic equilibrium between atoms, electrons, and radiation in an enclosure maintained at a temperature T are considered. The statistical equilibrium between the atoms is described by the law of Maxwell and Boltzmann, which may be applied to systems in which the total energy may assume only a certain number of discontinuous values. The equilibrium density of

radiation in the region of frequencies considered may be represented by Wien's law. The free electrons are considered as forming an ideal gas, with density proportional to $T^{\frac{3}{2}}$. The atomic coefficient of absorption of a substance is then shown to be given by $\mu = C\lambda^3 \sum_p n_p E_p^2$, where C is a constant, λ the wave-length, n_p the number of electrons in the level p (in the sense of Bohr's theory), and $E_p = h\nu_p$ the energy emitted when the atom passes from the ionised to the normal state. This result is compared with experiment.

J. R. P.

Stopping Power and Atomic Number. J. L. GLASSON (*Phil. Mag.*, 1922, [vi], **43**, 477—481).—By a discussion of known results it is shown that the stopping power of an atom is proportional to $N^{\frac{2}{3}}$, where N is the atomic number, rather than to $A^{\frac{1}{2}}$, where A is the atomic weight, as previously supposed. This agrees with the higher stopping power of hydrogen as compared with helium.

J. R. P.

Isotopy of the Radio-elements. M. L. NEUBURGER (*Nature*, 1921, **108**, 180).—Meitner's (this vol., ii, 15) nucleus model of the radio-elements permits of the division of the radioactive isotopes into four classes: (1) those which possess only the same nuclear charge and the same arrangement of their outer electrons, for example, radium and mesothorium-I, (2) those which have in addition the same atomic weight and the same total number of nuclear "building stones," for example, ionium and uranium-Y, (3) those having the same number of each nuclear building stone, but a different arrangement of these in the atomic nucleus, for example, radium-D and actinium-B, (4) those possessing the same arrangement of building stones, and thus the same probability of disintegration, for example, radium-G and actinium-D. Such elements cannot at present be designated isotopes since there is no available means of distinguishing between them.

A. A. E.

The Ionium Content of Radium Residues. ELIZABETH RONA (*Ber.*, 1922, **55**, [B], 294—301).—Ionium has been estimated in various radium residues according to the "indicator" method with the aid of uranium-X and the content has been compared with that of pitchblende. The final residues obtained during the extraction of radium in Austria still contain approximately 16% of the ionium present originally in the pitchblende. Thorough extraction of the latter with nitric acid on a laboratory scale gives insoluble residues which are almost completely free from ionium.

The importance of the estimation of ionium for that of protoactinium in uranium minerals and for the inter-relationships of the actinium series is discussed.

H. W.

Artificial Disintegration of the Elements. A Lecture delivered before the Chemical Society on February 9th, 1922. SIR ERNEST RUTHERFORD (*T.*, 1922, **121**, 400—415).

Luminescence of Flame Ions in the Air Spark. H. GREINACHER (*Physikal. Z.*, 1922, **23**, 65—69).—When a flame coloured

with a salt vapour is brought into a strong electric field, the ions may be caught on two platinum wires, outside the flame, on which they may afterwards be detected spectroscopically by heating. When a spark is passed between a wire in the flame and a brass sphere a few centimetres from the flame, or two wires similarly placed, the spectrum of the spark shows the lines of hydrogen and the metal ions. Lithium, sodium, potassium, rubidium, caesium, thallium, and strontium were examined. The metals move principally to the negative electrode, but partly to the positive. In the case of strontium, all the lines leave the flame, but in the other cases only a limited number. In spite of the strong field in the spark, only the lines with a small exciting potential (small $h\nu$) appear. The ions are partly produced in the flame and partly in the spark. An apparent change in wave-length occurs.

J. R. P.

Ionic Equilibria on Metallic Surfaces. H. VON EULER [with ARVID HEDELIUS and ZIMMERLUND] (*Z. Electrochem.*, 1922, **28**, 2—6).—An account is given of the sorption of gold, silver, and mercury ions on the surfaces of the metals. The method consisted in determining analytically the change in the concentration of solutions of silver nitrate and silver sulphate after they had been in contact with metallic silver and gold respectively. Similar experiments are described for solutions of mercuric chloride in contact with mercury. It is shown that 1 sq. metre of silver surface absorbs 0.35 mg. ion from silver nitrate and 0.5 mg. ion from potassium chloride solution, whilst the same area of gold absorbs 0.063 mg. ion from silver nitrate. A sq. metre of mercury surface absorbs 0.004 mg. ion from mercuric chloride solution. The results are discussed in connexion with the charge of an electric double layer.

J. F. S.

Evidence for the Existence of Homogeneous Groups of Large Ions. P. J. NOLAN (*Physical Rev.*, 1921, **18**, 185—198).—Using, as did Blackwood (*ibid.*, 1920, **16**, 85), the Zeleny method for the measurement of the mobilities of ions, instead of that previously employed by McClelland and Nolan (*Proc. Roy. Irish Acad.*, 1919, **35**, [A], 1, and previous papers), evidence has been adduced to confirm the author's original statement that when large ions are produced in air in various ways, the ions can be divided into a number of groups, each group having a definite mobility. It is considered that Blackwood's negative results were due to ions changing from group to group when the time spent in the measuring chamber is relatively long.

A. A. E.

The Scattering of Electrons by Nickel. C. DAVISSON and C. H. KUNSMAN (*Science*, 1921, **54**, 522—524).—When a nickel target is bombarded by a stream of electrons, there is observed, besides the emission of slowly moving secondary electrons characteristic of all metals, an appreciable emission of electrons of higher speed. After experimental and mathematical examination of

the phenomenon, it is suggested that the sharp deflexions experienced by these scattered electrons must result from their penetration into the atomic structure and their deflexion by the strong field which they encounter.

A. A. E.

Dielectric Constants of some Esters at Low Temperatures.

L. C. JACKSON (*Phil. Mag.*, 1922, [vi], **43**, 481—489).—A method is described for the determination of the dielectric constants of solid and liquid substances by the use of triode valve circuits. The results, with a frequency of 4.7×10^5 per second, were, at the absolute temperatures indicated, as follows: methyl formate, 2.56 at 78.65° ; ethyl formate, 2.40 at 81.3° ; *n*-propyl formate, 2.39 at 79.5° ; *n*-butyl formate, 2.43 at 78.7° ; methyl acetate, 2.58 at 77.3° ; ethyl acetate, 2.48 at 79.15° ; *n*-propyl acetate, 2.42 at 80.9° ; *n*-butyl acetate, 2.41 at 77.6° . The values are smaller than those found at the ordinary temperature (5 to 9). The acid radicle apparently contributes but little to the value of the dielectric constant. The dielectric constant of *n*-butyl acetate increases linearly with decrease of temperature to the melting point at which there is a sudden fall, followed by a very gradual rise as the temperature is still further lowered.

J. R. P.

Conductivity of Concentrated Solutions of Sodium and Potassium in Liquid Ammonia.

CHARLES A. KRAUS and WALTER W. LUCASSE (*J. Amer. Chem. Soc.*, 1921, **43**, 2529—2539).—The specific conductivity of solutions of sodium and potassium in liquid ammonia at its boiling point (-33.5°) has been measured for concentrations from 0.6*N* to saturated solutions. It is shown that as the concentration increases, the specific conductivity increases enormously, reaching the values 0.5047×10^4 and 0.4569×10^4 for saturated solutions of sodium and potassium respectively. The specific conductivity of solutions of sodium and potassium at the same equivalent concentration is very nearly the same. The equivalent conductivity of saturated solutions of sodium and potassium in liquid ammonia is of the same order of magnitude as that of such metals as strontium and iron. The solubility of sodium and potassium in liquid ammonia at its boiling point has been found to be 5.367 and 4.866 mols. of ammonia per atom of sodium and potassium respectively. The general result of the work is the furnishing of further evidence in support of the hypothesis that the conduction process in metals consists in a motion of negative carriers of sub-atomic dimensions, which carriers are identical for all metals.

J. F. S.

Potentials at the Junctions of Univalent Chloride Solutions.

DUNCAN A. MACINNES and YU LIANG YEH (*J. Amer. Chem. Soc.*, 1921, **43**, 2563—2573).—Using a slightly modified form of Lamb and Larson's flowing junction apparatus (*A.*, 1920, ii, 347) the contact potentials of the type, $MCl|M'Cl$, in which *M* and *M'* are either hydrogen or an alkali metal (lithium, sodium, potassium, caesium, or ammonium) have been determined. The measurements were made at 25° and were for solutions of equal concentrations.

Tables of results of all possible combinations are given for the concentrations 0.1*N* and 0.01*N*, and the values compared with those calculated by Lewis and Sargent's formula (A., 1909, ii, 369). In all cases reproducible values were obtained, within a few hundredths of a millivolt. The Lewis and Sargent form of Planck's original equation $E_e = RT/F \log_e \Lambda_c/\Lambda_c'$ expresses the results for most of the cases studied and gives a qualitative agreement in all cases. The experimentally determined potentials can, however, be obtained from the differences between numbers which are characteristic for each ion at each concentration. This is equivalent to the expression given above, except that for the lithium and potassium ions, values of Λ which are slightly different from those obtained from conductivity measurements would have to be used.

J. F. S.

A Quick Acting Hydrogen Electrode. P. J. MOLONEY (*J. Physical Chem.*, 1921, 25, 758—761).—A new form of hydrogen electrode is described. The electrode consists of a short length of platinum wire sealed into the end of a glass tube and projecting 4 mm. from the end; the tube should have an internal diameter of about 4 mm. A loop of 1 mm. diameter glass rod is sealed to the end of the tube so that the platinum wire occupies the centre of the loop. A glass tube, of slightly greater diameter than the electrode tube, blown into the form of a bell at one end and having a bulb a little higher up which is pierced near the top by a small hole, fits over the electrode tube and is kept in position by a piece of rubber tube. The platinum wire is platinised in the usual way. The object of the electrode is to ensure a rapid equilibrium between the hydrogen in the platinum and the hydrogen ion in the solution. To use the electrode it is drawn up the tube until the wire and glass loop are in the middle of the bulb in the jacket tube and the whole is immersed in the liquid to be measured until the tube connecting the bell and bulb is filled, then the electrode is pushed down until the wire and loop are in the bell, hydrogen is admitted under the bell, and the whole adjusted so that the wire is surrounded by hydrogen whilst the lower end of the loop just dips into the main bulk of the liquid. In this way only a small volume of liquid, namely, that held in the loop, has to be saturated with hydrogen and be in equilibrium with the wire. Equilibrium values are rapidly reached with this electrode.

J. F. S.

Behaviour of a Non-attackable Electrode in the Process Leading to the Equilibrium $3\text{HNO}_2 \rightleftharpoons 2\text{NO} + \text{HNO}_3 + \text{H}_2\text{O}$. ALFONS KLEMENC (*Z. Elektrochem.*, 1922, 28, 55, 56); H. PICK (*ibid.*, 56—57).—Polemical; cf. A., 1920, ii, 409; 1921, ii, 297.

J. F. S.

Overvoltage on Electrodes and its Connexion with the Hydration of Ions. N. ISGARISCHEV and SOPHIE BERKMANN (*Z. Elektrochem.*, 1922, 28, 40—47).—The decomposition voltage of *N*- and *N*/10-solutions of sulphuric acid and the sulphates of rubidium, aluminium, potassium, ammonium, sodium, lithium,

magnesium, zinc, copper, manganese, and nickel has been determined and the values have been compared with the degree of dissociation, the surface tension, the molecular hydration and the ionic hydration. It is shown that there is only one break in the anode current-voltage curve, and this is attributed to the discharge of the SO_4'' ion. The results show that the surface tension is in no way related to the discharge potential of the anion (E); the degree of dissociation also stands in no direct relationship to the value of E ; in some cases it is found that an increase in the value of the degree of dissociation is accompanied by an increase of E . It is concluded, therefore, that the discharge voltage is dependent on the velocity of the anode process, that is, a lower potential will be required for decomposition the greater the velocity of the anode process. To investigate the cause of the difference in the velocity of the anode process in different cases, the authors have compared the value of E with the hydration of the molecules and the ions. It is shown that there is no connexion between the value of E and the number of molecules of water combined with the molecules of the electrolyte. The more hydrated the kations the smaller is the decomposition voltage found to be, and since the more hydrated the kation the less hydrated is the anion, it follows that the lower is the potential required to discharge it. The anode process is expressed by the scheme, (a) $\text{SO}_4'' + 2\oplus = \text{SO}_4$; (b) $\text{SO}_4 = \text{SO}_3 + \text{O}$; (c) $\text{Na}_2\text{SO}_4(\text{H}_2\text{O})_r = 2\text{Na}(\text{H}_2\text{O})_{66} + \text{SO}_4''(\text{H}_2\text{O})_m$; (d) $\text{SO}_4''(\text{H}_2\text{O})_m = \text{SO}_4'' + m\text{H}_2\text{O}$. The cause, therefore, of the retardation of the anode process is the insufficiently rapid formation of SO_4'' ions from the hydrate. It is shown that there is a definite periodicity between the value of E and the atomic weight of the kation.

J. F. S.

Influence of Colloids on Overvoltage. N. ISGARISCHEV and SOPHIE BERKMANN (*Z. Elektrochem.*, 1922, **28**, 47—50).—The discharge potential of the hydrogen ion on copper, silver, and platinum cathodes has been measured in 2*N*-sulphuric acid containing various concentrations of gelatin (0—6%). It is shown that the nature of the cathode has no influence on the discharge potential. The value of this quantity at 18° rises to a maximum with increase in the gelatin concentration and then commences to fall. There is a corresponding increase in the anode discharge voltage with increase in the gelatin concentration. The change is explained as due to the formation of a complex between the hydrogen ion and the gelatin which is slowly decomposed at the electrode (see preceding abstract). The maximum potential represents the point where all the ions have combined with gelatin and a calculation based on an approximate value of the molecular weight of gelatin shows that a complex consisting of one hydrogen ion and 1173 molecules of gelatin is formed.

J. F. S.

Free Energy of Dilution and the Activities of the Ions of Potassium Bromide in Aqueous Solutions. J. N. PEARCE and HARRY B. HART (*J. Amer. Chem. Soc.*, 1921, **43**, 2483—2492).—Measurements of the *E.M.F.* of cells of the type $\text{Ag}|\text{AgBr}, \text{KBr}(c)|$

KHg_x have been made for various concentrations ($c=2.0-0.001N$) at 25° , 30° , and 35° . The decrease of free energy and the decrease in heat content attending the reaction in these cells have been calculated. The free energy decrease accompanying the transfer of 1 mol. of potassium bromide from various concentrations (c) to $0.10N$ have also been calculated. The *E.M.F.* of concentration cells with ion transference of the type $\text{Ag}|\text{AgBr}, \text{KBr}(c_1)|\text{KBr}(c_2), \text{AgBr}|\text{Ag}$ and of concentration cells without ion transference of the types $\text{Ag}|\text{AgBr}, \text{KBr}(c_1)|\text{KHg}_x-\text{Hg}_x\text{K}|\text{KBr}(c_2), \text{AgBr}|\text{Ag}$ and $\text{KHg}_x|\text{KBr}(c_1), \text{AgBr}|\text{Ag}-\text{Ag}|\text{AgBr}, \text{KBr}(c_2)|\text{Hg}_x\text{K}$ have been determined and from these values the transport number of the potassium ion has been calculated. The results show that dilution has very little influence on the transport number of potassium and there is only a very gradual increase with increasing dilution, whilst the effect of temperature is practically negligible between 25° and 35° . The decrease of free energy and heat content accompanying the transference of 1 mol. of potassium bromide from a concentration c_1 to a concentration c_2 have been calculated. The activity coefficients of the bromide ion have been calculated and a comparison made of the activity coefficients of the chloride and bromide ions. For all concentrations up to $0.5N$, the activity coefficients of these two ions are practically equal.

J. F. S.

Electro-chemical Behaviour of Metallic Conducting Compounds. G. TAMMANN (*Z. Elektrochem.*, 1922, 28, 36-40).—A discussion on the electromotive behaviour of compounds which exhibit a metallic conductivity. It is shown that of the five cobalt silicides, only those are attacked by acids which contain more than one atom of cobalt to one atom of silicon. In the case of the lead palladium intermetallic compounds, it is found that they have the palladium potential, but if there is an excess of lead over that required for the formation of a compound in the lead palladium alloy the mixture shows the lead potential. A number of other cases are cited and discussed.

J. F. S.

Activity Coefficients and Colligative Properties of Electrolytes. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1922, 44, 252-267).—A theoretical paper in which on the basis of the empirical equation $\log F_a' = \alpha'c - \beta'c^m$ (A., 1920, ii, 664) which connects the activity coefficient of an electrolyte with the molecular concentration at a given temperature, and Duhem's equation, equations are derived for calculating the vapour pressures of solutions at this temperature. The validity of the above equation has been rigorously tested, and it is found to hold for all electrolytes over the whole range where data were examined with the exception of sulphuric and hydrochloric acids. In these cases, it holds up to a concentration $3M$. The activity coefficients of solutions of hydrochloric acid, sodium chloride, and potassium chloride have been investigated and the values of the parameters of the above equation for these electrolytes and others have been collected and tabulated, from which the vapour pressures and osmotic pressures of their solutions may be calculated. It is suggested that the

equation and method employed here, although empirical and an approximation, will prove useful in testing the consistency and accuracy of activity data and also will be of service in organising the colligative data of concentrated solutions. J. F. S.

Ghosh's Theory of Electrolytic Solutions. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1921, **43**, 2514—2528).—A theoretical paper in which the hypothesis of electrolytic solutions put forward by Ghosh (T., 1918, **113**, 449, 627, 777, 790) is discussed. Ghosh's equation expressing the conductivity of solutions of electrolytes as a function of the concentration is compared with the experimental values in aqueous and non-aqueous solutions. On plotting the values of $\log A$ against those of the cube root of the concentration, the experimental points lie on a curve which is concave toward the axis of concentration. If Ghosh's equation were applicable, the points should lie on a straight line. The deviation of the points from a linear relation is consistent throughout, and cannot be accounted for by errors in the original observations. It is held that in its present form Ghosh's hypothesis does not satisfactorily account for the properties of solutions of electrolytes. The postulates and assumptions on which the hypothesis is based are discussed and several inconsistencies indicated. The use of Maxwell's law for the distribution of velocities and Clausius's virial theorem to systems of charged particles is open to serious objections. J. F. S.

Distribution of Thermal Energy in the Quadrivalent Chlorides of Carbon, Silicon, Titanium, and Tin. WENDELL M. LATIMER (*J. Amer. Chem. Soc.*, 1922, **44**, 90—97).—The specific heats of carbon, silicon, titanium, and tin tetrachlorides have been measured from the temperature of liquid air to 298° Abs., and, in addition, the specific heat of carbon tetrachloride was measured at still lower temperatures down to 39.1° Abs., in order to determine the whole specific heat curve for these compounds. The following values of $C_p M/5$ are recorded: Carbon tetrachloride, solid I, 39.1°, 0.60; 40.7°, 0.65; 63.8°, 2.05; 79.6°, 2.81; 91.0°, 3.40; 99.5°, 3.60; 199.5°, 5.84; 208.0°, 5.90; solid II, 229.4°, 6.20; 235.6°, 6.25; 238.0°, 6.77; liquid, 253.8°, 6.40; 265.1°, 6.30; and 290°, 6.34. Silicon tetrachloride, solid, 77.4°, 3.60; 86.6°, 3.83; 94.8°, 4.14; 131.3°, 4.80; 168.6°, 5.68; 181.0°, 5.95; liquid, 208.8°, 6.74; 294.3°, 6.94. Titanium tetrachloride, solid, 86.7°, 4.26; 92.8°, 4.40; 194.6°, 6.19; 231.8°, 6.31; 247.7°, 6.21; liquid, 251.6°, 7.26; 294.3°, 7.32. Tin tetrachloride, solid, 89.0°, 4.59; 95.9°, 4.71; 161.2°, 5.89; 200.7°, 6.33; 227.3°, 6.62; liquid, 266.1°, 7.56; 294.0°, 7.86. All temperatures are in absolute degrees. The heat of transition of solid I to solid II in the case of carbon tetrachloride at 224.6° Abs. is 7.10—7.19 cal./gram. The heat of fusion has been determined as follows: carbon tetrachloride, 4.1—4.22 cal./gram at 249°; silicon tetrachloride, 10.85 cal./gram at 203.3°; titanium tetrachloride, 11.77 cal./gram at 248.0°, and tin tetrachloride 8.38—8.42 cal./gram at 239.9°. The entropy, S_{298} , of each of the compounds at 298° Abs. and the entropy change

in the formation, ΔS_{298} , of each compound from its elements have been calculated. The following values are recorded: carbon tetrachloride, S_{298} , 49.06, ΔS_{298} , -50.84; silicon tetrachloride, S_{298} , 56.43, ΔS_{298} , -48.27; titanium tetrachloride, S_{298} , 59.51, ΔS_{298} , -47.09; tin tetrachloride, S_{298} , 61.84, ΔS_{298} , -49.66.

J. F. S.

Relation between Statistical Mechanics and Thermodynamics. RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1922, 44, 75—90).—A theoretical paper in which the relationship between statistical mechanics and thermodynamics is investigated by a method which is based, like that of Boltzmann and Planck, on a consideration of the arrangement of the elements or molecules of a system. Instead, however, of arbitrarily defining entropy by the equation $S = k \log W$ as do Planck and Boltzmann, an attempt is made to discover a statistical mechanical quantity which has the same derivatives with respect to energy, volume, and number of molecules as does the thermodynamic quantity entropy. In this way, an expression for entropy is developed which differs from that of Planck by an additive term; it is further shown that the addition of such a term is necessary in order that the derivative of the entropy of the system with respect to number of molecules shall have its correct value. The equation thus developed has the form $S = (N\epsilon - N\psi)/T$, in which N is the number of molecules, ϵ has a significance defined below, and T is the temperature. In connexion with the derivation of the above expression, it is shown that the quantity ϵ occurring in the Maxwell-Boltzmann distribution law $dN = Ce^{-\epsilon/kT} dq_1 \dots dp_n$ must be taken, not as the energy of a molecule having co-ordinates and momenta falling in the region $dq_1 \dots dp_n$, but rather as the rate of increase in the total energy of the system per molecule added in the region $dq_1 \dots dp_n$, when the system is in its configuration of maximum probability. These two quantities are the same for dilute gases, but for concentrated systems may be quite different. Hence the new methods introduced may be of considerable importance in dealing with the properties of imperfect gas or rather concentrated systems. It is pointed out that the equations developed which connect the statistical mechanical quantities with thermodynamic quantities do not agree with the equations of Marcelin and Adams (*A.*, 1915, ii, 328; 1921, ii, 628).

J. F. S.

Relation between Entropy and Probability. Integration of the Entropy Equation. GEORGE A. LINHART (*J. Amer. Chem. Soc.*, 1922, 44, 140—142).—Two equations are deduced which express the change of specific heat of an element or compound with the entropy. The equations are based on the assumptions that the change depends on the probability of the "randomness" of the individual particles, the certainty that particles will have a fixed position at the point of zero kinetic energy, and the zero probability that this condition persists at high temperatures. The equations deduced are tested by means of recently published work on the specific heat of copper when a good agreement between the

observed and calculated values of the specific heat over the range $14.51-390.0^{\circ}$ Abs. is found. J. F. S.

Latent Heats of Fusion. I. Benzophenone, Phenol, and Sulphur. (MRS.) K. STRATTON and J. R. PARTINGTON (*Phil. Mag.*, 1922, [vi], 43, 436-446).—The following values of the latent heats of fusion, in gram-calories per gram, were measured at the melting points by electrical heating: benzophenone, 21.70; phenol, 29.06; sulphur (monoclinic), 8.85. In a theoretical discussion, it is suggested that intramolecular vibrations as well as rotations are indicated in the case of some liquid molecules.

J. R. P.

The Freezing Points of Pure Organic Liquids as Thermometric Constants at Temperatures below 0° . JEAN TIMMERMANS, (MLLE) H. VAN DER HORST, and H. KAMERLINGH ONNES (*Compt. rend.*, 1922, 174, 365-367).—The following organic liquids have been carefully purified and their boiling points, densities, and freezing points accurately determined, so that these constants may be used as references by working with specimens kept in sealed tubes. All boiling points are given at 760 mm. pressure, and f. p. is the freezing point obtained under conditions where the thermodynamic equilibrium between the liquid and crystalline phases can be maintained for a long time to within 0.01° .

Carbon tetrachloride, b. p. 76.75° ; d_4^{20} 1.63255; f. p. -22.9° ; chlorobenzene, b. p. 132.00° ; d_4^{20} 1.12795; f. p. -45.2° ; chloroform, b. p. 61.2° ; d_4^{20} 1.52635; f. p. -63.5° ; ethyl acetate, b. p. 77.15° ; d_4^{20} 0.92450; f. p. -83.6° ; toluene, b. p. 110.70° ; d_4^{20} 0.88445; f. p. -95.1° ; carbon disulphide, b. p. 46.25° ; d_4^{20} 1.29270; f. p. -111.6° ; ethyl ether (stable form), b. p. 34.60° ; d_4^{20} 0.73625; f. p. -116.3° ; (unstable form), f. p. -123.3° ; methylcyclohexane, b. p. 100.3° ; d_4^{20} 0.78640; f. p. -126.4° ; isopentane, b. p. 27.95° ; d_4^{20} 0.63950; f. p. -159.6° . W. G.

Hydration of Ions. S. ASCHKENASI (*Z. Elektrochem.*, 1922, 28, 58-59).—A theoretical paper in which Fajans's treatment of the hydration of ions (*Naturwiss.*, 1921, 729) is discussed and a possible connexion with the known irregularities in the vapour pressure curves of aqueous solutions of electrolytes suggested.

J. F. S.

A Receiver for Fractionation in a Current of Gas or under Reduced Pressure. T. S. WHEELER and E. W. BLAIR (*J. Soc. Chem. Ind.*, 1922, 41, 59-60T).—The device consists essentially of an upper and a lower receiver connected together through a two-way tap which makes the connexion alternatively with the top or bottom of the upper receiver. In the former case, the vacuum is maintained in, or the gas is passed through, the upper and lower receivers, whilst the distillate collects in the upper receiver. When it is desired to collect a new fraction, the two-way tap is turned into the second position and the fraction which has collected in the upper receiver passes into the lower one, which is then detached, another put in its place, and evacuated (if neces-

sary), and the distillation continued with the two-way tap in the first position as before. If it is desired to keep the distillate out of contact with air, the lower receiver is provided with inlet and outlet taps, which are turned off before detaching it from the apparatus, and the liquid thus remains enclosed in the inert atmosphere in which it was distilled. G. F. M.

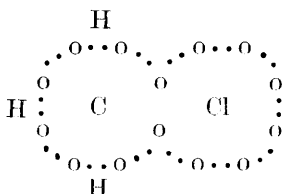
Comparison of the Linking of Carbon Atoms in Graphite and in Aromatic Hydrocarbons. J. P. WIBAUT (*Rec. trav. chim.*, 1922, **41**, 96—102).—A theoretical paper based on the work of Fajans (A., 1920, ii, 354), and criticising the theory put forward by von Steiger (A., 1920, ii, 355) that the linking of the carbon atoms in aromatic hydrocarbons is, from the point of view of energy, equivalent to the linking in graphite. H. J. E.

Atomic Linkings in the Carbon Compounds. I. and II. HANS BEUTLER (*Z. anorg. Chem.*, 1921, **120**, 24—30, 31—47).—I. Assumptions that periodic oscillations of melting points and boiling points in homologous series are due to heteropolar linking of the carbon atoms in the chain (cf. Cuy, A., 1921, ii, 429), are shown to be untenable, on account of the non-dissociation of the carbon compounds. The heats of combustion also vary in an oscillatory manner in homologous series, and this may be explained by considering the lattice-energy of the crystal structure. Compounds with an even number of carbon atoms probably have a more highly symmetrical lattice than those with an odd number, and as a result they have higher melting points and lower heats of combustion. Even in liquids, a kind of potential lattice structure probably exists, and influences the periodically varying physical properties. As the critical temperature is approached, the influence of the lattice is weakened by the strong thermal forces and the differences between odd and even members of the series disappear.

The electron structure of stable ions such as the Cl' or SO_4'' ion is discussed, and it is shown that ion formation is due to the splitting of a compound into parts each of which has an electron structure similar to that of a noble gas, with an outer shell of eight electrons. (This is identical with the Lewis-Langmuir theory, to which, however, no reference is made.) The structure of a non-dissociating substance of the type of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ is probably such that the co-ordinated groups are attached tetrahedrally to the central atom; in the electron system, the central atom is surrounded by eight electrons forming the corners of a cube, four edges of which are common each to one edge of the electron cubes of one of the co-ordinated groups. The possibility of two isomerides is at once apparent in this arrangement.

II. In the preceding section it was shown that isomerism is possible in the compound of the formula $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$; this is due to the fact that free rotation about the central Pt atom is inhibited probably by directing forces from the inner layers of electrons in the Pt atom. In carbon compounds $\text{CR}_1\text{R}_1\text{R}_2\text{R}_2$ free rotation is possible, since only two electrons are contained within the shell of eight electrons and restraining forces are absent. The electron

structures of methane, its halogen substitution products, ethylene, acetylene, and aromatic hydrocarbons are discussed. The methane molecule is represented by a central carbon nucleus surrounded by four electrons and four hydrogen nuclei arranged tetrahedrally at the eight corners of a cube with the other four electrons between the



carbon and hydrogen nuclei. In CH_3Cl there are fourteen electrons, two of which are common to the eight surrounding the carbon atom and the eight surrounding the chlorine atom. Diagrammatically the electron structure can be represented thus, where the electrons of the outer shell are represented by small circles. In ethylene it is supposed that the eight electrons

which are not situated directly between the hydrogen and carbon nuclei, revolve in an elliptical path of which the major axis is parallel to the C—C axis. The observed paramagnetism attributed to the double bond confirms this view. The electron structural formula for benzene shows three electrons between each pair of adjacent carbon atoms. In naphthalene, three electrons are shown between each pair of adjacent carbon atoms except between the carbons common to both rings, where there are only two. Reduction to 1:4-dihydronaphthalene, however, converts one ring into a true benzene ring, and a true ethylenic bond appears between the carbon atoms 2 and 3 in the other ring. E. H. R.

A Method for Measuring Vapour Densities for the Determination of Atomic Weights. A. MAGNUS and E. SCHMID (*Z. anorg. Chem.*, 1921, **120**, 232—240).—An apparatus is described for the measurement of vapour densities, the distinguishing feature of which is the total enclosure of the manometer and measuring vessel in a double-walled chamber which can be kept constant at the temperature of boiling water. The apparatus was used for determining the relation between the pressure p and pv/mT , where v is the volume, m the weight of the vapour, and T the absolute temperature for benzene and chloroform. Contrary to the results of Ramsay and Steele, the relation was found to be truly linear. The molecular weights calculated from the results are 78.096 for benzene and 119.380 for chloroform, whilst the atomic weight of chlorine calculated from these is 35.455, showing that the apparatus gives results of a high degree of accuracy. E. H. R.

Regularities in the Molecular Volumes of Inorganic Compounds. FR. A. HENGLEIN (*Z. anorg. Chem.*, 1921, **120**, 77—84).—It was recently shown by Biltz (*A.*, 1921, ii, 437) that there is a linear relationship between the molecular volumes of the halogens and of their compounds. This is now shown to be a particular case of a more general law that the molecular volumes of certain groups of inorganic compounds of like crystalline form bear a linear relation to constant magnitudes characteristic of their kations or anions. For the halogens, these magnitudes x may be expressed by the constants $F' : 0.8525$, $\text{Cl}' : 1.000$, $\text{Br}' : 1.066$, $\text{I}' : 1.179$, and

the magnitudes y for the alkali metals, $\text{Li}^{\cdot}:1.000$, $\text{Na}^{\cdot}:1.428$, $\text{K}^{\cdot}:2.108$, $\text{Rb}^{\cdot}:2.478$. The molecular volumes of the haloids of the alkali metals can be calculated from the general equation $\text{mol. vol.} = 14.67x \cdot y + 0.73x + 56.65y - 51.60$. Cæsium is abnormal in this series, its constant being smaller than that of rubidium although in other series, for example in the sulphates, selenates, manganates, and chlorates, it is normal. The cubic haloids of copper, silver, and thallium form a good series in which the following constants appear, $\text{Cu}^{\cdot}:1.00$, $\text{Ag}^{\cdot}:0.920$, $\text{Tl}^{\cdot}:1.40$. Hexagonal silver iodide does not fit in with the other cubic substances. The same law is shown to hold for numerous other isomorphous series containing metals of the second and fourth groups. The following density determinations were made: lithium fluoride, $d^{20.4} 2.597$; sodium fluoride, $d^{20.2} 2.726$; potassium fluoride, $d^{18.8} 2.369$.

E. H. R.

The Variation of the Mechanical Properties of Metals and Alloys at Low Temperatures. LÉON GUILLET and JEAN COURNOT (*Compt. rend.*, 1922, **174**, 384—386).—The hardness and resilience of a number of metals and alloys have been measured at 20° , -20° , -80° , and -190° . The results show that there is, in general, an increase in the hardness with cooling, there being a fairly big jump from the value at -80° to that at -190° . Fragility at low temperatures is a characteristic of ferrite, the rapidity of the fall in resilience as a function of the temperature being greater as the ferrite content is higher. Nickel and copper, on the other hand, do not lead to fragility and aluminium, if present to any great extent, tends to produce a slight increase in the resilience. Pure austenite sufficiently rich in nickel does not show fragility at low temperatures. Special perlitic steels containing nickel have a high fragility in liquid air, but the addition of nickel retards the lowering of the fragility with decrease in temperature.

Measurements of hardness and resilience after a specimen has been kept for sixteen hours at -190° and then for twenty-four hours at $+20^{\circ}$ give evidence of a return to normal properties at the ordinary temperature.

W. G.

Surface Tension of Corresponding States. RICHARD LORENZ and W. HERZ (*Z. anorg. Chem.*, 1922, **120**, 320—328).—The expression $\gamma_s/\gamma_e = (1 - T_s/T_k)/(1 - T_e/T_k) \cdot (V_e/V_k)^{2/3}$ is deduced. T_s/T_k and T_e/T_k have been shown by Lorenz (*A.*, 1916, ii, 311) to be practically constant. According to the best average values, $T_s/T_k = 0.64$, $T_e/T_k = 0.44$, $(V_e/V_s) = 0.855$, and therefore $\gamma_s/\gamma_e = 0.578$. This was tested on results obtained by Jaeger (*A.*, 1917, ii, 33) and figures are given for 89 organic compounds. The average value for γ_s/γ_e was found to be 0.52, 75% of compounds agreeing very closely. Twenty-one inorganic compounds of known boiling points gave an average for $\gamma_s/\gamma_e = 0.58$. Assuming $\gamma_s/\gamma_e = 0.578$, the authors have calculated the boiling points of several salts. The higher the critical temperature the further does γ_s/γ_e deviate from the mean.

W. T.

Surface Tension of Aqueous Solutions of Night-blue. R. DE IZAGUIRRE (*Anal. Fis. Quím.*, 1922, **20**, 40—55; cf. Traube, A., 1912, ii, 740, 741).—The surface tension of aqueous solutions of night-blue of varying concentrations and with the addition of different electrolytes was investigated by means of the stalagmometer. The increase of surface tension with concentration is fairly rapid at first, but then slows down. In the experiments with addition of electrolytes, it was found that an abrupt fall in surface tension to that for pure water took place at the point where coagulation of the solution occurred. The coagulating power of various ions can thus be studied by means of the stalagmometer. Other physical properties, including the aspect under the ultramicroscope, do not show this abrupt change at the point of coagulation. Solutions purified by dialysis give results analogous to those obtained with unpurified material, but the stability of the solutions obtained is less, since smaller concentrations of salts are necessary for coagulation. G. W. R.

Theory of Adsorption Processes. A. EUCKEN (*Z. Elektrochem.*, 1922, **28**, 6—16).—A theoretical paper in which the process of physical adsorption is considered. By physical adsorption is understood that adsorption, for example, of argon by charcoal, where it is unlikely that the adsorbed molecules are held by the attractions of chemical forces. It is shown that the adsorption forces are similar to the forces which are responsible for condensation phenomena. They are practically independent of the temperature and are operative over a relatively small distance which is of the same order as the molecular radius. J. F. S.

Adsorption of Ammonia by Silica Gel. L. Y. DAVIDHEISER and W. A. PATRICK (*J. Amer. Chem. Soc.*, 1922, **44**, 1—8).—A continuation of previous work (A., 1920, ii, 417). The adsorption of ammonia by silica gels containing respectively 4.98% and 0.33% of water has been determined for a series of pressures at 0°, 30°, 40°, and 100°. A smaller amount of ammonia is adsorbed by the less hydrated gel than by the more hydrated compound, although the less hydrated gel is still capable of adsorbing large amounts of ammonia. It is shown that the adsorption of ammonia may be satisfactorily explained on the basis of capillary condensation, provided corrections are made for the amount of gas which dissolves in the water. J. F. S.

Adsorption by Precipitates. V. Adsorption during the Precipitation of Colloids by Mixtures of Electrolytes. HARRY B. WEISER (*J. Physical Chem.*, 1921, **25**, 665—683; cf. A., 1919, ii, 269; 1920, ii, 228; 1921, ii, 625).—The precipitation of colloidal ferric hydroxide and colloidal arsenious sulphide by the simultaneous addition of pairs of electrolytes, and the adsorption of ions during the precipitation of the colloids by mixtures of electrolytes, have been investigated. The precipitation experiments were carried out with pairs of the electrolytes, potassium chloride,

barium chloride, strontium chloride, potassium oxalate, potassium sulphate, and potassium bromate. The adsorption of the oxalate ion in the presence of the chloride and sulphate ion respectively and the barium ion in the presence of the potassium ion was investigated. It is shown that the precipitating action of mixtures of pairs of electrolytes is approximately additive if the precipitating power of each is of the same order of magnitude, but may be far from additive if the electrolytes have widely varying precipitating power. In the latter case, the action of the electrolytes is antagonistic in the sense that relatively more of each is necessary than if the other were absent. In the simultaneous adsorption by solids from mixtures of two electrolytes having no common ion, the most strongly adsorbed kation and anion are taken up most and the other pair least readily; from mixtures having one common ion the oppositely charged ions are each adsorbed less than if the other were absent, but the most readily adsorbed ion is displaced the least. Factors which influence the precipitating action of mixtures of electrolytes are the effect of the presence of each precipitating ion on the adsorption of the other and the stabilising action of the ions with the same charge as the colloid. The second factor is of minor importance with mixtures of electrolytes that have similar precipitation values and have stabilising ions in common. The precipitating action of mixtures of electrolytes with similar precipitating power is additive, since the adsorption of the precipitating ions is similar and consequently the adsorption of each is affected but slightly by the presence of the other within the limits of the precipitation concentration. With mixtures of electrolytes of widely varying precipitating power, the precipitating action may be approximately additive when the influence of both factors, mentioned above, is small, but may be far from additive when the influence of both factors is large. These extreme cases are realised experimentally.

J. F. S.

Use of the Water Interferometer as a Pressure Gauge.

L. VAN DOREN, H. K. PARKER, and P. LOTZ (*J. Amer. Chem. Soc.*, 1921, **43**, 2497—2501).—The Zeiss water interferometer can be modified so as to serve as a pressure gauge. The modification consists in replacing the two water cells by two brass cells fitted with stout plate glass windows at the ends. One cell is filled with water at atmospheric pressure and the other with water under pressure. On calibrating the instrument, it was found that pressures up to sixty atmospheres could be measured. The range of the instrument may be increased by inserting a thin glass plate in the path of the beam passing through the non-pressure chamber of such a thickness that it will compensate for a pressure of sixty atmospheres in the other chamber. Thus by means of a series of glass plates of different thickness the range of the instrument can be extended to almost any pressure. In the calibration of the instrument for pressures up to 270 atmospheres at 20° and 30° it is found that at the higher temperature the effect of increased pressure on the refractive index diminishes.

J. F. S.

Osmotic Pressures of Concentrated Solutions of Sucrose as Determined by the Water Interferometer. PAUL LOTZ and J. C. W. FRAZER (*J. Amer. Chem. Soc.*, 1921, **43**, 2501—2507).—The authors describe a modification of the method used by Frazer and Myrick for measuring the osmotic pressure (*A.*, 1916, ii, 603). The principal feature of the new apparatus is the use of the water interferometer (preceding abstract) for determining the magnitude of the pressures developed. The apparatus is a decided improvement on that of Frazer and Myrick, being more rapid in action and more trustworthy. Pressures up to 273 atmospheres have been measured, but the instrument has been calibrated up to 330 atmospheres. Pressure measurements are recorded for sucrose solutions of concentrations up to saturated solutions at 30° and 55.7°. Attention is directed to the results of Woods as calculated for vapour-pressure measurements, and it is shown that his results (*Trans. Faraday Soc.*, 1915, **11**, 29) showing a decrease in osmotic pressure with rise in temperature in concentrated solutions are relatively correct, although his actual values for the osmotic pressure appear to be high when compared with these direct measurements. J. F. S.

System: Ammonia-Water as a Basis for a Theory of the Solution of Gases in Liquids. BENJAMIN S. NEUHAUSEN and W. A. PATRICK (*J. Physical Chem.*, 1921, **25**, 693—720).—A static method has been developed for measuring the partial pressure of a component of a liquid mixture which has a very small partial pressure compared with that of the second component. This method has been used to determine the partial pressures of water and ammonia solutions at 0°, 20°, and 40° at partial pressures of ammonia varying from 1000 mm. to 4000 mm. The measurements in the case of ammonia are made to 2—4 mm., and in the case of water to 0.08 mm. The solubility of ammonia in water was determined at 0°, 20°, and 40° at pressures from 750 mm. to 3600 mm., and the densities of the saturated solutions were also measured. A theory of the nature of solutions of gases in liquids first advanced by Graham has been amplified, and solutions of various gases in liquids classified on the basis of some of the physical and chemical properties of the gas. The formula $V = K(P\sigma/P_0)^{1/n}$ has been found to represent the solubility of ammonia, hydrogen chloride, sulphur dioxide, and carbon dioxide in water at various temperatures and pressures. In this formula V is the volume occupied by the liquefied gas dissolved per gram of water, P_0 is the vapour pressure, and σ the surface tension of the liquefied gas at the temperature, whilst P is the equilibrium gas pressure. The constant K for ammonia has value 0.49 and $1/n$ the value 0.69. The solubility data of hydrogen chloride, sulphur dioxide, and carbon dioxide have been plotted according to this formula. J. F. S.

Change of State of Aggregation and Polymorphism. KARL SCHAUM (*Z. anorg. Chem.*, 1921, **120**, 241—260).—The assumption of Ostwald that there is a relatively broad region of metastability, below the normal melting point, in which spontaneous crystallisation

is impossible, appears unnecessary. On the other hand, it is highly improbable that, in a small quantity of liquid in a limited time, the necessary number of molecules in the correct space-lattice orientation to form a nucleus in equilibrium with the liquid at a given temperature will ever come together. It is reasonable to assume with Ostwald the existence of "anisotropic" molecules, but these cannot alone have a "resonance" effect on other "isotropic" molecules and so cause crystallisation. The ageing of a liquid by keeping it some time above its melting point, whereby the tendency to supercooling is increased, is doubtless due to the change of anisotropic molecules into the isotropic form. Anisotropic molecules probably become associated with one another to form space-lattice fragments, and when a crowd of these come together they may cause a field of force strong enough to bring about the formation of a crystal nucleus. As the temperature falls, this process is facilitated through the slowing down of translatory and rotatory motion, but, on the other hand, the probability of the crowding together of anisotropic molecules and space-lattice fragments is lessened.

[With ELLI RIFFERT.]—The crystallisation process is investigated statistically by counting the number of nuclei formed when a thin film of liquid is allowed to crystallise between microscope slide and cover-glass under different conditions. A large number of organic substances were used for the purpose. There is a strong tendency for the nuclei to form in the outer zone of the cover-glass, particularly at the edge, and sometimes they will form again and again at a particular spot. The tendency to nuclei formation at boundary surfaces, especially a triple boundary such as air-glass-liquid, is probably a surface tension phenomenon. The number of nuclei formed increases as the temperature is lowered, finally reaching a maximum. In these experiments, the melted substance was brought suddenly down to the temperature at which the nuclei were to be formed. Pressure may cause the development of nuclei. The substances examined (about 200) fall into five different types, according to the manner in which they crystallise; the states of aggregation assumed by crystallisation from nuclei are described as radiating, bunching, star-like, tabular, and mosaic.

E. H. R.

The K_α Doublet, with New Determinations of the Lattice Constants of some Crystals. WALTHER GERLACH (*Physikal. Z.*, 1922, 23, 114—120).—When a somewhat coarse powder is used in the Debye-Scherrer method, the K_α lines appear double. A method for the measurement of the fine structure of Röntgen lines is described. The lattice constants, in 10^{-8} cm., of the following crystals were determined: silicon (identical, within the limits of error, with "amorphous," graphitoid, and crystalline silicon): 5.415 ($\pm 0.3\%$) with copper radiation; 5.410 ($\pm 0.3\%$) with nickel radiation; regular zinc blende 5.390 ($\pm 0.3\%$) with copper radiation; calcium fluoride 5.455 ($\pm 0.1\%$) with copper radiation; 5.478 ($\pm 0.2\%$) with nickel radiation. The doublet distance $K_{\alpha_1-\alpha_2}$

was determined with an accuracy of about 3% as 3.842 X.U. (1 "X-Unit" = 10^{-11} cm.) for copper, and 3.772 X.U. for nickel. Bragg's model for fluorite was confirmed. J. R. P.

Freezing of Hydrosols. A. LOTTERMOSER (*Kolloid Z.*, 1922, 30, 133).—A complaint that Gutfier (this vol., ii, 142) has used the author's statements in connexion with the influence of freezing on sols in a manner opposite to that which the author has intended. This has arisen because the author's statements have not been understood in the sense demanded by the context. J. F. S.

Influence of the Concentration of Colloids on their Precipitation by Electrolytes. HARRY B. WEISER and HENRY O. NICHOLAS (*J. Physical Chem.*, 1921, 25, 742—757).—The precipitation of colloidal chromic oxide, Prussian blue, ferric oxide, and arsenious sulphide of various concentrations by electrolytes with precipitating ions of different valency has been investigated. With colloidal chromic oxide, Prussian blue, and ferric oxide, the precipitating values of all electrolytes decrease as the concentration of the colloid decreases, irrespective of the valency of the precipitating ion; but the decrease is least marked with electrolytes having univalent precipitating ions. With colloidal arsenious sulphide, the precipitating value of electrolytes with univalent precipitating ions increases as the concentration of the colloid is decreased. The manner in which the precipitation value of an electrolyte varies with the concentration of colloid is determined to a large extent by the relative adsorbability of the precipitating ion and the stabilising ion. If the adsorption of the stabilising ion of an electrolyte is negligible and the adsorption of the precipitating ion is very large, the precipitation value varies almost directly with the concentration of the colloid. This condition may be realised experimentally with electrolytes which have trivalent and quadrivalent ions which precipitate in extremely low concentration. If the adsorption of the stabilising ion of an electrolyte is appreciable, the precipitating value is increased. This effect is more pronounced the greater the dilution of the colloid, since the decreased opportunity both for the collision and the coalescence of particles combines to render the colloid proportionately more stable so that relatively more of the precipitating ion must be added for complete coagulation. The influence of adsorption of the stabilising ion is more marked with electrolytes having univalent precipitating ions which precipitate only in very high concentration. Under these conditions, the precipitation value decreases much less sharply than under the conditions obtaining when the stabilising ion is only slightly adsorbed, and may even increase as the concentration of the colloid is decreased. The laws put forward by Burton and Bishop (*A.*, 1921, ii, 176) in connexion with the variation in the coagulative power of ions with the concentration of the disperse phase are shown to be quite limited in their applicability. The hypothesis of Kruyt and van der Spek (*A.*, 1919, ii, 498) on the nature of the process of coagulation

ation is inadequate, since it fails to take into account the influence of the stabilising ions of electrolytes. J. F. S.

Relation of Anomalous Osmosis to the Swelling of Colloidal Material. F. E. BARTELL and L. B. SIMS (*J. Amer. Chem. Soc.*, 1922, **44**, 289—299).—The authors discuss some seven hypotheses put forward previously to account for the swelling of colloids, and find none of them is applicable to all cases of swelling. The relationship of the swelling of gels to the osmotic effects is considered, and as a working hypothesis it is assumed that a gel may be considered as composed essentially of a framework of membranes and that the hypothesis which accounts for the flow of a liquid through membranes also accounts to a certain extent for the flow of a solution into a cellular gel. The view is held that swelling is the result of imbibition together with the operation of effects which produce anomalous osmosis. It would therefore follow that in swelling the tendency for normal osmosis is always operative, solution in the membrane may take place in some instances, forces of attraction and repulsion are operative, capillarity plays a part, negative or positive adsorption of solute may have an effect, electrical effects due to electrical orientation of the system may enter in, and swelling unaccompanied by electrical effects may occur, as with solutions of non-electrolytes with some gels. For the purpose of comparing anomalous osmotic effects with swelling effects, a series of osmotic pressures using parchment membranes and a series of swelling experiments using *Laminaria* have been carried out with solutions of potassium citrate (0.05*M*), sodium hydroxide (0.0001*N*), hydrochloric acid (0.0001*N*), and aluminium chloride (0.05*M*). The results show that those solutions which exhibit a negative osmotic tendency with parchment produce a swelling effect with *Laminaria*, and those which have a positive osmotic tendency produce a shrinking of the *Laminaria*. A further series of experiments with solutions of various electrolytes of several concentrations confirms the foregoing results. In all cases, the osmosis-concentration curves have the exactly opposite form to those of the concentration-swelling curves. J. F. S.

Lecture Experiment. Protective Colloids. J. NEWTON FRIEND (*Nature*, 1922, **109**, 341).—It appears to be a general law that protective colloids or organic emulsoids tend to retard the velocities of such reactions, whether chemical or physical, as involve a change of state in one or more of the components. Examples of such retardation, the rate of which conforms in many cases to the requirements of the adsorption law, are to be found in the solution of metals in acids, corrosion in neutral media, solution and precipitation of salts, and replacement of one metal by another. An illustration is afforded by the precipitation of mercuric iodide from solutions of mercuric chloride and potassium iodide, the unstable yellow form first precipitated ordinarily turning rapidly into the more stable red variety. In the presence, however, of 1% of gelatin, after a momentary formation of colloidal mercuric iodide, a fine, canary-yellow precipitate is produced, and remains

practically unchanged for half an hour or more. The slow change to the red variety is markedly accelerated by sunlight. A. A. E.

Pure Aniline and Water Emulsions. SHANTI SWARUPA BHATNAGAR (*J. Physical Chem.*, 1921, **25**, 735—741).—The rate of coagulation of aniline-water emulsions by potassium chloride, sodium chloride and sulphate, barium, strontium, chromium, and aluminium sulphates has been investigated at 46°. The results show that in general the precipitating power of electrolytes is the same as in the case of many sols, trivalent ions being more effective than bivalent ions and these more so than univalent ions. The order of the precipitating efficiency of the kations is given as $\text{Al} > \text{Cr} > \text{Ba} > \text{Sr} > \text{K} > \text{Na}$. The effect of dilution on the emulsions is to increase the time required for precipitation; thus an emulsion which is normally precipitated in ten minutes by barium chloride requires eighteen minutes seven seconds when diluted by an equal volume of water saturated with aniline, and when again diluted by the same volume of saturated water forty minutes. J. F. S.

The Detergent Power of Soap Solutions. R. T. A. MEES (*Chem. Weekblad*, 1922, **19**, 82—85).—The conception of Martin Fischer of a soap solution as a two-phase system is inadequate, since it does not exclude other gels, for example, gelatin solutions. Similarly, the orientation theory of Langmuir and Harkins does not exclude other substances possessing polarity within the molecule. The unique power of soap solutions to stabilise emulsions can be explained by combining the two theories, since only soaps have the necessary polar character within the molecule without at the same time having molecules soluble as such in oil and water. A soap such as sodium palmitate has the reactive sodium ion, which tends to confer solubility in water, opposed within the molecule to the inert, saturated carbon-hydrogen chain, which tends to confer solubility in oily substances. When such a soap is intimately admixed with an oily substance and water, it forms a bounding layer between the particles of each, its molecules being orientated with the sodium ion towards the water, the carbon-hydrogen chain towards the oil, acting as a layer possessing polar solubilities; in such a system, surface tension disappears.

Earthy impurities, such as clays, resemble soaps in stabilising water-oil emulsions, being lyophil towards both; in presence of soap solution, they are adsorbed by the latter in the bounding surfaces between the particles of oily matter and water.

The detergent power of soaps is therefore primarily a chemical property due to the polarity of molecules insoluble as such in oil and water. S. I. L.

Cellulose Nitrate as an Emulsifying Agent. HARRY N. HOLMES and DON H. CAMERON (*J. Amer. Chem. Soc.*, 1922, **44**, 66—70).—The use of cellulose nitrate as an emulsifying agent has been studied. It is shown that this substance serves as an excellent emulsifying agent in dispersing water or glycerol throughout

amyl acetate, acetone, or other solvents for the nitrate. Visible concentration films of cellulose nitrate were observed round large drops of water emulsified in amyl acetate-benzene mixtures. An increase in concentration of cellulose nitrate at the acetone-glycerol interface was observed and studied quantitatively. The properties of an ideal emulsifying film are discussed. J. F. S.

Chromatic Emulsions. HARRY N. HOLMES and DON H. CAMERON (*J. Amer. Chem. Soc.*, 1922, **44**, 71-74).—Two immiscible liquids can be emulsified with suitable emulsifying agents, such as cellulose nitrate, to produce a transparent emulsion when the refractive index of the two phases is the same, and when the dispersive power ($n_F - n_C$) of the two phases is the same. A chromatic (structural colour) emulsion is produced when the refractive index of both phases is the same and the dispersive power of one phase is much greater than that of the other phase. The greater the difference the more intense the resulting colour.

J. F. S.

Application of Statistics to Chemical Equilibria. K. F. HERZFELD (*Physikal. Z.*, 1922, **23**, 95-100; cf. A., 1921, ii, 313).—Statistical principles have been applied to chemical equilibria, in connexion with polymorphic substances and equilibria in gaseous systems at low temperatures and at high temperatures. A reason is advanced for the good agreement found between experimental results and those calculated by the Nernst approximation formula, and it is shown to be probable that the conventional chemical constant is always about 3.

J. F. S.

Equilibrium in Mixtures of Binary Electrolytes. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1921, **43**, 2507-2514).—A theoretical paper in which it is shown that the isohydric principle, when applied to mixtures of electrolytes, leads to a functional relationship of the form $(C_i)^2/C_u = F(\Sigma C_i)$ in which C_u is the concentration of the undissociated fraction, C_i the ion concentration, ΣC_i the sum of the concentrations of all the negative and positive ions in the solution, and $F(\Sigma C_i)$ any explicit function of the total ion concentration of the solution. As the concentration of the second electrolyte diminishes, the function $P_i/C_u = F(P_i)$, in which P_i is the ion product, reduces, in the limit, to the same form as the function resulting from the isohydric principle. The values of the specific conductivity of mixtures of sodium chloride and hydrochloric acid as calculated according to this principle are shown to furnish a better agreement with the measured values than are those on the isohydric principle.

J. F. S.

Partition of Chlorine between Water and a Gaseous Phase. W. S. TITOV (*Nachr. Physik.-chem. Lab. Semsoinsés*, 1917, 102-110; from *Chem. Zentr.*, 1921, iii, 1222).—The partition of chlorine at 20° between water and air containing this gas is given by the formula $(y - 1.748)^3 x^2 = (72.52)^3$, where x is the volume of chlorine per thousand volumes of air and y is the volume dissolved in the water under the corresponding partial pressure. For example,

when $x=10$ parts per thousand, $y=74.27$ under a partial pressure of 7.6 mm.

G. W. R.

Nature of Secondary Valency. III. Partition Coefficients in the System Water-Ethyl Ether. HOMER W. SMITH (*J. Physical Chem.*, 1921, **25**, 605—615, 616—627; cf. A., 1921, ii, 315, 324).—In the first paper, details are given of the determination of the partition coefficient of forty-nine organic acids and fifteen organic bases at 25° in the system water-ethyl ether. The results obtained from a comparative treatment of these partition coefficients in terms of molecular volume are in good agreement with the results obtained previously (*loc. cit.*) in the systems water-xylene, and water-chloroform. The results are discussed in connexion with the principles laid down in previous papers. The second paper is a supplementary note on the method of correction employed in the earlier papers. Corrected values for the partition of chloroacetic acid in the system water-chloroform and for a number of organic acids and bases in the systems water-ether are given.

J. F. S.

Nature of Secondary Valency. IV. Partition Coefficients in the System Glycerol-Acetone. HOMER W. SMITH (*J. Physical Chem.*, 1921, **25**, 721—734; cf. preceding abstract).—The partition coefficients of fifty acids, amines, and amine acid phthalates have been determined in the system acetone-glycerol. The present results are in excellent agreement with those obtained in the systems previously investigated (*loc. cit.*). In the present series of experiments, a fact, which has not been observed previously, is noted, namely, that under certain conditions, concerning the nature of the solvents and the solutes, a solute is not distributed, but is concentrated entirely in one or other of the solvents. The series constants for the acids and amines have the same absolute value in this system, as contrasted with the different values found in systems containing water as one solvent. Of the substances examined in the system glycerol-acetone, benzoic acid, benzoic acid, $\alpha\beta$ -dibromopropionic acid, 2:4-dinitrobenzoic acid, diisobutylamine, salicylic acid, 2:4:6-trinitrobenzoic acid, and *n*-valeric acid pass completely into the acetone layer.

J. F. S.

Equilibrium in the Reaction between Sulphur Dioxide and Water. F. RUSSELL BICHOWSKY (*J. Amer. Chem. Soc.*, 1922, **44**, 116—132).—The reactions between liquid sulphur and aqueous sulphuric acid have been investigated over a wide range of conditions. At low concentrations of sulphuric acid, two reactions occur simultaneously, namely, (1) $S_{(\lambda\mu)} + 2H_2SO_4(aq) = 2H_2O(liq) + 3SO_2(gas)$ and (2) $4S_{(\lambda\mu)} + 4H_2O(liq) = 3H_2S(gas) + H_2SO_4(aq)$. Both reactions are reversible. In the acids of a greater molecular fraction than 0.05, and at temperatures up to the critical temperature of water, the second reaction becomes negligible. Equilibrium pressures for the first reaction have been measured for acids of molecular fractions ranging from 0.041 to

0.363 and at temperatures from 527° Abs. to 613° Abs., using an apparatus of a new type. The vapour pressures of sulphuric acid of various concentrations have been measured. Using these and other existing data, the free energy for the reaction $S_{(s)} + 2H_2SO_4(M) = 2H_2O(gas) + 3SO_2(gas)$ has been calculated to be 31500 cal. at 25° and standard conditions. From the data the free energy of both aqueous sulphuric acid and sulphur dioxide may be calculated. A new type of apparatus for measuring equilibrium or vapour pressures of corrosive liquids up to high pressures and temperatures is described. This consists of a quartz tube contained in a mercury-filled steel bomb which communicates with a pressure gauge. The quartz tube is constructed so that the material is contained in a chamber at the top; this communicates through a quartz capillary with a second chamber filled with mercury which is in contact with the mercury in the steel jacket. The upper part of the bomb only is heated. J. F. S.

Equilibria in the Systems: Carbon Disulphide-Methyl Alcohol and Carbon Disulphide-Ethyl Alcohol. E. C. McKELVY and D. H. SIMPSON (*J. Amer. Chem. Soc.*, 1922, **44**, 105—115).—The temperature of complete mutual miscibility of mixtures of carbon disulphide with ethyl and methyl alcohols respectively have been determined. The critical solution temperature of the system carbon disulphide-methyl alcohol is 35.7° and the critical concentration is about 85% of carbon disulphide; solid methyl alcohol separates from the layer rich in alcohol at -99.6°. The critical solution temperature of the system carbon disulphide-ethyl alcohol is -24.4° and the critical concentration about 83% by weight of carbon disulphide. All mixtures freeze at -111.7°. It is shown that the critical solution temperature offers an extremely sensitive criterion of the purity or changes of purity of either component, provided that the other component is either pure or of constant composition. Distillation of carbon disulphide from ceresin is shown to remove the impurities and yield a perfectly pure product. J. F. S.

The Quaternary System: Ammonium Chloride-Sodium Sulphate-Ammonium Sulphate-Sodium Chloride-Water. ALBERT CHERBURY DAVID RIVETT (*T.*, 1922, **121**, 379—393).

Induction Periods in Reactions between Thiosulphate and Arsenite or Arsenate. A Useful Clock Reaction. GEORGE SHANNON FORBES, HOWARD WILMOT ESTILL, and OSMAN JAMES WALKER (*J. Amer. Chem. Soc.*, 1922, **44**, 97—102).—The precipitation of arsenious sulphide from an acidified solution (acetic acid) containing sodium thiosulphate and arsenite is preceded by an exceedingly sharp and reproducible induction period. The duration of the induction period is strictly in inverse proportion to the concentration of thiosulphate and is practically independent of the concentration of the arsenite or the acetic acid. Hydrochloric acid prolongs the induction periods and is much better for experimental demonstration of induction periods, of the relationship

between concentration and reaction velocity, and of the temperature coefficient of the reaction velocity, than the familiar sulphurous acid and iodate reaction. The prolongation of the periods by strong acids, the limiting concentrations yielding precipitates when arsenates are used, and the speed of precipitation were also investigated. J. F. S.

The Combustion of Complex Gaseous Mixtures. WILLIAM PAYMAN and RICHARD VERNON WHEELER (T., 1922, **121**, 363—379).

Oxidation of Nitric Oxide and its Catalysis. CHARLES LALOR BURDICK (*J. Amer. Chem. Soc.*, 1922, **44**, 244—251).—The rate of oxidation of nitric oxide by oxygen in the presence of glass, pumice, pumice impregnated with tungstic acid, nickel oxide, cobalt oxide, nickel, cobalt, and manganese dioxide, platinised pumice, platinised asbestos, coke, charcoal, and coconut charcoal, has been investigated at temperatures from 0° to 100°. It is shown that the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ is not catalysed by ordinary porous material either impregnated or unimpregnated, but that in the presence of the highly absorptive forms of carbon or charcoal the rate of the reaction may be accelerated as much as five hundred times. The presence of water vapour in the gaseous mixtures greatly decreases the activity of the charcoal catalysts. Increase of temperature above the point at which the aqueous vapour condenses counteracts this effect to some extent. The temperature coefficient of the velocity of reaction for both the catalysed and uncatalysed change is generally negative. In the presence of water vapour the temperature coefficient of the catalysed reaction is apparently positive. This is probably due to the decreased absorption of water by the catalyst at elevated temperatures. J. F. S.

The Transformation of Ammonia into Carbamide. C. MATIGNON and M. FRÉJACQUES (*Compt. rend.*, 1922, **174**, 455—457; cf. A., 1921, ii, 33).—In continuation of previous work (*loc. cit.*), the yields of carbamide from ammonium carbamate at the equilibrium point at different temperatures are given. Applying the law of mass action to the system in equilibrium the authors calculate the heat of the reaction to be -6 cal., the experimental value being -7.7 . The progress of the reaction with time at different temperatures from 130° to 145° has been studied. The curves indicate that the water formed has an effect on the velocity of the reaction. The effect of certain catalysts such as thorium oxide, aluminium oxide, kaolin, etc., has been examined. The results indicate that whilst they may accelerate the reaction at low temperatures, they are without benefit at about 150°. W. G.

The Processes $\text{NH}_2 \cdot \text{CO} \cdot \text{ONH}_4 + \text{H}_2\text{O} \rightleftharpoons (\text{NH}_4)_2\text{CO}_3$ and $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$. CARL FAURHOLT (*Z. anorg. Chem.*, 1921, **120**, 85—102).—Experiments on the velocity of the conversion of ammonium carbamate into carbonate indicated that the reaction proceeded first with liberation of carbon dioxide, and this con-

clusion was confirmed by an investigation of the velocity of the reaction $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$. A new method was devised for estimating the proportion of hydrated carbon dioxide, that is, of carbonic acid, in a solution of the gas. When an aqueous solution of carbon dioxide is added to a large excess of ammonia, the anhydrous carbon dioxide immediately forms carbamate, which is so stable in the concentrated ammonia that there is time to precipitate the carbonate as barium carbonate, filter, wash, and titrate it. By this method the dissociation constant of carbonic acid to $\text{H}^+ + \text{HCO}_3^-$ was found to be 10^{-13} , against 10^{-37} to 10^{-44} found by Thiel and Strohecker (A., 1914, ii, 361). This method was applied to making approximate determinations of the velocity of hydration of carbon dioxide in solutions of sodium hydroxide, sodium carbonate, and mixtures of carbonate and hydrogen carbonate. At 0° , hydration is immediate in sodium hydroxide solution, but in a solution containing $\text{Na}_2\text{CO}_3 : \text{NaHCO}_3$ in the ratio 6:4 only 77% of the carbon dioxide added is hydrated in the first eighty seconds. Hydration is thirteen times as rapid at 18° as at 0° . Velocity of hydration is inversely proportional to hydrogen-ion concentration. By strong acids, carbonic acid is immediately dehydrated, but by weak acids much more slowly.

The same method of analysis was used for investigating the decomposition of ammonium carbamate in acid, aqueous, ammoniacal, and alkaline solution. Before analysis, the solutions were made alkaline with 0.1N sodium hydroxide to stabilise the carbamate. In aqueous solutions containing ammonia and ammonium chloride, the proportion of carbamate present at equilibrium increases with the concentration of either. The equilibrium constant for the reaction $\text{NH}_2 \cdot \text{CO} \cdot \text{O}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{NH}_3$ at 0° had an average value of about 0.34. By even very weak acids, carbamate is immediately decomposed. On adding alkali again, however, some carbamate is re-formed, since two reactions proceed simultaneously with nearly the same velocity, carbamate being formed from ammonia and carbon dioxide, and carbonate from carbonic acid, which is formed at once by hydration of part of the carbon dioxide by the alkali added.

In a 0.05 mol. solution of carbamate in water at 0° , equilibrium is reached in about a day; in a 0.1N-ammonia solution, three days are required, in a 0.4N-ammonia solution, ten days; at 18° the reaction is twenty times as fast. In sodium hydroxide solution, the reaction is much slower, requiring about three days in a 0.1N-solution and a month in a 1.0N-solution, at 18° . E. H. R.

The Velocity of Formation of Barium Peroxide. NOBUJI SASAKI (*Mem. Coll. Sci. Kyoto*, 1921, 5, 9—96).—For the investigation of the velocity of formation of barium peroxide from barium oxide and oxygen at high temperatures, 400—625°, a special balance was devised, so constructed that the specimen under examination could be weighed at any time, being suspended from one arm of the balance, which was totally enclosed and operated from outside by means of magnets. A new type of gas washer was also devised.

It consists of a U-tube of glass, one arm being narrow and the other expanded into an elongated bulb. The two arms are bridged by a narrow glass spiral in such a manner that the gases, entering by the narrow arm, bubble through the liquid in the spiral and escape at the top of the wide arm, which acts as a reservoir for the washing liquid. The velocity curves for the formation of barium peroxide were of an unusual form. The greater part of the paper is devoted to a mathematical analysis of these curves, and it is shown that they may be explained on the assumption that the oxide consists of a great number of very small, equal spherical particles which begin to react one after another, the number of spheres becoming active in unit time being proportional to the quantity of peroxide already formed. E. H. R.

The Influence of Protective Colloids on the Corrosion of Metals and on the Velocity of Chemical and Physical Change. JOHN ALBERT NEWTON FRIEND and REECE HENRY VALLANCE (T., 1922, 121, 466—474).

Influence of Temperature on Two Alternative Modes of Decomposition of Formic Acid. C. N. HINSHELWOOD, H. HARTLEY, and B. TOPLEY (*Proc. Roy. Soc.*, 1922, [A], 100, 575—581).—The thermal decomposition of formic acid has been investigated at 283°, and from the results an hypothesis has been formulated in connexion with the mechanism of the reaction. Sabatier and Mailhe (A., 1911, i, 515) have shown that formic acid may decompose according to the equations (a) $\text{H}\cdot\text{CO}_2\text{H}=\text{CO}_2+\text{H}_2$, (b) $\text{H}\cdot\text{CO}_2\text{H}=\text{CO}+\text{H}_2\text{O}$, and (c) $2\text{H}\cdot\text{CO}_2\text{H}=\text{H}\cdot\text{CHO}+\text{CO}_2+\text{H}_2\text{O}$. Assuming that in the decomposition certain molecules are activated, either by collision with other molecules or by the absorption of quanta of radiation, the question arises whether every molecule which possesses the necessary critical energy reacts at once or whether, in addition to possessing this, it must be in a certain phase. Under the conditions of the experiments described, only reactions *a* and *b* come into consideration. If E_1 and E_2 are the critical energies for the two alternative reactions and N is the total number of molecules, it follows from the kinetic theory that the number of molecules possessing these respective energies are $N_1=N\epsilon^{-E_1/RT}$ and $N_2=N\epsilon^{-E_2/RT}$, taking the system as of two degrees of freedom. Then $N_1/N_2=\epsilon^{-(E_1-E_2)/RT}$, so that if one mode of reaction is associated with a slightly lower critical energy it would predominate very largely if the number of active molecules were the only factor. Actually it is found that although the two alternative modes of decomposition of formic acid proceed with the same velocity, yet the critical increments are so different that one reaction should predominate almost entirely unless a phase restriction is introduced, and an interpretation of the phase factor is suggested for this case, as follows. The critical increments for the two reactions are calculated to $E_{\text{CO}}=16000$ cal./mol. and $E_{\text{CO}_2}=28000$ cal./mol. The numbers of molecules activated for the two reactions are proportional to $\epsilon^{-28000/RT}$ and $\epsilon^{-16000/RT}$, respectively, that is about ϵ^{10} molecules should yield carbon monoxide for one yielding the

dioxide, but since the rates of both reactions are identical a phase restriction must govern the reaction yielding the monoxide. If the formic acid molecule is assumed to be adsorbed on the glass surface by the residual affinity of the carbonyl group, then in the case of a sufficiently activated molecule a violent collision between the hydrogen- and hydroxyl-groups may occur, and a molecule of hydrogen be split off. Although the requisite degree of activation may be attained but rarely, nevertheless a high percentage of these collisions in activated molecules may result in this type of decomposition. On the other hand, for water to be eliminated and carbon monoxide left, a high degree of activation is not necessary, possibly since the removal of a hydroxyl group, as a whole, from an organic compound is a much less profound change than the fission of the hydrogen and oxygen, but very few of the activated molecules may decompose, because it is necessary to await the contingency that the forces holding the hydroxyl and hydrogen to the carbon should be weak enough to allow the simultaneous "uncoupling" of the molecule. J. F. S.

The Replacement of Halogen in 4-Chloro-3-nitrobenzonitrile and in 4-Bromo-3-nitrobenzonitrile. II. T. J. F. MATTAAR (*Rec. trav. chim.*, 1922, **41**, 103—111; cf. this vol., i, 251; also Conrad, Hecht, and Brückner, A., 1890, **4**, 327, and 1046; A., 1891, 796).—In order to measure the effect of the cyanogen group on the replacement of halogen the velocity of reaction of 1-chloro-2 : 4-dinitrobenzene, 4-chloro-3-nitrobenzonitrile, 1-bromo-2 : 4-dinitrobenzene and 4-bromo-3-nitrobenzonitrile with sodium methoxide, with sodium ethoxide, and with sodium phenoxide in both ethyl alcohol and methyl alcohol solution has been investigated. The following conclusions are drawn: (1) the halogen atom is more active in the substituted dinitrobenzene than in the substituted nitrobenzonitrile, (2) chlorine is more reactive than bromine in corresponding compounds, (3) sodium ethoxide reacts more quickly than sodium methoxide, (4) the reaction in ethyl alcohol takes place about twice as quickly as that in methyl alcohol.

H. J. E.

The Effect of Temperature and the Concentration of Hydrogen Ions on the Rate of Destruction of Antiscorbutic Vitamin (Vitamin-C). V. K. LAMER, H. L. CAMPBELL, and H. C. SHERMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 172—181; cf. *ibid.*, 165).—Using the quantitative method previously described (*loc. cit.*), the authors claim to have shown that, under the experimental conditions, the velocity of destruction of vitamin-C by heat decreases with the time and in greater degree than would be expected if the reaction followed the unimolecular law, or the square root rule of Schutz. The temperature coefficient is of low order, namely, $Q_{10}(60-80^{\circ})=1.23$; $Q_{10}(80-100^{\circ})=1.12$. The effect of reducing the hydrogen-ion concentration from $p_H=4.3$ to $p_H=5.2-4.9$ is to increase the destruction during one hour at 100° from 50% to about 58%. When the material was made alkaline, $p_H=10.9-8.3$, the destruction was 61—65%. If re-acidification after heating in

alkaline solution was omitted, there was still further destruction, if the material was allowed to remain alkaline for five days at 10°. The material used as the source of vitamin-*C* was tomato juice.

W. G.

The Influencing of Catalysts and Specifically Active Catalysts. E. ABEL (*Ber.*, 1922, 55, [B], 322—323).—A final reply to Rosenmund and Zetzsche (cf. Abel, A., 1921, ii, 542; Rosenmund and Zetzsche, A., 1921, ii, 320, 392, 393; this vol., ii, 41).

H. W.

The Oxygen-Hydrogen Catalysis by the Platinum Metals and the Contact Potentials in Presence of Aqueous Electrolytes. K. A. HOFMANN (*Ber.*, 1922, 55, [B], 573—588).—Since previous experiments (A., 1920, ii, 240) were performed with platinised porous earthenware tubes, whilst Willstätter and Waldschmidt (A., 1921, ii, 185) employed platinum black, these investigators are not justified in concluding that their results are incompatible with the views of Hofmann and Zipfel (*loc. cit.*). In the present work, no indication could be discovered of the peroxide-hydride, to which Willstätter and Waldschmidt ascribe the favourable effect of oxygen on the catalytic activity of hydrogen (D.R.-P. 301364, Willstätter and Waldschmidt, *loc. cit.*). The volume of oxygen occluded by platinised earthenware is shown to be so small that any peroxide produced cannot bear any relation to the actual effect of oxygen on catalysis, which is rather due to its influence on the catalyst surface. At the same time, the small amounts of gas adsorbed by porous surfaces render them much more suitable than platinum for determinations of variations of contact potential during catalysis. Measurements of the potential difference between such an electrode and one of platinum in contact with hydrogen at atmospheric pressure show that, whether the electrolyte be 17% sulphuric acid or 4% sodium hydrogen carbonate solution, contacts impregnated with platinum, palladium, or iridium in contact with a mixture of hydrogen and oxygen are electrically modified in the opposite sense to that of their previous treatment (with one or other of the gases), and the more rapidly this occurs the more rapidly is water-formation catalysed. The activity diminishes on prolonged treatment with hydrogen or, especially in the case of palladium, with oxygen. It is improved by repeated variation of this treatment, by repeated use with the stoichiometrical mixture of the gases, and by varying galvanic polarisation. Light and moderate temperature changes are much less effective. Hydrogen exerts a greater effect on the catalysis potentials with increased hydrogen-ion concentration of the electrolyte, whilst the reverse is true of oxygen. These results indicate that neither pure hydrogen nor hydrogen-oxygen mixtures produce any special oxidising or reducing compound on the catalyst surface of the kind suggested by Willstätter which determines the potential. Direct instantaneous determinations of the effect on the same electrode potentials of the addition of hydrogen peroxide show that this always acts as a strong oxidising agent, and renders it

highly improbable that any peroxide-hydride could exert a strong reducing influence, apart from the extreme rapidity with which the known peroxides are decomposed by platinum metals. Although it is not improbable that hydrogen peroxide is an intermediate product in the formation of water, its existence is so transient as to elude all attempts to detect it. J. K.

Atomic Structure. N. BOHR (*Nature*, 1921, **108**, 208—209; cf. *ibid.*, 1921, **107**, 104, 170).—Further examination of the orbits of the electrons postulated in the previous communication has shown that the conception of the atom there outlined cannot be reconciled with that which assumes the atom to be composed of a number of well-defined spherical shells of electrons moving in sharply separated regions. The electrons in the atom are still regarded as being arranged in groups in such a way that the orbit of every electron within a particular group is characterised by the same total number of quanta. In proceeding outwards from the nucleus, the number of quanta characterising a certain group of orbits is larger by one unit than that of the preceding group. The electrons of certain sub-groups will also penetrate into the region of the orbits of electrons of inner groups, giving rise to group-coupling, which is reflected in the stability of the atom. These considerations are applied to the cases of the iron group and the rare earths.

A. A. E.

A Magnetic Model of Atomic Constitution. J. K. MARSH and A. W. STEWART (*Nature*, 1921, **109**, 340).—If the central magnetic pole in a tank is maintained at a strength always exactly equal and opposite to the combined powers of a number of floating magnets, and if the number of the latter corresponds with units of atomic weight in various elements, the magnets arrange themselves in two clearly defined and sharply separated groups, termed for convenience the nucleus and ring, respectively. It is a remarkable coincidence that the series of groupings obtained corresponds exactly with Aston's suggestions regarding the atomic structure of a number of elements and isotopes. In the case of boron-11 and carbon, both nuclei contain six magnets arranged in two pairs of concentric triangles, a peculiarity which seems to have some connexion with certain chemical and physical similarities. A. A. E.

Correlation of Atomic Structure and Spectra. HAROLD S. KING (*J. Amer. Chem. Soc.*, 1922, **44**, 323—328).—A theoretical paper in which it is shown that Bury's modification (this vol., ii, 43) of Langmuir's hypothesis of the structure of elements is confirmed in addition to the relationship between the atomic diameter and the number of electron shells, also by the relationship between the atomic number and the number of lines in the arc and spark spectra, respectively. J. F. S.

Motion of Electrons in Atoms. J. S. TOWNSEND and V. A. BAILEY (*Phil. Mag.*, 1922, [vi], **43**, 593—600).—It is shown that when an electron moving with a velocity of the order of 10^8 cm. per second collides with a molecule of argon it loses only about

one ten-thousandth of its energy, whereas previous experiments showed that in collision with oxygen, nitrogen, or hydrogen, it loses more than 1% of its energy. The mean free path of an electron moving with these velocities in argon is about ten times that in the other gases at the same pressure.

J. R. P.

Relationship between the Internal Friction and the Chemical Constitution of Gases. HARRY SCHMIDT (*Z. Elektrochem.*, 1922, **28**, 50—55).—A theoretical paper in which the author has deduced equations by means of which the atomic radius of the elements and the mean cross-section of the simpler molecules may be calculated. Using the formula $r = \sqrt{4k \sqrt{M/7\pi\eta}}$, in which r is the atomic radius, k a constant, M the molecular weight, and η the coefficient of viscosity, the following values of the radii have been obtained: oxygen, 1.000; nitrogen, 1.035; hydrogen, 0.752; chlorine, 1.491; sulphur, 1.477; bromine, 1.841; helium, 0.795; neon, 0.946; argon, 1.336; krypton, 1.553; xenon, 1.794. The mean cross-section of a number of simple compound molecules are also calculated and tabulated.

J. F. S.

Atomic Radius and Ionisation Potential. MEGH NAD SAHA (*Nature*, 1921, **107**, 682—683; cf. Basu, *Phil. Mag.*, 1920, [vi], **40**, 619).—The radius, a_x , of an atom (the distance from the nucleus to the outermost electron of the Rutherford-Bohr model) may be calculated from the ionisation potential, V_x , of an element x , from the equation: $a_x = 10^{-8} \times (0.532 \times 13.56) / V_x$ cm. The atomic radii calculated in this way are smaller than those calculated either from crystal data or from the kinetic theory. The following values, expressed as $a \times 10^8$, were obtained, those derived from other methods being placed within brackets: hydrogen, 0.530; helium, 0.28 (1.08); neon, 0.33 (0.65, 1.01); lithium, 1.34 (1.50); sodium, 1.41 (1.77); potassium, 1.67 (2.07); rubidium, 1.73 (2.25); caesium, 1.86 (2.37); copper, 0.94 (1.37); silver, 0.95 (1.77); gold, 0.83; magnesium, 0.95 (1.42); calcium, 1.18 (1.70); strontium, 1.27 (1.95); barium, 1.39 (2.10); zinc, 0.77 (1.32); cadmium, 0.81 (1.60); mercury, 0.69; thallium, 0.99 (2.25); manganese, 0.98 (1.47).

A. A. E.

New Method of Determining Molecular Diameters by the Electromagnetic Rotation of the Discharge in Gases. C. E. GUYE and R. RÜDY (*Compt. rend.*, 1922, **174**, 382—384).—By applying the theory of ionisation by shock to the phenomenon of rotation of the electric discharge in gases, the velocity of rotation is given by $V = eH/12\pi\sigma^2mM$. Thus with a constant magnetic field and for the same gas, the product of the pressure and the velocity observed must be a constant. A new series of measurements has been made on a number of carefully purified gases. The molecular diameters obtained by this method show a close agreement in value with those deduced from viscosity measurements. Contrary to the general opinion, the observed velocity of rotation is not inversely proportional to the density of the gas,

but to the product of the square of the molecular diameter and the density. W. G.

Atomic Weights and Frequencies. A. REYCHLER (*Bull. Soc. chim. Belg.*, 1922, **31**, 67—72).—Warrington's formula for calculating atomic weights (A., 1915, ii, 160) gives too low a value for elements of the two short series. The author's formula, $A = 2N + 0.007N^2$, gives better values, but is not applicable to hydrogen and is not very satisfactory for elements of the first short series. Attention is directed to the relation of this formula to the equation $\nu = \gamma (N - c)^2$, which expresses frequency of radiation of an element when used as an anticathode. H. J. E.

Qualities of Valency. R. M. CAVEN (*Nature*, 1921, **108**, 210—211).—Polemical. Langmuir's (*ibid.*, 1921, **108**, 101) view that the sodium and chlorine atoms in sodium chloride are not united by a chemical bond is attacked, and criticism offered regarding the postulation of covalency and electrovalency in certain cases. A. A. E.

A Theoretical Derivation of the Principle of Induced Alternate Polarities. ARTHUR LAPWORTH (T., 1922, **121**, 416—427).

An Explanation of the Property of Induced Polarity of Atoms and an Interpretation of the Theory of Partial Valencies on an Electronic Basis. WILLIAM OGILVY KERMAK and ROBERT ROBINSON (T., 1922, **121**, 427—440).

Friend's Theory of Valency. J. D. MAIN SMITH (*Chem. News*, 1922, **124**, 84—86).—Friend's theory of valency as extended in a recent paper (T., 1921, **119**, 1040) is subjected to a detailed criticism. In particular, the direct translation of Thomson's physical conception of "ionised" and "non-ionised" valency into chemical terms is criticised, on the ground that residual valency may partake of the properties of both. Friend's criticisms of some aspects of Werner's theory are discussed. E. H. R.

Space-filling and the Equation of Condition. J. J. VAN LAAR (*Z. anorg. Chem.*, 1921, **120**, 203—208).—A theoretical discussion of the theory of space-filling numbers in relation to van der Waals's equation. E. H. R.

Inorganic Chemistry.

Active Modifications of Hydrogen and Nitrogen produced by α -Rays. F. H. NEWMAN (*Phil. Mag.*, 1922, [vi], **43**, 455—462).—The α -rays from polonium were allowed to act on nitrogen at different pressures in the presence of sodium, potassium, sulphur, phosphorus, iodine, magnesium, arsenic, mercury, and an alloy

of sodium and potassium. Some gas was absorbed. Similar experiments with hydrogen gave absorptions with sulphur, phosphorus, and iodine. The absorption was shown to be due, at least in some cases, to the formation of nitrides and hydrides. The chemical activity of the gases is due to active modifications, probably consisting of neutral atoms and triatomic molecules, and not to ions. The α -rays are the only ones effective in the rays from radioactive substances.

J. R. P.

Constitution of Hydrogen Peroxides. B. ODDO and R. BINAGHI (*Gazzetta*, 1921, **51**, ii, 343—348).—See this vol., i, 314.

Separation of the Isotopes of Chlorine. J. N. BRÖNSTED and G. HEVESY (*Nature*, 1921, **107**, 619).—When a strong aqueous solution of hydrogen chloride is cooled to -50° and evaporated in a high vacuum, the mixture of water and hydrogen chloride being condensed on a surface cooled with liquid air, the condensed portion of the acid is found to be richer, and the remaining portion poorer, as regards the lighter constituent of chlorine, than ordinary hydrogen chloride. After repeated separations, the two portions were converted into sodium chloride, of which saturated aqueous solutions at 20° had d 1.20222 and 1.20235, respectively, corresponding with a difference of 0.024 unit in the atomic weights of the chlorine isotopes, if it is assumed that the latter have equal atomic volumes. Equal quantities of the isotopic sodium chlorides were also treated with a slight excess of silver nitrate solution, and the excess of silver salt accurately estimated. The results indicated a difference in the atomic weight of 0.021 unit.

A. A. E.

The Separation of Chlorine into Isotopes. WILLIAM D. HARKINS (*Nature*, 1921, **108**, 209; cf. Harkins and Broeker, *ibid.*, 1920, **105**, 230).—See Harkins and Hayes, this vol., ii, 140.

A. A. E.

Attempt to Separate the Isotopes of Chlorine. H. HARTLEY, A. O. PONDER, E. J. BOWEN, and T. R. MERTON (*Phil. Mag.*, 1922, [vi], **43**, 430—435).—According to Aston, ordinary chlorine consists essentially of a mixture of three parts of Cl^{35} and one part of Cl^{37} , and the molecules should be present in the proportions $\text{Cl}^{35}\text{Cl}^{35} : \text{Cl}^{35}\text{Cl}^{37} : \text{Cl}^{37}\text{Cl}^{37} = 9 : 6 : 1$. If light which has passed through a column of such chlorine enters a mixture of chlorine and hydrogen, the initial reaction should use up the three types of molecules in the proportions $1 : 10^9 : 10^{24}$, and the hydrogen chloride formed should be almost entirely HCl^{37} . The gas, after exposure, was treated with mercury to remove unchanged chlorine and the hydrogen chloride, absorbed in water, was converted into sodium chloride. The equivalent of the latter, determined by conversion to silver chloride, showed that no separation had occurred within the limits of experimental error. The circumstances which would prevent a separation of isotopes in the experiment are discussed.

J. R. P.

The Atomic Weight of the Chlorine in an Ancient Mineral, Apatite, from Balme. (MLLE) ELLEN GLEDITSCH and B. SAMDAHL (*Compt. rend.*, 1922, **174**, 746—748).—The chlorine in a sample of apatite from Balme (cf. Curie, A., 1921, ii, 396) was converted into sodium chloride which was carefully purified without possible contamination by chlorine from other sources. Atomic weight determinations gave the value for chlorine as 35.49 and 35.45. Thus taking into consideration the age and origin of the mineral, it may be concluded that the chlorine at the time of the formation of the minerals of the primary magma contained the two isotopes in the same proportion as it does to-day or that the two isotopes were then formed in constant proportions. W. G.

The Reaction between Iodine and Sulphurous Acid. ROBERT MILROY MACAULAY (T., 1922, **121**, 552—556).

Strength of Hypoiodous Acid. ADOLF FÜRTH (*Z. Elektrochem.*, 1922, **28**, 57—58).—Making use of the constants $[I']/[HIO][H']/[I_2] = 3 \times 10^{-13}$ (Bray, *Abegg's Handb.*, **4**, 2, 456) and $[I_2][I']/[I_3'] = 1.3 \times 10^{-3}$ (Jakowkin, A., 1899, ii, 593) and a series of determinations of the concentration of I_3 ions in a sulphuric acid solution of various concentrations of iodine in 0.1*N*-potassium iodide by a colorimetric method, the author has calculated the dissociation constant of hypoiodous acid. The values found lie between 1.8×10^{-11} and 4.4×10^{-11} , which are in good agreement with a value 4.8×10^{-11} calculated from experiments of Deventer (*Chem. Weekblad*, 1905, **2**, 135). This value shows that hypoiodous acid is about a thousand times weaker than hypochlorous acid.

J. F. S.

Preparation and Properties of the Persulphides of Hydrogen. JAMES H. WALTON and LEWELLYN B. PARSONS (*J. Amer. Chem. Soc.*, 1921, **43**, 2539—2548).—The preparation and properties of hydrogen disulphide and hydrogen trisulphide are described. The two compounds are prepared together by the action of hydrochloric acid on sodium polysulphide. Other acids decomposed the polysulphide completely into hydrogen sulphide and sulphur. Two kilos. of crystallised sodium sulphide and 300 grams of flowers of sulphur are placed in a 3-litre round-bottomed flask and mixed, 800 c.c. of water are added, and the flask is closed with a Bunsen valve. After all the sodium sulphide has dissolved, the flask is heated on a water-bath for three to four hours with occasional shaking, when the whole of the sulphur dissolves and a clear solution of polysulphide is obtained. The polysulphide solution is run into hydrochloric acid (d 1.19) which is cooled to -4° to -10° . The addition is made under the surface of the acid at the rate of 3 litres an hour, the solution being rapidly stirred. After a quantity of polysulphide has been added, a brown scum rises to the surface and decomposes with evolution of hydrogen sulphide. At this point, the addition is stopped and the emulsion allowed to settle when a crude oil separates. The oil is a mixture of the two sulphides and about 400—500 c.c. are obtained from

2 kilos. of polysulphide. The oil is separated and dried with phosphoric oxide. The dried mixture is distilled in a quartz glass apparatus fitted with two receivers in series. The first is cooled by cold water and the second by ice and salt. The distillation is carried out at 20—25 mm. pressure and the flask heated in a glycerol bath at 120°. From two volumes of the freshly prepared mixture 2/3 volume of hydrogen trisulphide is obtained in the first receiver and 1/3 volume of hydrogen disulphide in the second receiver, whilst a residue of sulphur dissolved in the trisulphide remains in the distilling flask. It is essential that quartz apparatus is used in the distillation, because the alkali in glass decomposes both sulphides very rapidly.

The analysis of the persulphides is effected as follows. A weighed quantity (2—3 grams) is placed in a tared quartz test-tube (75 mm.), corked, and weighed. The tube is almost filled with carbon disulphide and the contents are poured into a tared quartz dish (75 mm. diam.), and the tube washed with carbon disulphide. About 20—30 c.c. of carbon disulphide are sufficient. About 10 c.c. of pure acetone are added to the solution, and the dish is covered by a watch-glass. After the evolution of hydrogen sulphide has ceased, the cover-glass is rinsed with carbon disulphide and the contents of the dish are allowed to evaporate spontaneously and the residue of rhombic sulphur crystals is dried at 90° and weighed. This method is rapid and accurate.

Hydrogen trisulphide, H_2S_3 , is a mobile, yellow, oily liquid with an odour similar to that of camphor and sulphur monochloride. Its vapours have an irritating action on the eyes and nose. On cooling strongly, the yellow colour is lost and at the temperature obtained with solid carbon dioxide and ether it is quite colourless. It is soluble in benzene, toluene, chloroform, carbon disulphide, ether, and heptane, and is catalytically decomposed by alcohols, ketones, nitrobenzene, aniline, and pyridine. Hydrogen trisulphide behaves like glass on cooling, becoming more and more viscous as the temperature is reduced to -75° , but on warming again there is a short delay in the rise of temperature at -52° to -53° . It may be distilled in a vacuum, but at atmospheric pressure it foams, evolves hydrogen sulphide, and leaves a gummy residue of sulphur in the mixed sulphides.

Hydrogen disulphide, H_2S_2 , has not been obtained quite free from trisulphide, the amount of impurity is not large and is represented by a deficiency of 1—2% of hydrogen sulphide on decomposition. It is a colourless, mobile oil with a much more severe and irritating odour than the trisulphide, causing tears and a smarting sensation in the nostrils. It is soluble in the same solvents as the trisulphide, but is much more sensitive to impurities. Acetone catalyses the decomposition very violently, so that great care is required in the analysis. It boils at 74.5° and melts between -88° and -90° , but shows no sharp point of solidification. Hydrogen trisulphide has the same action on solutions of copper oleate, ferric chloride, stannic iodide, silver nitrate, and mercuric bromide in ether as hydrogen sulphide. Silver oxide, cupric

oxide, lead dioxide, and mercuric oxide decompose hydrogen trisulphide so violently and with such development of heat that it is ignited; lead oxide, stannic oxide, and magnetite decompose it violently, whilst arsenious, arsenic, ferric, and zinc oxides, barium dioxide, and manganese dioxide bring about only a slow decomposition. Potassium permanganate and potassium dichromate decompose it violently. Most metallic salts decompose the trisulphide, but massive metals have a very slow action. It dissolves readily in liquid hydrogen sulphide and one molecule of the trisulphide dissolves eight atoms of sulphur. J. F. S.

Influence of Freezing on Colloidal Selenium. III. A. GUTBIER and R. EMSLANDER (*Kolloid Z.*, 1922, **30**, 97—110; cf. A., 1921, ii, 693; this vol., ii, 142).—Further experiments on the effect of freezing on selenium sols are described. It is shown that selenium sols prepared by means of hydrazine hydrate are stable toward freezing when of suitable concentration, even in the presence of large concentrations of selenious acid. The stability of such sols is dependent on the temperature of formation to a marked extent. A particularly stable system is formed when a 0.002*M* solution of selenium dioxide is reduced by a 1 : 2000 solution of hydrazine hydrate at 60°, ten parts of selenium dioxide solution being reduced by one part of hydrazine hydrate. The coagulation of selenium sols is greatly accelerated by freezing. Selenium sols may be prepared by the solution of selenium in hydrazine hydrate at ordinary temperature and pouring this molecular disperse system into a large volume of water. With this system, it is shown that the stability of colloidal selenium depends mainly on the degree of dispersion. It is also shown that an optimum concentration of electrolyte is necessary for the stability of selenium hydrosols. In the absence of electrolytes, this system is quite unstable toward freezing. The protective action of the sodium salts of protalbic and lysalbic acids on selenium sols consists in a retardation of the spontaneous coagulation of the suspension. J. F. S.

Hydrates of Selenium Dioxide. WILHELM MANCHOT and KARL ORTNER (*Z. anorg. Chem.*, 1922, **120**, 300—309).—Crystallisation of solutions of selenium dioxide did not give trustworthy results, because the crystals obtained were very hygroscopic and could not be dried in a desiccator without undergoing decomposition. The freezing curve of hydrated selenium dioxide showed only one eutectic point at -23°; the eutectic mixture containing 57% SeO_2 , and consisting of ice and the hydrate $\text{SeO}_2 \cdot \text{H}_2\text{O}$. A maximum was found on the solubility curve corresponding with a composition of 86.07% SeO_2 , that is, $\text{SeO}_2 \cdot \text{H}_2\text{O}$. The vapour pressure curve indicated that $\text{SeO}_2 \cdot \text{H}_2\text{O}$ was the only hydrate present. Molecular weight was found by the freezing-point method. The degree of dissociation was found to be approximately the same as for tartaric acid. No evidence could be obtained of the existence of the associated selenious acid $(\text{H}_2\text{SeO}_3)_2$ in a
10*—2

freshly prepared solution as claimed by Rosenheim and Krause (this vol., ii, 47).
W. T.

The Elimination of the Heat of Reaction in the Synthesis of Ammonia by High Pressures. GEORGES CLAUDE (*Compt. rend.*, 1922, 174, 681—683).—The device adopted to remove the heat of reaction consists in having the catalyst in a thin-walled inner tube and allowing the oncoming cold gases to circulate through the annular space. The inner tube is so constructed that the amount of heat removed at any one point is just equal to the heat generated at that point. This is effected by varying the thickness of the inner tube along its length. With this new arrangement it is claimed that the life of the reaction tube is considerably increased and the catalyst can very easily be replaced when necessary.
W. G.

The Rôle of Gaseous Impurities in the Catalytic Oxidation of Ammonia. Influence of Hydrogen Phosphide. E. DECARRIÈRE (*Compt. rend.*, 1922, 174, 460—461; cf. A., 1921, ii, 503, 546).—Hydrogen phosphide when present in the ammonia-air mixture as the sole gaseous impurity and only to the extent of 0.00002% exercises a harmful effect and reduces the oxidation by nearly 30%. If the gas is present to the extent of 0.02%, the yield falls from 93.8% to 3.9%. In every case, however, the activity of the catalyst is regenerated when the impurity is removed, the regeneration being slower the greater the percentage of the impurity previously present. In some cases, however, industrial catalysts of the type of those of Ostwald may be destroyed by the momentary presence of traces of hydrogen phosphide in certain favourable circumstances.
W. G.

The Rôle of Gaseous Impurities in the Catalytic Oxidation of Ammonia Gas. EUGÈNE DECARRIÈRE (*Compt. rend.*, 1922, 174, 756—758; cf. preceding abstract).—It has previously been shown that hydrogen sulphide is capable of partly neutralising the injurious influence of acetylene in the catalytic oxidation of ammonia in the presence of finely divided platinum. It is now shown that it can also partly neutralise the injurious influence of hydrogen phosphide. This beneficial effect is not due to the dissociation of the sulphide with the consequent liberation of hydrogen, since hydrogen itself is incapable of neutralising the effect of the phosphide.
W. G.

Nitrous Anhydride. F. FOERSTER (*Ber.*, 1922, 55, [B], 490—491).—In a recent communication (A., 1921, i, 778) Wieland has shown that nitrous fumes behave in many respects as if constituted entirely as nitrous anhydride, N_2O_3 , and has assumed that, in spite of density determinations, a small proportion of this substance must be present in equilibrium with the mixture of nitric oxide and nitrogen peroxide. The experimental evidence on this point has been provided by Le Blanc (*Z. Elektrochem.*, 1906, 12, 544) and the author (A., 1910, ii, 1059).
H. W.

Magneto-chemical Investigation of the Constitutions in Mineral Chemistry. The Acids of Phosphorus. PAUL PASCAL (*Compt. rend.*, 1922, **174**, 457—460).—The method of magnetic analysis previously applied to the compounds of sulphur (A., 1921, ii, 692) has now been applied to compounds of phosphorus. The molecular susceptibilities of a number of phosphorus compounds are given. In all its incompletely saturated derivatives the diamagnetism of phosphorus or its oxy-groups is greatly weakened, and phosphorus and its oxy-radicles possess a constant magnetic individuality. In its saturated derivatives, phosphorus has a different but constant magnetic susceptibility. The results accord perfectly with the rational formulæ $\text{PO}(\text{OH})_3$, and $\text{RPO}(\text{OH})_2$ for the phosphoric and phosphinic acids. W. G.

The Use as a Drying Agent of Phosphoric Oxide Treated with Ozone. JOHN JOB MANLEY (T., 1922, **121**, 331—337).

Atomic Weight of Boron. G. P. BAXTER and A. F. SCOTT (*Science*, 1921, **54**, 524—525).—Boron was obtained by reduction of boric oxide with excess of magnesium, and extraction with either hydrochloric or hydrobromic acid. It was then converted into the haloid by passing over it at 700° either dry chlorine or helium saturated with bromine nearly at the boiling point of the latter. The excess of halogen having been removed, the haloids were repeatedly distilled with the use of Hempel fractionating columns in sealed, all-glass vessels, with the exclusion of air. Analysis was effected by comparison with silver in the usual way, and by each method gave a result of 10.83 ± 0.01 . This indicates the proportion of the heavier isotope to be about five times that of the lighter, a result which is more in accord with the observations of Aston (A., 1920, ii, 718) than the previous determination (10.900) by Smith and van Haagen (A., 1920, ii, 247). A. A. E.

Researches on the Chemistry of Coal. II. The Resinic Constituents and Coking Propensities of Coals. W. A. BONE, A. R. PEARSON, E. SINKINSON, and W. E. STOCKINGS (*Proc. Roy. Soc.*, 1922, [4], **100**, 582—598; cf. *ibid.*, 1917, [4], **96**, 119).—Strongly coking bituminous coals may be extracted for prolonged periods by organic resin solvents without impairing their coking propensities. It is shown that the pyridine-chloroform method of extracting coals does not, as stated by Clark and Wheeler (T., 1913, **103**, 1706), effect a complete, or nearly complete, separation between the resinous constituents and the degradation products of the celluloses of which coal is conglomerated; but that, on the contrary, it yields an admixture of resins with a predominance of non-resinous substances, which latter are chiefly of cellulosic origin, and have been provisionally designated "humic" substances in the present paper. It is shown that resins may be extracted and isolated in a pure condition from such coals by treatment with pyridine and amyl alcohol, in equal proportions, in an atmosphere of nitrogen, followed by successive treatments with ethyl ether and light petroleum. These resins do not normally much exceed

1% of the coal substance, and, although they may be a contributory, are not usually the chief cause of the coking propensities of coals. A series of non-resinous substances, amounting in many cases to as much as 4%, may be extracted from strong coking coals by a special pyridine or pyridine-amyl alcohol treatment. These substances for the most part are insoluble in ether but soluble in chloroform. On heating these substances out of contact with air, a strong exothermic reaction takes place between 275° and 375° which is accompanied by the elimination of water. This reaction is reminiscent of the behaviour of cellulose and shows these substances to be chiefly cellulosic in type and origin. The coking propensities of coals are principally due to the presence, or the formation in them by heat, of such non-resinous substances of cellulosic origin, the fusion temperatures of which are below those at which they undergo rapid decomposition. The still more complex substances, also of cellulosic origin, which constitute the main portion of the coal substance, but which decompose without fusion, have little or no direct influence on its coking propensities.

J. F. S.

Modifications of Silicon. Solubility of Silicon in Hydrofluoric Acid. WILHELM MANCHOT and HERBERT FUNK (*Z. anorg. Chem.*, 1922, **120**, 277—299).—Specimens of silicon obtained from an aluminium regulus have been examined and the influences of (1) temperature of the fusion, (2) concentration of silicon, and (3) rate of cooling investigated. The temperature of the fused mass was varied from 900° to 1650° and was found to have but little effect. The concentration of silicon could be varied from 0.25 to 10% without much effect, but a higher concentration (>10%) favoured the formation of crystals. Rapid cooling of the regulus gave a greyish-black, amorphous (no crystalline form could be detected at 960 magnification) silicon (d 2.23) which reacted briskly with hydrofluoric acid with evolution of hydrogen leaving a brown, amorphous residue (d 2.20) apparently insoluble in hydrofluoric acid. This brown variety was found to be very active—reacting violently with fuming nitric acid, sodium hydroxide, chlorine, and bromine at ordinary temperatures. This reactivity was found to be due to adsorbed hydrogen; after removing the hydrogen it reacted with hydrofluoric acid and behaved in the same way as the greyish-black, amorphous form. On cooling the regulus slowly, crystalline silicon was obtained (d 2.30); this form reacted but slowly with hydrofluoric acid. The aluminium could be replaced by a silver regulus. Silicon of 99% solubility in hydrofluoric acid as claimed by Moissan and Siemens (*A.*, 1904, ii, 560) could not be prepared. Silicon in the mixture (silicon and silica) was estimated by the volume of hydrogen liberated from potassium hydroxide solution. Silicon completely resistant towards hydrofluoric acid could not be prepared. Ordinary silicon heated at 2000° and suddenly cooled behaves in the same way as when slowly cooled. This leads the author to believe that the various forms obtained from the reguli are not allotropic modifications. The

sudden cooling of the solution and solidification of the metal solvent gives extremely fine particles ($d=1\mu$); the reactivity is ascribed to this fineness and not to a new form. Such a degree of fineness could not be obtained mechanically.

W. T.

Formation of Potassium Perchlorate from Potassium Chlorate. VICTOR LENHER, HOSMER W. STONE, and HELEN H. SKINNER (*J. Amer. Chem. Soc.*, 1922, **44**, 143—144).—The formation of potassium perchlorate from potassium chlorate by the action of acids has been investigated. On treating potassium chlorate with sulphuric acid, taking care to add the acid slowly and keeping the mixture cold until the yellow colour has disappeared, a yield of 11% of perchlorate is obtained. Evaporation to dryness of chlorate with nitric acid of various concentrations on a steam-bath gives a yield of 30% of perchlorate; fuming nitric acid yields no perchlorate under the same conditions. A 15% yield of perchlorate is obtained when potassium chlorate is boiled with 85% phosphoric acid. Potassium chlorate and chromium trioxide boiled with just sufficient water to maintain a solution give 11% of perchlorate. Chloric acid gives no perchlorate with potassium perchlorate. The following acids have no action of potassium chlorate even at the boiling point: saturated oxalic acid solution, 25% tartaric acid, acetic acid both glacial and dilute, 50% chloroacetic acid, 25% lactic acid, 50% arsenic acid, 20% permanganic and persulphuric acid. Formic, trichloroacetic, hydrofluoric, and hydrochloric acids decompose potassium chlorate without producing perchlorate.

J. F. S.

Preparation and Constitution of a Double Potassium Ammonium Orthophosphate. R. M. CORELLI (*Gazzetta*, 1921, **51**, ii, 380—385).—Attempts to prepare a salt analogous to sodium ammonium hydrogen orthophosphate by the interaction of dipotassium hydrogen phosphate and ammonium chloride or phosphate result in the elimination of ammonia and formation of potassium dihydrogen phosphate. This extreme instability indicates the compound formed to be a tertiary phosphate, and *potassium diammonium phosphate*, $K(NH_4)_2PO_4 \cdot 4H_2O$, may be obtained by passing ammonia into aqueous potassium dihydrogen phosphate solution cooled in ice and salt, filtering the solution quickly in an atmosphere of ammonia and pressing the crystals between filter-paper. The compound deliquesces and loses ammonia in the air, but may be preserved in sealed tubes.

T. H. P.

Crystal Structures of Potassium and Ammonium Stannichlorides. ROSCOE G. DICKINSON (*J. Amer. Chem. Soc.*, 1922, **44**, 276—288).—The crystal structures of potassium and ammonium stannichlorides have been determined from measurements of the X-ray reflection spectra and from unsymmetrical Laue photographs. The structure is shown to be similar for the two salts and of the calcium fluoride type. It has been found possible to carry out the analyses without making any quantitative assumption concerning "normal decline" of intensity, and with only

rough assumptions as to the relative reflecting powers of the atoms. The results lead to the conclusion that six equivalent chlorine atoms are grouped about each tin atom; and the structure is accordingly regarded as built up of SnCl_6'' ions and potassium or ammonium ions. The SnCl_6'' ion occupies the positions filled by calcium in fluorspar and the potassium or ammonium ions occupy the positions of the fluorine. It is shown that the general structure and cleavage of the crystals investigated are similar to those of fluorspar. The following distances between the atoms are recorded: potassium stannichloride, between tin and chlorine, 2.44 Å.U., tin and potassium, 4.31 Å.U., potassium and chlorine, 3.52 Å.U., ammonium stannichloride, tin and chlorine, 2.46 Å.U., nitrogen and tin, 4.35 Å.U., and nitrogen and chlorine, 3.55 Å.U. J. F. S.

Simple Method for the Preparation of Sodium Hydroxide Free from Carbon Dioxide. JACOB CORNOG (*J. Amer. Chem. Soc.*, 1921, **43**, 2573—2574).—Solutions of sodium hydroxide free from carbonate may be prepared as follows. Distilled water contained in an Erlenmeyer flask is boiled to remove carbon dioxide, after which, when the water has cooled sufficiently, a layer of ethyl ether 3—4 cm. deep is placed on the water. Pieces of metallic sodium, not exceeding 1 cm. in diameter, are dropped into the flask. They fall no further than the ether, where they remain suspended and are slowly attacked by the water dissolved in the ether and the sodium hydroxide passes into the water. After the desired quantity of sodium has reacted, the larger portion of the ether is pipetted off and the last traces are removed by boiling the solution. It is shown that there is no danger of fire if the depth of the ether is great enough to prevent the suspended sodium from being simultaneously in contact with the air and water. With the care usually employed in working with ether and by keeping the ether layer from three to four times as thick as the diameter of the pieces of sodium added, the reaction may be performed easily and without danger. A further advantage of using ether is that the oil adhering to the sodium is removed with the ether. The product gives no precipitate with solutions of barium hydroxide. J. F. S.

Sodium Hyposulphite. FREDERICK W. HEYL and FRANK E. GREER (*Amer. J. Pharm.*, 1922, **94**, 80—92).—The most satisfactory laboratory method for the production of sodium hyposulphite is by the action of sodium formaldehydesulphoxylate on sodium hydrogen sulphite. The former substance may be prepared by the method of D.R.-P. 256460, or more conveniently by the reduction of commercial "hydrosulphite" with zinc dust and zinc oxide in presence of formaldehyde solution, and recrystallising from water at a temperature not exceeding 70° the crystals first obtained. The purity of the product, which approximates to 100%, is best determined by direct titration of a hot solution with standard solution of methylene-blue. Sodium formaldehydesulphoxylate is soluble in glycerol to the extent of about 74 grams in

100 c.c. Administered intravenously, it apparently has no toxic action on white rats. It was not found possible to prepare analytically pure anhydrous sodium hyposulphite even by the method from the sulphonylate indicated above, and salting out the product with strong brine, although a purity of 97.7% is claimed in U.S. Pat. 990457. The yields obtained amounted to 55—60% of the theoretical with a purity of 80—85%, and neither by recrystallisation nor salting out from air-free aqueous solutions in an inert atmosphere could the salt be further purified. Unlike the sulphonylate, sodium hyposulphite and also its decomposition products are toxic in doses of about 200 mg. upwards per kilo. of body weight.

G. F. M.

The Density of Cæsium at the Absolute Zero. W. HERZ (*Z. anorg. Chem.*, 1921, **120**, 159).—In a previous paper (A., 1919, ii, 220), it was overlooked that, in calculating the density of a number of elements at the absolute zero, the value arrived at for cæsium, 1.791, is lower than the density at higher temperatures. The equation used cannot therefore be applicable to cæsium. A value harmonising better with that of the other alkali metals is obtained by taking the density at 27° as the density at the melting point d_e , and applying the relation $d_0 : d_e = 1.21$, when the value 2.222 is obtained, and the corresponding atomic volume 59.77. A correction must be made in a subsequent paper in which the atomic volume at absolute zero is used for calculating molecular volumes of cæsium salts (Lorenz and Herz, A., 1921, ii, 536).

E. H. R.

Highly Basic Lithium Salts of Weak Inorganic Acids.

ARTHUR ROSENHEIM and WERNER REGLIN (*Z. anorg. Chem.*, 1921, **120**, 103—119).—It has been shown that some highly basic salts of lithium, such as those of antimonious and periodic acids, have semi-colloidal properties (A., 1918, ii, 194 and 1919, ii, 508). Those lithium salts which are characterised by low solubility and negative temperature coefficient of solubility are generally those of weak acids which may be expected to form polymerised or associated molecules. A number of such lithium salts, including phosphite, hypophosphate, phosphate, vanadate, molybdate, tungstate, borate, and carbonate, have been examined with respect to their state of aggregation.

Dilithium hydrogen phosphite, $\text{Li}_2\text{HPO}_3 \cdot \text{H}_2\text{O}$, has a negative temperature coefficient of solubility in water, which ranges from 9.07 grams at 0° to 4.24 grams at 98° of anhydrous salt per 100 grams of solution, the solid phase being the monohydrate throughout. The hydrogen-ion concentration at 20° in a normal solution is $7.34 \cdot 10^{-9}$ ($P_{\text{H}} = 8.14$). The equivalent conductivity at dilutions from $v = 32$ to $v = 1024$ was measured, and also the freezing-point depression. The values for the latter do not indicate association in solution.

Lithium hypophosphate, $\text{Li}_2\text{PO}_3 \cdot 3.5\text{H}_2\text{O}$, does not form a clear, aqueous solution and its solubility would not be determined directly with accuracy. An estimate of the solubility was made from the conductivity, making use of known data to calculate the migration

velocities of the ions. The value obtained for the solubility was 0.1267 gram of Li_2PO_3 per litre at 25° , a value much lower than the apparent solubility determined directly. Whether the apparently colloidal solution is really colloidal or a non-colloidal suspension cannot be stated.

Lithium phosphate was obtained in the form of a dihydrate, $\text{Li}_3\text{PO}_4 \cdot 2\text{H}_2\text{O}$, which at 60° is slowly converted into $\text{Li}_3\text{PO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$. It also forms a cloudy solution; the solubility, determined by the conductivity method, is 0.297 gram of Li_3PO_4 per litre at 25° . Two compounds of lithium with vanadic acid were obtained. The first, $4\text{Li}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 4\text{H}_2\text{O}$, is precipitated when a solution of vanadium pentoxide in a large excess of a saturated solution of lithium hydroxide is heated. It appears to have a negative temperature coefficient of solubility, but at low temperatures when stirred with water it changes into $3\text{Li}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 18\text{H}_2\text{O}$ or $\text{Li}_3\text{VO}_4 \cdot 9\text{H}_2\text{O}$, transparent, rhombohedral needles. This appears to be identical with Ditte's $4\text{Li}_2\text{O} \cdot \text{V}_2\text{O}_5 \cdot 14\text{H}_2\text{O}$ (A., 1887, 705). The solubility coefficient of $\text{Li}_3\text{VO}_4 \cdot 9\text{H}_2\text{O}$ is positive, the maximum solubility being 6.25 gram of Li_3VO_4 per 100 grams of solution at 35.2° ; above this temperature, the monohydrate is stable and the temperature coefficient is negative.

Lithium molybdenate was found to have the composition $4\text{Li}_2\text{MoO}_4 \cdot 3\text{H}_2\text{O}$, not $5\text{Li}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (Wempe, A., 1913, ii, 59). Its solubility at 25° is 44.81 grams of Li_2MoO_4 per 100 grams of solution and the temperature coefficient is small and negative. The tungstate has a similar composition, $4\text{Li}_2\text{WO}_4 \cdot 3\text{H}_2\text{O}$, and its solution is rapidly decomposed by atmospheric carbon dioxide.

Lithium borate, $\text{LiBO}_2 \cdot 8\text{H}_2\text{O}$, has a positive solubility coefficient and shows normal depression of freezing point in solution.

Lithium carbonate when boiled in aqueous solution loses carbon dioxide, and finally a solution is obtained containing $\text{LiOH} : \text{Li}_2\text{CO}_3 = 1 : 1$ (approx.). It follows that the solubility determinations of Bewad (*J. Russ. Phys. Chem. Soc.*, 1884, 16, 591) are not trustworthy at higher temperatures.

E. H. R.

Crystallographic and Atomic Symmetries of Ammonium Chloride. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1922, [v], 3, 177—183).—The symmetry of ammonium chloride as indicated by the development of the external faces and by etch-figures on the faces is that of the enantiomorphous hemihedral class, whilst from the X-ray data, both with the spectrometer and the powder method, the internal structure is tetrahedral cubic with one chemical molecule to the unit cell. The latter is based on the ratio $n^3/m=1$, where n is the order of the reflection and m the number of molecules in the unit cell. Several more complex enantiomorphous groupings with several molecules in the unit cell are considered; but from a chemical point of view these are highly improbable, since they collected all the ammonium groups about one point in the unit and all the chlorine atoms about another point. The crystallographic observations are therefore regarded as requiring revision.

L. J. S.

Decomposition and Stabilisation of Ammonium Nitrate in Presence of Oxidisable Material. ALEXANDER FINDLAY and CYRIL ROSEBOURNE (*J. Soc. Chem. Ind.*, 1922, **41**, 58—59T).—The stability of mixtures of ammonium nitrate with small quantities of woodmeal and with starch was investigated by heating the mixture contained in a test-tube, provided with a capillary delivery tube leading below the surface of mercury to a graduated gas burette. The tube was exhausted and placed in a boiling water-bath. A mixture of 23.75 grams of ammonium nitrate and 1.25 grams of woodmeal gave 1.5 c.c. of a mixture of carbon dioxide (33.1%) and nitrogen (66.9%) in twenty-four hours, and 47.1 c.c. in fifty days. A mixture of the same amount of nitrate and 2 grams of soluble starch gave in one day 46.5 c.c. of a gas having the composition CO_2 27.04%, N_2 72.4%, and CO 0.56%. After some days, the rate of evolution slowed down considerably, and eventually the gas evolved appeared to consist of nitrogen only. In both cases, the addition of 0.25 gram of carbamide to the mixtures proved a most effective stabiliser, no appreciable evolution of gas occurring with the woodmeal mixture in a period of thirty-five days. Diphenylamine and phenyl benzyl ether also act as stabilisers, but they are not suitable for the purpose, owing to subsidiary reactions occurring between these substances and the ammonium nitrate. G. F. M.

Solubility of Silver Chloride in Dilute Chloride Solutions and the Existence of Complex Argentichloride Ions. II. GEORGE SHANNON FORBES and HARRIET ISABELLE COLE (*J. Amer. Chem. Soc.*, 1921, **43**, 2492—2497; cf. A., 1912, ii, 49).—To solutions of sodium, ammonium, hydrogen, rubidium, calcium, barium, strontium, and potassium chloride of concentrations not greater than 0.1N a 0.001N-solution of silver chloride was added at 25° until an incipient precipitation was observed. The total silver then in solution was invariably given by $2 \times 10^{-10}/(\text{MCl}) + 3.4 \times 10^{-5}(\text{MCl}) + b$, where 2×10^{-10} is the solubility product of silver chloride, 3.4×10^{-5} a constant possibly connected with a complex of the type AgCl_2 , and b is apparently the constant sum of silver chloride in precipitate, in dispersion, and in dissolved molecules. The great difference between this observed total and the minute silver content of filtrates from large precipitates of silver chloride is discussed. It is shown that silver chloride should be most insoluble at 25° in 0.0025N-chloride solutions. J. F. S.

Crystal Structure of Silver Oxide. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1922, [v], **3**, 184—188).—Silver oxide (Ag_2O), which crystallises as small, isotropic octahedra, was examined by the X-ray powder method, and the type of cubic structure deduced is the same as that assigned to cuprous oxide. The unit cube, containing two molecules of Ag_2O , has an edge of 4.768 Å.U.

L. J. S.

Vapour Pressure of Metallic Calcium. NORMAN B. PILLING (*Physical Rev.*, 1921, **18**, 362—368; cf. Langmuir, *ibid.*, 1913, **2**, 329; 1914, **4**, 377).—The vapour pressure of calcium was computed

with the aid of Langmuir's expression, which requires measurement of the rate of evaporation of a certain weight of metal of known surface area at constant temperature and in a vacuum. When the coefficient of reflection, s , of the calcium molecules from the enveloping walls is taken into consideration, the expression becomes $m = \sqrt{M/2\pi RT} \cdot p(1-s)$, where M is the molecular weight of the vapour, assumed to be monatomic, R the gas constant, T the absolute temperature, p the pressure in dynes per sq. cm., and m the rate of evaporation in grams per sq. cm. per second. The value of s was determined by control experiments with zinc and cadmium, the vapour pressures of these metals in the solid state being known (Egerton, *Phil. Mag.*, 1917, [vi], **33**, 33). Vapour-pressure curves are given for liquid and solid calcium, the vapour pressure at the melting point, 805° , being 2.0 mm. and the b. p./760 mm. being computed to be 1240° . The calcium employed contained 1.62% of magnesium, 0.009% of iron, and 1.25% of calcium chloride. A. A. E.

A Simple Process for Obtaining Crystallised Gypsum.

L. BOURGEOIS (*Bull. Soc. chim.*, 1922, [iv], **31**, 160—161).—Three volumes of nitric acid are diluted with one volume of water and this solution is saturated at just below its boiling point with calcium sulphate. The clear liquid is decanted off and allowed to cool. After eight days, crystals of gypsum begin to appear. W. G.

Some Compounds in the System $\text{CaO-P}_2\text{O}_5$ and their Relation to Basic Slag. TH. DIECKMANN and ED. HOUDRE-MONT (*Z. anorg. Chem.*, 1921, **120**, 129—149).—A number of compounds of calcium and phosphoric acid have been prepared and examined with respect to their physical properties and solubility in citric acid with the object of throwing some light on the constituents of basic slag. The solubility of tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$, in 2% citric acid was found to be affected by the temperature to which it was heated. Starting at 94.6° , it fell to 60% as the temperature was raised to 540° , and then rose steadily to 96.2% at the melting point. The composition of the insoluble residue varied in a similar manner, and at the point of minimum solubility had the composition of oxyapatite, $3(\text{Ca}_3\text{P}_4\text{O}_8), \text{CaO}$. Further heating to higher temperatures appeared to reconvert this into the normal phosphate. The melting point of tricalcium phosphate is 1670° . Oxyapatite was prepared from a mixture of tricalcium phosphate and calcium carbonate. Formation of the compound was complete at about 1450° , and its low solubility in citric acid, about 55%, confirmed the opinion that this compound is formed during the heating of tricalcium phosphate alone. By melting the oxyapatite with the calculated quantity of insoluble pyrophosphate according to the equation $3(\text{Ca}_3\text{P}_2\text{O}_8), \text{CaO} + 2\text{CaOP}_2\text{O}_5 = 4\text{Ca}_3(\text{PO}_4)_2$, a highly soluble tricalcium phosphate was obtained. The melting point of oxyapatite is 1540° , d 2.99; it crystallises in doubly refracting needles.

Tetracalcium phosphate, $4\text{CaO}, \text{P}_2\text{O}_5$, has a high solubility in

citric acid, but if heated for some time at 1000° the solubility falls to about 25% and the insoluble residue has the composition of oxyapatite. This observation explains earlier statements that tetracalcium phosphate has a low solubility. Its m. p. is 1630° . It is decomposed by boiling water into lime and oxyapatite. Calcium pyrophosphate is practically insoluble in citric acid; m. p. 1230° , d 3.09. Calcium metaphosphate is also insoluble in citric acid. The molten substance when cooled forms a glass and is difficult to crystallise. The melting point is between 970° and 980° , d 2.82 (crystals) and 2.65 (amorphous). Calcium silicophosphate, $5\text{CaO}, \text{P}_2\text{O}_5, \text{SiO}_2$, has the same solubility in citric acid as tricalcium phosphate, and is probably therefore a compound of the latter with the normal orthosilicate, $\text{Ca}_3(\text{P}_2\text{O}_4)_2, 2\text{CaO}, \text{SiO}_2$. Its melting point is 1760 — 1780° . Synthetic fluorapatite, $\text{CaF}_2, 3\text{Ca}_3(\text{PO}_4)_2$, has a low solubility, about 10%, in citric acid; m. p. 1630 — 1650° , d 3.18. The above observations show the importance of adding sufficient silica to basic slag to neutralise any excess of lime if a soluble phosphate is to be obtained, since the silicophosphate, unlike tetracalcium phosphate, does not decompose during slow cooling to form insoluble oxyapatite. [See *J. Soc. Chem. Ind.*, 1922, April.] E. H. R.

Calcium Silicides. LOTHAR WÖHLER and F. MÜLLER (*Z. anorg. Chem.*, 1921, **120**, 49—70).—It has been shown by a number of workers that, besides the calcium silicide, CaSi_2 , corresponding with ordinary calcium carbide, a second calcium silicide exists, but various formulæ have been ascribed to it, for example, Ca_3Si_2 (Hackspill, A., 1908, ii, 589) and $\text{Ca}_{11}\text{Si}_{10}$ (Kolb and Formhals, A., 1910, ii, 35). It is now shown that the second compound is calcium monosilicide, CaSi or Ca_2Si_2 . The compound is formed free from disilicide when a mixture of calcium and silicon in atomic proportions or with excess of silicon up to 100% is heated in a magnesia boat in an atmosphere of carbon dioxide at 1050° . After a quarter of a minute, a violent reaction takes place and the mass becomes incandescent. It must then be cooled rapidly. The mass breaks up readily into small, lustrous, metallic leaflets and larger crystals. The density of the substance, containing a small proportion of uncombined silicon, is 2.346. By dilute acids it is attacked readily with evolution of a spontaneously inflammable silicon hydride and formation of hydrated silica. It is only slowly attacked by concentrated acids, with evolution of hydrogen, and by cold water, more readily by warm water and by dilute ammonia. By contrast, the disilicide dissolves in hydrochloric acid with formation of yellow silicone and without production of spontaneously inflammable silicon hydride. When, in the preparation of the substance, so large an excess of silicon is used as to prevent the necessary rise in temperature during the reaction, a mixture of mono- and di-silicides is formed. From this it was concluded that the monosilicide is formed endothermically from the disilicide. This was confirmed by an experimental determination of their heats of combustion and calculation of their heats of

formation, which were found to be, for Ca_2Si_2 , +166.3 cal. and for CaSi_2 , +208.7 cal.

Pure calcium disilicide can be prepared by heating the monosilicide at 1000–1010° in a current of hydrogen. If excess of silicon is present, this reacts with the calcium hydride formed to give a further quantity of the disilicide. The pure disilicide evolves only hydrogen and no silicon hydride with dilute acid. The disilicide is stable at least up to 1050°, for at this temperature the monosilicide, in absence of air, dissociates with development of heat into disilicide and calcium.

The silicon hydride formed by the action of dilute acids on the monosilicide is probably silicoethylene formed according to the equation $\text{Ca}:\text{Si}:\text{Si}:\text{Ca} + 4\text{HCl} = 2\text{CaCl}_2 + \text{H}_2:\text{Si}:\text{Si}:\text{H}_2$. E. H. R.

System Ammonia-Magnesium-Mercury. Formation of Magnesium Hexammoniate. ALBERT G. LOOMIS (*J. Amer. Chem. Soc.*, 1922, **44**, 8–19).—When dilute magnesium amalgam is brought into contact with ammonia, a solid phase separates slowly which has a bright metallic lustre and is decomposed on exposure to air or by reducing the ammonia pressure to below two atmospheres. If the magnesium amalgam contains more than 0.15% of magnesium, the whole becomes completely solid with excess of ammonia, whilst richer magnesium amalgams become solid if more ammonia than 0.035 mol. per 100 grams of amalgam is added. The determination of the composition of the solid phase has been attempted. It is shown that magnesium dissolves in mercury to the extent of 0.323% at 23°. The vapour pressure of the system at 0° has been studied by removing measured volumes of ammonia. The vapour-pressure curve shows a gradually decreasing ammonia pressure as ammonia is removed from which it is concluded that in addition to the vapour phase there are only two phases present, one at least of which is of variable composition. The ratio of ammonia to magnesium has been determined in the crystals and the formula $\text{Mg}(\text{NH}_3)_6\text{Hg}_x$ given to the compound. The solubility of the crystals at 22.4° in pure mercury has been determined and is represented by 0.00593 gram of magnesium per 100 grams of mercury. The ammonia pressure of the crystals has been measured at 22.4°. From the experimental results the value of x in the above formula is calculated as 17.5–18.4. From the large value thus obtained for the amount of mercury, it is concluded that solid solutions are formed by the molecular compound, magnesium hexammoniate, with the excess of mercury present. J. F. S.

Variously Coloured Modifications of Colloidal Copper. C. PAAL and HERMANN STEYER (*Kolloid Z.*, 1922, **30**, 88–97).—Colloidal copper exists in the following differently coloured modifications: reddish-brown (Lottermoser, A., 1899, ii, 558), blue (Gutbier, A., 1903, ii, 81; 1905, ii, 327), ruby-red (Paal and Leuze, A., 1906, ii, 356), brown (Billitzer, A., 1902, ii, 454), olive (Ehrenhaft, *Anz. Wiener Akad.*, 1902, **39**, 241), and green (Paal and Leuze, *loc. cit.*). The ruby-red variety exists in two forms known as the α - and β -modification, respectively. The

present paper gives a description of the preparation and properties of the α - and β -ruby-red and the blue modifications of copper hydrosol by the use of sodium lysalbate and protalbate and the free acids. The method of converting the ruby-red variety into the blue variety is described. J. F. S.

German Silver. WALTER VOIGT (*Z. anorg. Chem.*, 1922, **120**, 309—319).—The equilibrium diagram of the copper-nickel-zinc alloys was investigated by Tafel (A., 1908, ii, 846). All alloys except those rich in zinc were easily worked. The electric resistance was determined after heating the wires to the temperatures of minimum resistance (cf. Credner, A., 1913, ii, 280). If the ratio of copper to nickel remains constant, then increasing amounts of zinc have but little effect. The resistance increases much more rapidly on increasing the nickel content. As regards the thermoelectric effect, if the ratio copper:nickel is constant then increasing amounts of zinc increase it. Increase in the ratio of zinc to copper alone decrease it; a considerable decrease was observed on increasing the nickel content, the copper-zinc ratio being kept constant. In general, the surface of the thermoelectric effect (on diagram) runs parallel to that of the reciprocal of resistance, that is, conductivity. All the alloys showed a solution tension approximately equal to that of copper. They all precipitated copper gradually from a solution of copper sulphate. The passivity of nickels protects the alloy only when its content is 31 mol.% and 43 mol.%. W. T.

Crystal Structures of the Cuprous Haloids. RALPH W. G. WYCKOFF and EUGEN POSNJAK (*J. Amer. Chem. Soc.*, 1922, **44**, 30—36).—The crystal structure of cuprous chloride, bromide, and iodide have been deduced from the examination of X-ray reflection spectra using films of powder. They are shown to possess the zinc sulphide arrangement and the length of the side of the unit cube is 5.49, 5.82, and 6.10 Å.U. respectively. J. F. S.

Separation of Isotopes. Theory of Resolution of Isotopic Mixtures by Diffusion and Similar Processes. Experimental Separation of Mercury by Evaporation in a Vacuum. ROBERT S. MULLIKEN and WILLIAM D. HARKINS (*J. Amer. Chem. Soc.*, 1922, **44**, 37—65).—The various phenomena of diffusion and effusion in gases are discussed in connexion with the separation of isotopes. It is shown that for the processes of molecular diffusion through a porous membrane, molecular effusion, and non-equilibrium evaporation, the relative rates of escape of isotopes are proportional to their respective molecular fractions and inversely proportional to the square roots of their molecular weights. In all the above processes, the molecules move independently. As collisions between molecules become more frequent, molecular diffusion passes into capillary transpiration, or mass motion, and non-equilibrium evaporation passes into ordinary distillation. In either case practically no separation of isotopes occurs. If a gaseous mixture of isotopes diffuses into another gas, with no convective mixing, the diffusion coefficients of any two isotopes

are probably in the ratio $x_1/x_2 \sqrt{M_2/M_1}$, where c is a variable quantity usually in the neighbourhood of 1 or 2. The theory is complicated, but indicates a higher rate of separation than for molecular diffusion and evaporation, for which c is always 2. A further possible method of separation is that of "initial diffusion," which would take advantage of the fact that the front layer of molecules diffusing into a gas or a vacuum should be enriched in the lighter isotopes. The theory of non-equilibrium evaporation is discussed. If the vapour pressures of isotopes when pure are equal, a separation must occur when an isotopic liquid is evaporated in a vacuum in such a way that practically all the evaporating molecules are condensed. For an efficient separation, good mixing must take place in the surface and body of the liquid. This consideration makes the method inapplicable to solids, but solutions or liquid alloys might be used. Simple and closely approximate equations are developed for the change in the molecular fraction of any isotope and for the change of atomic weight in a mixture of any number of isotopes, when the latter is separated into fractions by a diffusion or evaporation process. A number of equations are evolved which apply to various sets of conditions. The rate of separation of two isotopes as measured by the change of atomic weight for a given operation is proportional to the square of the interval between the molecular weights of the two isotopes, inversely proportional to the ordinary molecular weight and proportional to the product of the molecular fractions of the isotopes. Similar relations also hold for a mixture of any number of isotopes. For a given element, the separation coefficient (equal to the decrease of atomic weight of the isotopic mixture for the first small portion of diffusate or condensate) is inversely proportional to the molecular weight of the compound in which that element is combined. A table of separation coefficients is given, calculated from atomic weights and the results of positive ray analysis. The value given for mercury has been calculated from the present experimental data. Most of the equations developed apply to the separation by diffusion of any gaseous mixture, whether it consists of isotopes or not. In systematic fractionation the diffusate or condensate, being formed at any time has an atomic weight less than that of the corresponding residue, which becomes denser as the diffusion proceeds, by a constant amount. Thus the enrichment of the light fraction is a maximum at the beginning. The atomic weight of the residue increases indefinitely, however, in proportion as the logarithm of its quantity decreases, whilst at the same time the atomic weight of the total diffusate approaches that of the original material. The use of cuts of two gives equal and opposite enrichments for the two fractions, equal in magnitude to 0.693 times the separation coefficient, or initial enrichment for the light fraction. Formulæ are given for calculating the proportions and numbers of isotopic species in compounds containing several isotopic atomic species. Zinc chloride contains twelve molecular isotopes, and if, for example, tin has six isotopes, the compound SnCl_4 is a mixture of thirty and SnCl_2Br_2 of fifty-four different molecular isotopes.

The existence of many new isomerides due to isotopism is pointed out. Experimental work on the partial separation of mercury into isotopes by non-equilibrium evaporation is described. Calculation based on data for a very efficient evaporation gives the value 0.0057 for the separation coefficient of mercury. The results agree with those of Brönsted and Hevesy (this vol., ii, 149), but the efficiency of the present separation is better. By making four successive cuts of approximately two, on both light and heavy fractions, a much larger decrease, of 64 parts per million, or 0.013 unit of atomic weight, has been obtained on the lightest fraction and a corresponding increase of 69 parts per million or 0.014 unit on the extreme heavy fraction. The results are in complete agreement with the theory developed. The total difference in density between the extreme fractions is 133 parts per million and a difference of 0.027 unit in the atomic weight. Data are given which show that a slight separation of isotopes occurs during an ordinary distillation under reduced pressure. A classification of the possible methods of separating isotopes is given in outline.

J. F. S.

Chromates of Thallium. G. CANNERI (*Gazzetta*, 1922, 52, i, 33—36).—Gröger's method of obtaining basic chromates (A., 1920, ii, 313) yields with thallous salts only normal thallous chromate. The action of dilute acid on thallous chromate yields thallous dichromate, but if a quantity of sulphuric acid insufficient to dissolve the chromate is employed and the boiling solution is filtered and concentrated, the double salt, $\text{TlHCrO}_4 \cdot \text{Tl}_2\text{CrO}_4$, is obtained in cinnabar-red crystals, which often form cruciform twins.

Thallic chromate may be obtained pure as a golden yellow, crystalline powder by dissolving freshly precipitated thallic oxide in excess of chromic anhydride solution.

The *E.M.F.* of the electrode, mercury amalgam|saturated thallous chromate solution varies continuously with the temperature, the curve exhibiting no characteristic point corresponding with the change in colour which thallous chromate crystals undergo when heated at 60°. Similarly the conductivity of saturated thallous chromate shows no sudden variation between 25° and 90°

T. H. P.

Molecular Condition of Metals Dissolved in Mercury. FRANZ SKAUPY (*Z. Elektrochem.*, 1922, 28, 23—27).—A theoretical discussion on the views which are at present held with regard to the condition of metals dissolved in mercury.

J. F. S.

Atomic Weight of Yttrium. H. C. FOGG and C. JAMES (*J. Amer. Chem. Soc.*, 1922, 44, 307—316).—The atomic weight of yttrium has been determined from the ratio $\text{YtCl}_3 : 3\text{Ag}$, and as a mean of twenty-one analyses the value 89.03 is obtained, the extreme values being 88.97 and 89.08. It is shown that to obtain very pure yttrium it is essential to use, finally, such a method as the cacodylate separation, in which the yttrium is precipitated whilst the more basic cerium earths remain in the form of quite

soluble salts. The material employed in the present work was obtained from Norwegian gadolinite and was submitted to a long process of purification which consisted in converting the oxalates of the rare earths into sulphates and these into bromates which were subjected to fractional crystallisation. A fraction containing yttrium and erbium bromates and practically no holmium was further purified by fractional precipitation as basic nitrate, which was continued until the erbium bands had practically disappeared. Further fractional precipitations by means of sodium nitrite and potassium ferricyanide were also carried out. The oxide obtained at the end of this series of purifications had a pale cream colour, due to a minute trace of praseodymium oxide, and this was removed by converting into acetate and precipitating as cacodylate, which effectually removed the last trace of impurity. The final purification was attempted by precipitation as the dimethyl phosphate, or *p*-sulphobenzoate and also by crystallisation of the acetate. The two former methods effected no purification, but the crystallisation of the acetates concentrated the coloured oxide in the mother-liquors. It was found, however, to be too wasteful and tedious.

J. F. S.

[Revision of the Atomic Weight of Lanthanum.] Correction.

G. P. BAXTER (*J. Amer. Chem. Soc.*, 1922, **44**, 328).—A correction of some eight figures in a table contained in a paper by Baxter, Tani, and Chapin on the atomic weight of lanthanum (*A.*, 1921, ii, 454). The following corrected values are given: $\text{LaCl}_3 : 3\text{Ag} = 0.757895$; atomic weight of lanthanum = 138.914 (mean); $\text{LaCl}_3 : 3\text{AgCl} = 0.570413$; atomic weight of lanthanum = 138.913 (mean).

J. F. S.

The Separation of the Rare Earths by Basic Precipitation.

WILHELM PRANDTL and JOHANNA RAUCHENBERGER (*Z. anorg. Chem.*, 1921, **120**, 120—128).—In a previous paper (*A.*, 1920, ii, 434) a method was given by which lanthanum could be separated from neodymium and praseodymium by regulated precipitation of the basic chlorides by ammonia in presence of ammonium chloride. The investigation has now been extended to samarium and it is found that the solubility of samaria in ammonia-ammonium chloride solutions at different concentrations and temperatures approximates closely to that of the didymia earths, being generally somewhat lower. Attempts to discover an unknown element between neodymium (atomic number 60) and samarium (62) by fractional precipitation of neodymia and samaria were unsuccessful.

With the object of applying the basic precipitation method more widely, the solubilities of lanthana, praseodymia, neodymia, and samaria were examined in presence of ammonia and ammonium nitrate at different temperatures, by adding the calculated quantity of ammonia, according to the equation $\text{M}'''(\text{NO}_3)_3 + 3\text{NH}_3 + 3\text{H}_2\text{O} \rightleftharpoons \text{M}'''(\text{OH})_3 + 3\text{NH}_4\text{NO}_3$ to the neutral nitrates in 1, 2, 3, 4, and 5*N*-ammonium nitrate solutions, and shaking for a day in a thermostat to attain equilibrium. The biggest separation of the solubility curves was found in 4—5*N*-ammonium nitrate solu-

tion at 100° , instead of $2-3N$ at 50° as in the case of the chlorides. The separation therefore depends on the nature of the anion, showing that it is due to the formation of basic salts of varying composition and solubility. The solubilities were then further examined in presence of an equivalent quantity of magnesium or zinc nitrate under similar conditions. The presence of magnesium offered no advantage for the separation of lanthanum from the other earths, but the solubilities of the last differed more among themselves at high concentrations of ammonium nitrate in presence of magnesium nitrate. The presence of zinc nitrate, however, increased the solubilities markedly, especially that of lanthana, which became four times that of the other earths. The practical application of this result will be reported later. E. H. R.

The Minimum Solubility of Aluminium Hydroxide in Water. A. MASSINK (*Chem. Weekblad*, 1922, 19, 66).—Since the minimum solubility of an amphoteric electrolyte lies at the isoelectric point, which for aluminium hydroxide requires $p_H \pm 7$, waters which are treated with aluminium compounds as coagulants should have a hydrogen-ion concentration close to that value.

S. I. L.

Tempering. A. POUCHOLLE (*Compt. rend.*, 1922, 174, 611—613).—Curves are given showing the variation in length of steel wires as a function of the time of cooling after different treatments. Tempering is characterised by the absence of the transformation point Ar_1 at low temperature. The transformation of γ -iron into α -iron only takes place at the point Ar_2 , that is, at about 200° . Over the temperature range $650-200^{\circ}$, from the point Ar_1 to the point Ar_2 , the curves do not show any angular point. However, invariably in this region, and only in this region, mechanical tensions appear, being manifested by sharp cracks and accompanied by the projection of the thin skin of oxide. The transformation point Ar_1 is lowered if the annealing observed follows a tempering. Similarly, the temperature at which tempering is obtained is lowered by successive temperings. The amplitude of the inflection Ar_1 diminishes (a) by rise in temperature until it becomes nil, (b) by the duration of the heating if the temperature remains constant. W. G.

Reduction of Ferric Chloride. A. PICKLES (*Chem. News*, 1922, 124, 93—94).—When hydrogen is passed through ferric chloride solution containing pieces of fine copper gauze, the ferric chloride is reduced rapidly; varying quantities of cuprous chloride are produced at the same time, and the reaction, which appears to be one of adsorption, is accelerated when the gauze is so arranged that it comes into intimate contact with the hydrogen. W. P. S.

The System Ferric Oxide-Sulphuric Acid-Water. MALCOLM PERCIVAL APPLEBEY and SIDNEY HERBERT WILKES (T., 1922, 121, 337—348).

Examination by the X-Ray Spectrum of Metallic Oxides which are Stable at Red Heat (Prepared by Different Methods and having Different Properties). J. A. HEDVAL (*Z. anorg. Chem.*, 1922, 120, 327—340).—That the properties of certain oxides prepared by different methods vary as regards colour, density, etc., is generally explained by assuming the existence of allotropic modifications. As this seems highly improbable, these oxides have been examined by the X-ray spectrum. The author shows that identical spectra can only be obtained from the same modification, and vice versa. The following oxides were examined. Ferric oxide (27), ferrosiferrous oxide (2), alumina (5), cobaltous oxide (2), cobaltocobaltic oxide (3), nickel oxide (6), magnesia (7), zinc oxide (6), cupric oxide (11), stannic oxide (3). The numbers in brackets give the number of different methods employed in their preparation. No oxide was found to exist in the amorphous form; they were all crystalline or cryptocrystalline. The different preparations of the same oxide gave identical spectra, which were the same as for the minerals. Many oxides were heated at 1150° for some time; this caused a change in some of their properties, but the X-ray spectrum remained unchanged. These changes in properties are not caused by changes in structure. W. T.

Properties of Subsidiary Valency Groups. III. The Preparation, Properties, and Molecular Volume Relationships of the Hydrates and Ammines of Cobalt Fluoride, Bromide, Iodide, Nitrate, Carbonate, and Citrate. GEORGE L. CLARK and HENRY K. BUCKNER (*J. Amer. Chem. Soc.*, 1922, 44, 230—244; cf. A., 1921, ii, 116).—The preparation and properties of a number of hydrates and ammines of several salts of cobalt are described. *Cobaltous fluoride trihydrate* is prepared by the action of hydrofluoric acid on cobalt carbonate; it forms rose-red crystals which only lose the last of the water at 300° in a current of nitrogen; $d=2.583$. *Cobaltous fluoride hexammine*, prepared by passing dry ammonia over the anhydrous fluoride placed on a balance pan until the requisite weight has been absorbed, which required about twenty-four hours, is a reddish-brown liquid at 25° which solidifies in ice and salt. It is easily soluble in water without hydrolysis, and has $d=1.744$. *Cobaltous fluoride triammine* is produced as a light pinkish-brown compound by keeping the hexammine in dry air; at 40° it loses all its ammonia. *Cobalt citrate tetrammine* is prepared by dissolving cobalt citrate in concentrated ammonia and evaporating spontaneously in a vacuum. It is a pink, very stable, crystalline compound, $d=1.686$. The preparation of many other compounds which have previously been prepared is also described. The molecular volume of all the above-named compounds is tabulated and the apparent volume of the subsidiary group calculated. The present work furnishes further evidence of the existence of cavities in the space lattice of solids, which may hold secondary valency groups, the sizes of the cavities depending on the relative volumes of cation and anion and varying in a parallel fashion with the stability of secondary

valency compounds. The constant relationship of physical properties among the halogens, free and combined, is shown by the linearity of the molecular volumes of the cobalt haloids, as well as by those of numerous other metal haloids, when plotted against the atomic volume of the halogens at the boiling point. Such linearity is not maintained after the formation of hydrates or amines. The great importance of the percentage contraction in the formation of hydrates, amines, and polyhaloids is shown by a straight line proportionality to stability. J. F. S.

Electrometric Study of the Hydrolysis of some Complex Cobaltamines under the Action of Barium Hydroxide.

PAUL JOB (*Compt. rend.*, 1922, **174**, 613—616).—Electrometric titration of complex cobaltamines with barium hydroxide gives a clear indication when the whole of the water of constitution of the cobalt complex has been replaced by the hydroxyl group. This method is capable of much wider application than the electrical conductivity method previously employed (cf. A., 1920, ii, 320). The curve obtained with the sulphatopentammine nitrate is quite regular and shows no inflexion, whereas the curves obtained with roseopentammine chloride and diroseotetrammine chloride both show marked inflexions and indicate when the replacement of the water of constitution is complete. W. G.

The Equilibrium of Tungsten and its Oxides with Hydrogen and Water Vapour; Carbon Monoxide and Carbon Dioxide and Oxygen.

J. A. M. v. LIEMPT (*Z. anorg. Chem.*, 1921, **120**, 267—276).—The measurements of Chaudron (A., 1920, ii, 379) are used to calculate the equilibrium constants for the reactions $\text{WO}_2 + 2\text{H}_2 \rightleftharpoons \text{W} + 2\text{H}_2\text{O}$; $\text{W}_2\text{O}_5 + \text{H}_2 \rightleftharpoons 2\text{WO}_2 + \text{H}_2\text{O}$; and $2\text{WO}_3 + \text{H}_2 \rightleftharpoons \text{W}_2\text{O}_5 + \text{H}_2\text{O}$; and the equilibrium curves are constructed. Making use of the water-gas constant $p_{\text{CO}} \cdot p_{\text{H}_2\text{O}} / p_{\text{CO}_2} \cdot p_{\text{H}_2}$, the constants for the three reactions $\text{WO}_2 + 2\text{CO} \rightleftharpoons \text{W} + 2\text{CO}_2$; $\text{W}_2\text{O}_5 + \text{CO} \rightleftharpoons 2\text{WO}_2 + \text{CO}_2$; $2\text{WO}_3 + \text{CO} \rightleftharpoons \text{W}_2\text{O}_5 + \text{CO}_2$ are also calculated. Further, from the known thermal dissociation of water, the vapour pressures and heats of formation of the three oxides of tungsten are calculated. The vapour pressures at 1773° are: $\text{WO}_2 \rightleftharpoons \text{W} + \text{O}_2$, $p = 10^{-8.2}$; $2\text{W}_2\text{O}_5 \rightleftharpoons 4\text{WO}_2 + \text{O}_2$, $p = 10^{-8.0}$; $4\text{WO}_3 \rightleftharpoons 2\text{W}_2\text{O}_5 + \text{O}_2$, $p = 10^{-6.7}$ atm. The heats of reaction are: $\text{W} + \text{O}_2 = \text{WO}_2 + 122,800$ cal.; $4\text{WO}_2 + \text{O}_2 = 2\text{W}_2\text{O}_5 + 121,400$ cal.; $2\text{W}_2\text{O}_5 + \text{O}_2 = 4\text{WO}_3 + 123,000$ cal. E. H. R.

Relationships between the Different Oxides of Uranium.

PIERRE JOLIBOIS and ROBERT BOSSUET (*Compt. rend.*, 1922, **174**, 386—388).—The decomposition of uranium trioxide, when heated in a vacuum is irreversible and yields the oxide U_3O_8 at 502° . The dioxide when heated in oxygen is oxidised very rapidly, the action commencing at about 185° . The only product is the oxide U_3O_8 . When heated in a current of hydrogen, the oxide U_3O_8 shows signs of reduction at 625° and the reduction can be completed at 650° . The only product is the dioxide UO_2 . In three hours at 1000° in a vacuum the oxide U_3O_8 only loses a very small

fraction of its oxygen. To obtain the dioxide by simple dissociation, the oxide U_3O_8 must be calcined at 2000° in a vacuum. W. G.

The Oxides of Uranium. P. LEBEAU (*Compt. rend.*, 1922, 174, 388—391; cf. preceding abstract).—From a consideration of the work done on the oxides of uranium the author concludes that the only oxides which have a definite existence are UO_3 , U_3O_8 , and UO_2 . The so-called black oxides have the composition U_3O_8 . They are stable in air and can be heated at 1000° under atmospheric pressure without decomposition. The green oxides prepared at temperatures below 800° contain varying amounts of uranium trioxide and can undergo change when exposed to moist air, the uranium trioxide present undergoing hydration (cf. Staehling, this vol., ii, 106). W. G.

The Amphoteric Character of Stannic Hydroxide and its Bearing on the Isomerism of the Stannic Acids. GEORGE ERNEST COLLINS and JOHN KERFOOT WOOD (*T.*, 1922, 121, 441—449).

Germanium. III. Germanium Tetrabromide and Germanium Tetrachloride. L. M. DENNIS and F. E. HANCE (*Chem. News*, 1922, 124, 66—69, 82—84; *J. Amer. Chem. Soc.*, 1922, 44, 299; cf. this vol., ii, 150).—When bromine vapour is passed over germanium, prepared by reduction of the dioxide with hydrogen, superficial reaction takes place in the cold, but the most favourable temperature for the reaction is about 220° . The germanium tetrabromide which distils over is best purified from bromine by fractional distillation. It has b. p. 185.9° (corr.) and m. p. 26.1° . It crystallises in small, white, flattened octahedra belonging to the cubic system. The liquid substance can be supercooled considerably, as low as -18° , without crystallising; n_D^{25} , 1.6269; d_{25}^{25} = 3.1315; specific conductivity < 0.000078 reciprocal ohm. It is very sensitive to water and fumes in air. With dry ammonia gas, it forms a white, solid compound.

Germanium tetrachloride was prepared by passing chlorine over germanium. Reaction started at 80° , was rapid at 180° , and at 360° the metal became incandescent. The crude product could not be freed from chlorine by fractional distillation, but the chlorine was removed by passing dry air through the liquid in a suitable apparatus with a condenser to keep back the germanium tetrachloride. The tetrachloride is a colourless, mobile liquid which fumes in air, b. p. 86.5° (corr.), m. p. -49.5° , n_D^{27} , 1.3606, d_{25}^{25} , 1.874. When the liquid is placed in water, reaction takes place slowly with a peculiar crackling sound. E. H. R.

Are Tantalum and Columbium Pentachlorides Conductors of Electricity in the Fused State ? WILHELM BILTZ and ARTHUR VOIGT (*Z. anorg. Chem.*, 1921, 120, 71—76).—According to Hampe (*A.*, 1888, 211), tantalum pentachloride is a good conductor, whilst columbium pentachloride is an insulator. To test the accuracy of these observations the two pentachlorides have been prepared in such a manner that moisture was altogether excluded and the

substance was distilled out of contact with air directly into the conductivity apparatus. The tantalum pentachloride was prepared by passing chlorine over a heated mixture of tantalum pentoxide and sugar carbon and distilling the pentachloride. It formed a snow-white mass of crystals which, when melted at $230\text{--}240^\circ$, had a conductivity $\kappa=0.30 \cdot 10^{-6}$. The platinum electrodes were strongly attacked, but the liquid appeared clear and unchanged. Columbium pentachloride was obtained by passing a current of chlorine over columbium sulphide, and, after removal of the sulphur chloride, distilling the columbium pentachloride. It crystallised in long, yellow needles, and its conductivity at $220\text{--}235^\circ$ was $\kappa=0.22 \cdot 10^{-6}$. The electrodes were attacked also in this case. The two compounds are therefore both insulators of about the same order as the best conductivity water.

E. H. R.

Action of Selenium on Gold. H. PÉLABON (*Compt. rend.*, 1922, 174, 391—392).—It is now shown that gold is attacked by selenium if immersed in the latter at a temperature just below its boiling point. The gold fixes some of the selenium, which is only removed with difficulty on heating, and at the same time some of the gold passes into the selenium. The β -selenium previously recorded (this vol., ii, 141) is, therefore, not a pure compound, its low electrical resistance being explained by the presence in it of gold dust held in suspension and by the crystalline configuration of the selenium.

W. G.

Preparation of Chloroplatinic Acid by Means of Hydrogen Peroxide. PAUL RUDNICK (*J. Amer. Chem. Soc.*, 1921, 43, 2575—2577).—Details of a method for working up platinum residues are given. The residues from the determination of potassium are extracted with the smallest possible quantity of hot water and filtered hot to remove asbestos and paper fibre. On cooling, pure potassium chloroplatinate is obtained as crystals. The filtrate from the crystals and all other aqueous filtrates are reduced with zinc and hydrochloric acid, and after removing the platinum black the filtrates are exposed to sunlight for several weeks, whereby further quantities of platinum black separate. Alcohol filtrates are treated as above after the alcohol has been expelled. The granular platinum black is washed and suspended in hydrochloric acid, treated with concentrated hydrogen peroxide, and stirred by passing in a stream of hydrogen chloride. The solution of the metal is complete in a few hours. The solution is treated with the necessary amount of potassium chloride and the potassium platinichloride added to the quantity obtained above. The material is stocked in this form. The reagent is prepared by reducing a weighed amount of potassium platinichloride with alkaline sodium formate, washing the platinum black, and dissolving as above. The solution is then made up so that 10 c.c. of the reagent contains 1 gram of metallic platinum.

J. F. S.

Mineralogical Chemistry.

The Relation of Chalcedony to other Forms of Silica. EDWARD W. WASHBURN and LOUIS NAVIAS (*Proc. Nat. Acad. Sci.*, 1922, 8, 1—5).—Chalcedony from Yellowstone Park and black pebble flint from France were examined in comparison with quartz, cristobalite, tridymite, and silica-glass, and determinations are given of d , n , inversion-temperature, coefficient of cubical expansion on either side of the inversion-temperature, and change in volume on inversion. The results suggest that the raw materials consist of quartz, but that after calcination the material is cristobalite. This is fully confirmed by the X-ray spectra. After calcination at 1450° for two hours, the chalcedony gave 99.87% SiO_2 and the flint 99.6% SiO_2 . L. J. S.

Camsellite, a New Borate Mineral from British Columbia. H. V. ELLSWORTH and E. POITEVIN (*Trans. R. Soc. Canada*, 1921, Sect. IV, [iii], 15, 1—8).—This is found as white, fibrous masses, intermixed with chrysotile and dolomite, filling shear zones in serpentine near Douglas Lake in the Nicola mining division. The blades give straight extinction with negative elongation and are probably orthorhombic; refractive indices α 1.575, γ 1.649. Analyses I, II, and III are of the camsellite, dolomite, and chrysotile respectively, separated from one another as far as possible; after deducting considerable amounts of impurities these are reduced to Ia, IIa, IIIa.

	SiO_2	CO_2	B_2O_3	Al_2O_3	Fe_2O_3	FeO	MnO	CaO	MgO	H_2O (at 110°)	H_2O ($>110^\circ$)	Total
I.	7.65	5.64	29.07	0.26	0.86	0.95	0.85	3.69	41.72	0.52	9.88	100.12*
II.	1.15	46.10	trace	0.09	—	0.29	0.66	29.05	20.98	0.03	0.69	100.05†
III.	39.95	1.15	trace	0.32	1.44	0.13	0.06	0.75	41.43	1.80	13.04	100.08§
Ia.	—	—	40.40	0.29	0.85	1.28	1.09	—	45.24	0.26	10.55	100.00†
IIa.	—	47.25	—	0.09	—	0.30	0.68	29.77	21.50	—	0.41	100.00
IIIa.	40.80	—	—	0.33	1.48	0.13	0.06	—	41.90	1.84	13.35	100.00

* Also Na_2O , K_2O 0.03, NiO trace. † Also MgO (insol.) 1.01. § Also Cr_2O_3 0.01, NiO , B_2O_3 , Na_2O , K_2O traces. ‡ Also Na_2O , K_2O 0.04. || Also Cr_2O_3 0.01.

The formula $2\text{MgO} \cdot \text{B}_2\text{O}_3 \cdot \text{H}_2\text{O}$ given by Ia, corresponds with that of the manganese borate sussexite. Up to 550° only 2.95% H_2O is lost. The mineral readily fuses to a black, opaque globule; and it is soluble in acids. L. J. S.

Tschermigite (Ammonium-Alum) from Wyoming. E. THEODORE ERICKSON (*J. Washington Acad. Sci.*, 1922, 12, 49—54).—Tschermigite occurs as colourless to white, columnar masses and imperfect crystals in brown bituminous shale near Wamsutter, Wyoming. It is optically isotropic, n 1.457, d 1.645. Associated are a pale yellow ammoniacal jarosite (containing $(\text{NH}_4)_2\text{O}$ 1.25%) and crystals of gypsum. Analysis gave (also traces of Fe_2O_3 , CaO , K_2O , Cl):

Al_2O_3	$(\text{NH}_4)_2\text{O}$	Na_2O	MgO	SO_3	H_2O	Insol.	Total
11.57	5.23	0.21	0.13	35.11	47.82	0.06	100.13

At 105°, the mineral fuses in its water of crystallisation and loses three-fourths of its water; nearly all the water is lost at 200°. The ammonium sulphate commences to decompose at 360°, and on ignition the total loss is 88.06%. Sodium alum when ignited gives $\text{Na}_2\text{O} + \text{Al}_2\text{O}_3$ presumably as sodium aluminate.

L. J. S.

Melanovanadite, a New Mineral from Peru. WALDEMAR LINDGREN, L. F. HAMILTON, and CHARLES PALACHE (*Amer. J. Sci.*, 1922, [v], **3**, 195—203).—A repetition of the earlier paper (this vol., ii, 155) giving some additional details. The mineral is hygroscopic; material which had been exposed to a moist atmosphere contained up to 16.6% H_2O , of which about 10.5% is lost over sulphuric acid or at 105°. A new analysis of such material gave:

V_2O_4 .	V_2O_5 .	CaO.	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$.	H_2O (above 105°).	Total.
33.48	49.38	10.65	1.39	5.90	100.80

The melanovanadite has probably been derived from a vanadium sulphide which is present in the black shale; and by its own alteration it gives rise to pascoite ($\text{Ca}_2\text{V}_6\text{O}_{17}, 11\text{H}_2\text{O}$). A microscopical examination of polished sections of patronite shows that this is a mixture of three minerals which are probably vanadium sulphides. Measurements of the monoclinic crystals of melanovanadite give the axial ratios $a : b : c = 0.4737 : 1 : 0.5815$, $\beta = 88^\circ 37\frac{1}{2}'$.

L. J. S.

Dewindtite, a New Radioactive Mineral. ALFRED SCHOEP (*Compt. rend.*, 1922, **174**, 623—625).—This occurs at Kasola, Katanga, Belgian Congo, as a canary-yellow powder intimately mixed with torbernite and a white, powdery material (which resembles impure talc, but contains much alumina—a partial analysis is given). Under the microscope, it is seen to consist of minute scales of rectangular or square outline, d 4.8. In the closed tube it yields water and becomes brown, returning to yellow on cooling. Before the blowpipe in the oxidising flame it fuses to a black globule, and in the reducing flame yields beads of lead. It is soluble in nitric acid, and decomposed by hydrochloric or sulphuric acid. The mean of several analyses is given under I;

	P_2O_5 .	UO_3 .	PbO.	$\text{Al}_2\text{O}_3(\text{Fe}_2\text{O}_3)$.	CaO.	MgO.	H_2O .	Insol.	Total.
I.	10.01	55.50	21.74	2.06	1.32	2.75	5.82	0.40	99.60
II.	10.84	60.13	23.55	—	—	—	5.46	—	[99.98]

deducting impurities (represented by the white powdery material), II corresponds with $4\text{PbO}, 8\text{UO}_3, 3\text{P}_2\text{O}_5, 12\text{H}_2\text{O}$.

L. J. S.

Japanese Minerals containing Rare Elements. III. Analyses of Beryl of Naegi, Mino Province. YŪJI SHIBATA and TAKU UEMURA (*J. Chem. Soc. Japan*, 1922, **43**, 48—62).—Beryl (d 2.6 and having no radioactivity) from Naegi in Mino Province gave on analysis:

SiO_2 .	Fe_2O_3 .	Al_2O_3 .	GLO.	CaO.	MgO.	Na_2O .	Ignition.	Total.
60.69	0.77	20.79	11.10	1.00	0.99	1.57	2.75	99.66

No alkali metals other than sodium were detected. The authors deduce the formula, $5\text{GlO} \cdot 2\text{Al}_2\text{O}_3 \cdot 10\text{SiO}_2$, the constitution $\text{Gl}[\text{SiO}_3 \cdot \text{Al}(\text{OH}) \cdot \text{SiO}_3 \cdot \text{Gl} \cdot \text{SiO}_3 \cdot \text{Al} \langle \text{SiO}_3 \rangle \text{Gl}]_2$ being suggested.

K. K.

Thortveitite, a Silicate of Scandium. JAKOB SCHETELIG (*Norsk Geol. Tidsskr.*, 1922, 6, 233—244).—Thortveitite (A., 1912, ii, 56; 1920, ii, 627) is found in felspar quarries in Sætersdalen, Norway, as large, greyish-green, prismatic crystals resembling epidote in appearance. These are monoclinic ($a:b:c = 0.7674:1:0.5569$, $\beta = 77^\circ 28'$) and usually twinned on $m(110)$; H 6—7, optically negative, α 1.7561, β 1.7926, γ 1.8093 (Na). Analysis I by J. SCHETELIG, II by J. ŠTĚRBA-BÖHM, and III by F. TAUCHERT.

	SiO_2	Sc_2O_3	Yt_2O_3	$(\text{Di}, \text{Er})_2\text{O}_3$	Fe_2O_3	FeO	GlO	Ign.	Total	<i>d.</i>
I.	42.9	37.6	17.7*		2.1	0.8	—	0.4	100.9	3.57
II.	45.45	42.06	8.89†		2.83	—	0.51	0.54	100.28	3.566
III.	45.55	38.61	10.47‡	4.26§	3.13	—	—	—	100.02	—

* Mol. wt. 270. † Mol. wt. 320. ‡ Mol. wt. 226. § Mol. wt. 380.

These lead to the diorthosilicate formula $(\text{Sc}, \text{Y})_2\text{Si}_2\text{O}_7$, analogous to that of thalenite (A., 1899, ii, 766). Spectroscopic analysis shows the presence of several other rare-earths, but an absence of cerium, zirconium, etc.

L. J. S.

The Anaheim Meteorite. R. A. A. JOHNSTON and H. V. ELLSWORTH (*Trans. R. Soc. Canada*, 1921, [iii], 15, sect. IV, 69—92).—This iron, weighing 11.84 kilos., was found in 1916 and probably represents the meteor observed on January 21, 1914. The structure is that of a coarse octahedrite, and the different constituents were studied in detail by the metallographic method. I is the bulk analysis of the iron (also insol. in nitric acid 0.003; Ti, V, Al, Sn absent); II of the kamacite groundmass readily dissolved in 10% hydrochloric acid. The constituents insoluble in this dilute acid were separated into: III, bright, tin-white lamellæ of ténite rich in nickel; IV, tin-white, uncrystallised phosphide (schreibersite) giving ratios near $\text{Fe}_5(\text{Ni}, \text{Co})_2\text{P}_2$; V, long, slender crystals of phosphide (rhabdite?), $(\text{Fe}, \text{Ni}, \text{CO})_3\text{P}$. VI, central portion of a nodule of chromiferous troilite, which in the outer portion is intergrown with 38.71% graphite.

	Fe.	Ni.	Co.	Cu.	Mn.	Cr.	Si.	P.	S.	C.	Total.	<i>d.</i>
I.	91.51	7.84	0.46	0.08	trace	0.001	0.002	0.219	0.012	0.01	100.12	7.873
II.	93.10	6.39	0.48	0.03	—	—	—	—	—	—	100.00	—
III.	60.74	37.38	0.67	0.64	nil	nil	nil	0.65	—	trace	100.08	7.9
IV.	61.28	25.62	0.47	0.09	—	—	—	13.06	—	—	100.52	7.2
V.	40.28	41.36	0.23	0.77	—	—	—	15.35	—	n. d.	98.68*	—
VI.	62.91	0.28	trace	0.16	—	0.96	—	—	35.47	—	99.76	4.814

* Also SiO_2 0.69.

L. J. S.

The Pitts Meteorite. S. W. MCCALLIE (*Amer. J. Sci.*, 1922, [v], 3, 211—215).—This meteorite was observed to fall on April 20, 1921, at Pitts in Wilcox Co., Georgia. Four fragments, weighing

Analytical Chemistry.

Phenol-red as an Indicator for Acidity of Media. A. MASSINK (*Pharm. Weekblad*, 1921, 58, 1133—1136).—The colorimetric determination of p_H in the region 7—8 by means of phenol-red is affected by the electrolyte-content of the solution, the values being too low with low salt-content, and too high with high salt-content. S. I. L.

Continuous Reading Electro-titration Apparatus. KENNETH H. GOODE (*J. Amer. Chem. Soc.*, 1922, 44, 26—29).—An electro-titration apparatus for the determination of hydrogen-ion concentration is described by means of which the *E.M.F.* between a calomel electrode and a hydrogen electrode may be read continuously. The voltmeter consists of a three electrode vacuum valve ("audion"). The three electrode valve consists of a highly exhausted glass bulb containing an incandescent filament surrounded by a grid of fine wire, which is itself surrounded by a metallic plate. A battery of 20—100 volts connected between the plate and filament, through a d'Arsonval galvanometer, produces a current through the plate circuit, the magnitude of which is proportional to the potential of the grid. The filament is connected to a 6-volt circuit containing a resistance which adjusts the current to 1.06 amperes. The current in the plate circuit, I_p , may be considered as the sum of a constant current, I_0 , which is independent of the grid potential and a current $(I_p - I_0)$ which is a linear function of the grid potential. The current I_0 is balanced by an equal current in the opposite direction and $(I_p - I_0)$ is measured with the galvanometer which is calibrated to read either volts or Sørensen units directly. The calomel cell is connected to the negative pole of the filament circuit and the hydrogen electrode to the grid. The apparatus as described with a d'Arsonval galvanometer of sensitivity of 10.1×10^{-6} amperes for one scale division is sensitive to 0.1 Sørensen unit or 0.006 volt. J. F. S.

Titration in Ethyl Alcohol as Solvent. EDNA R. BISHOP, ESTHER B. KITTREDGE, and JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1922, **44**, 135—140).—Alcoholic solutions of acetic, maleic, palmitic, and sulphuric acids, *p*-chlorophenol, and phenol have been titrated with an alcoholic solution of sodium ethoxide, using the hydrogen electrode as indicator. The hydrogen electrode was measured against the electrode $\text{HgHg}_2\text{Br}_2/N/10\text{KBr}$ in alcohol. Similar titrations of alcoholic solutions of ammonia and aniline by alcoholic hydrogen chloride were also carried out. Sharp and accurate end-points were obtained, but the titrations take much longer than titrations in aqueous solutions by the same method, since the hydrogen electrode requires ten minutes before it reaches a constant value. The hydrogen potentials at which a series of indicators changes colour was determined by titrating pairs of the above-named substances and using the indicators and then measuring the potential of the mixture which just gives the colour change. The potential range 0.14—0.45 was measured with aniline and hydrogen chloride, 0.45—0.70 and 0.90—0.97 with acetic acid and sodium ethoxide and 0.75—0.98 volt with *p*-chlorophenol and sodium ethoxide. The positions of most of the indicators in alcohol are close to their positions in water; some exceptions occur, for example, cyanine is displaced very much to the acid side, and some indicators which are useful in water cannot be used in alcoholic solution. The following colour changes and potentials are recorded: Benzaldehyde-green, green 0.69 colourless. Bromophenol-blue, yellow 0.34, green 0.47 blue. Cresol-red, pink 0.20 orange 0.30. Curcumin, greenish-yellow 0.66 red 0.85 orange 0.91 golden. Cyanine, colourless 0.24 blue; gallein, rose 0.68 violet-blue. Iodeosin, golden brown 0.20 pink; methyl-green, blue 0.66 lavender. Methyl-orange, pink 0.20 orange 0.23 yellow. Methyl-violet, violet 0.95 colourless. Methyl-red, red 0.54 orange 0.62 yellow. Naphthol-benzoin, light brown 0.70 blue. *p*-Nitrophenol, colourless 0.61 yellow green. Phenolphthalein, colourless 0.68 red. Resorcin-blue, red 0.39 blue. Rosolic acid, golden 0.58 orange 0.67 pink. Sodium alizarin-sulphonate, greenish-yellow 0.50 orange 0.55 rose 0.82 violet. Thymol blue, red 0.30 golden. Thymolphthalein, colourless 0.82 blue. Trinitrobenzene, colourless 0.68 golden-orange. Tropæolin salmon-pink 0.20 orange 0.23 golden, and tropæolin OO, pink 0.15 orange 0.20 yellow. Palmitic acid in the presence of tripalmitin may be titrated in alcoholic solution with sodium ethoxide, using thymolphthalein as indicator. J. F. S.

Simple Theory of the Nephelometer. P. V. WELLS (*J. Amer. Chem. Soc.*, 1922, **44**, 267—276).—The theory of the nephelometer and its use are considered. It is shown that although the depth ratios by reflection and by transmission are equal, both methods cannot be used in nephelometry except for an intermediate range of concentrations. For extremely dilute suspensions, for example, less than 10^{-5} gram/c.c., the transmissions are quite insensitive, whilst the reflection measurement remains sensitive down to the limit of vision. On the other hand, for very turbid suspensions

the transmission probably follows less complicated laws. Although masses in suspension much too small to be detected by the most delicate balance can be easily measured in a Tyndall beam, the precision of such a measurement can never exceed that of the best photometry, that is, about 0.2%. For sensitive and rapid work nephelometry takes its place with other volumetric methods. The phenomena of diffuse reflection and transmission are much more complicated than is represented in the present considerations, but the simple theory presented gives a general idea of the phenomena and may serve as a starting point of a future investigation.

J. F. S.

Nephelometry. A Nephelometer with Constant Standard.

A. A. WEINBERG (*Biochem. Z.*, 1921, **125**, 292—310).—A new nephelometer and point-source of light are described which embody the best features of the Kober (A., 1917, ii, 266) and Kleinmann (A., 1920, ii, 634) nephelometers, the most striking feature being the introduction of the Lummer-Brodhun prism whereby the two fields are rendered concentric. Nephelometric estimations with such an instrument are comparative and a modified nephelometer is described with a permanent standard. This is attained by replacing one of the tube systems by two Nicols, the lower of which can be rotated relatively to the upper, thus reducing the light to any degree as recorded by a scale on the Nicol prism. For coloured solutions, a slip of coloured glass can be inserted.

H. K.

Quantitative Analysis by Centrifuge. OLOF ARRHENIUS (*J. Amer. Chem. Soc.*, 1922, **44**, 132—134).—The estimation of calcium, magnesium, and phosphoric, sulphuric and nitric acids may be effected by precipitating the various substances in the usual way and transferring the precipitate and mother-liquor to tubes 2.5 cm. diameter at the top and provided with a steep funnel below leading to a capillary tube 4 cm. long and 1 mm. diameter. The precipitate is allowed to settle and by means of gentle shaking is, for the most part, caused to settle in the capillary stem. The tube is then centrifuged until the height of the column of precipitate is constant; this usually requires thirty minutes. The height of the column is then read and reduced to the weight standard by comparison with a precipitate similarly obtained from a known weight of the same substance. The method claims no great degree of accuracy, and is suggested as a suitable method of analysis for soil and similar substances.

J. F. S.

The Penetrability of Filter-paper. R. C. GRIFFIN and H. C. PARISH (*J. Ind. Eng. Chem.*, 1922, **14**, 199—200).—An apparatus is described for testing the penetrability of filter-paper by observing the time required to pass 100 c.c. of distilled water at 20° through a 2-inch disk of the paper under a constant head of 9 inches of water. The apparatus, which is constructed mostly of lead, consists of an overflow cup connected by a pipe to the under side of a

wire gauze which supports the disk of filter-paper, and is placed 9 inches below the top of the overflow cup. The distilled water is fed into the connecting pipe at such a rate that it overflows at the cup as well as through the outlet pipe of the apparatus after passing through the filter-paper, and the number of seconds required to collect 100 c.c. at the outlet is timed with a stop watch. It was found that the temperature of the water had a marked bearing on the speed of filtration, water at 30°, for example, passing through more than twice as rapidly as water at 0° under otherwise similar conditions. The time factor is also important, and even when distilled water is used the filtration slows down after a time owing to the hydration and expansion of the fibres. A paper which initially had a penetrability of twenty-five seconds had slowed down after two hours to one thousand seconds. G. F. M.

Estimation of Perchlorate by Rothmund's Method. FRITZ KÖNIG (*Z. anorg. Chem.*, 1921, **120**, 48).—In the estimation of perchlorate by reduction with titanous sulphate by Rothmund's method (A., 1909, ii, 434), it is unnecessary to pass a current of hydrogen or carbon dioxide through the flask if a long, narrow glass tube is adapted to the reflux condenser to prevent circulation of air. For the oxidation of excess of titanous sulphate, ferric ammonium sulphate is better than permanganate in view of the fact that the latter may attack the hydrochloric acid, and that in the back-titration of silver nitrate in the chlorine determination by the Volhard process a ferric salt must be present. Soluble titanic sulphate is now a commercial product and can be reduced electrolytically, using lead electrodes, to titanous sulphate.

E. H. R.

Comparative Values of Different Specimens of Iodine for Use in Chemical Measurements. C. W. FOULK and SAMUEL MORRIS (*J. Amer. Chem. Soc.*, 1922, **44**, 221—229).—Iodine purified by several methods, including wet and dry sublimation and drying in the presence of sulphuric acid and phosphoric oxide, has been compared by direct titration with sodium thiosulphate with iodine prepared by Baxter's atomic weight method (A., 1905, ii, 81, 579). Using some new forms of titration flasks and other pieces of apparatus for handling iodine, it is shown that the maximum difference between the various specimens and the highly purified iodine is 0.024%. It is shown that a rubber stopper may be used in place of a glass stopper for closing the flask in which the iodine is titrated. The usual method, as given in text-books of analytical chemistry, of drying iodine by exposing it in a desiccator with a drying agent, is open to criticism if the iodine has previously solidified in the presence of water. Powdered iodine when exposed under a bell-jar with water takes up 0.09% of its weight in forty-eight hours, whilst crystals take up only 0.05% under the same conditions in five days. An exposure to sulphuric acid for ten days removes the whole of the water in both cases. It is suggested that solids like iodine, which have a measurable vapour pressure at ordinary

temperatures, possess peculiar adsorptive properties, due to the fact that a fresh surface is being continually exposed. J. F. S.

Method of Determining Traces of Oxygen in Hydrogen.

ALFRED T. LARSON and ERNEST C. WHITE (*J. Amer. Chem. Soc.*, 1922, **44**, 20—25).—A rapid and accurate method of estimating traces of oxygen in nitrogen-hydrogen mixtures such as are used in the synthetic manufacture of ammonia is described. The method consists, essentially, in passing the gas mixture through a platinised platinum catalyst which is heated at 305° in a carefully regulated diphenylamine vapour-bath, and measuring the rise in temperature due to the combustion of the hydrogen by means of a thermo-element. The deflexions of a sensitive galvanometer attached to the thermo-element give a measure of the oxygen content of the gas mixture. Concentrations of oxygen as low as 0.001% may easily be determined with an error of 3%. The apparatus was calibrated for a rate of flow of 500 c.c. per minute by adding electrolytic oxygen from an alkali electrolysis to the oxygen-free mixture of nitrogen and hydrogen. By the use of a less sensitive galvanometer, the apparatus may be used for concentrations of oxygen up to about 1%. Precautions necessary for efficient working of the apparatus are indicated. J. F. S.

The Estimation of Sulphur in Iron Pyrites. G. CHAUDRON

and G. JUGE-BOIRARD (*Compt. rend.*, 1922, **174**, 683—685).—During the dissolution of pyrites in nitric acid or aqua regia, there is always a separation of free sulphur if the temperature exceeds 60°, in the case of marcasite or pyrites containing other metallic sulphides. If, however, the acid is allowed to act at the room temperature, there is no separation of sulphur, but the time required is much longer. W. G.

A New Method of Estimating Sulphur in Organic Compounds. H. TER MEULEN (*Rec. trav. chim.*, 1922, **41**, 112—

120).—The substance is vaporised or decomposed by heating in a current of hydrogen and the mixture of vapours and hydrogen then passed through a heated quartz tube containing platinised asbestos. All the sulphur is thus converted into hydrogen sulphide, which is led into an alkaline solution and estimated iodometrically. In the case of very small quantities, colorimetric estimation by means of sodium plumbite is suitable. Experimental errors are avoided by using small quantities of material, heating gently, and not allowing the hydrogen to pass too quickly. It is occasionally necessary to burn off a deposit of carbon from the catalyst.

The results obtained by this method are in good agreement with the theoretical values. H. J. E.

Volumetric Method for the Estimation of Hyposulphurous and Sulphoxylic Acids. FERRUCCIO DE BACHO (*Giorn. Chim.*

Ind. Appl., 1921, **3**, 501—502).—This method is based on the property possessed by formaldehyde of forming with hyposulphite a solution highly resistant to oxidation by means of atmospheric oxygen [cf. *J. Soc. Chem. Ind.*, 1922, 250A.] T. H. P.

Microchemical Estimation of Nitrogen. C. VALLÉE and M. POLONOWSKI (*Compt. rend. Soc. Biol.*, 1921, **84**, 900—901; from *Chem. Zentr.*, 1921, iv, 1080).—For microchemical estimation of nitrogen, the substance is heated with 1 c.c. of sulphuric acid, 1 gram of potassium sulphate, and a small piece of quartz, and diluted with 6 c.c. of water. After addition of 3 c.c. of sodium hydroxide solution, the ammonia is carried over by a current of air into 0.02N-sulphuric acid. G. W. R.

Estimation of Small Quantities of Nitrogen by Kjeldahl's Method. J. K. PARNAS and RICHARD WAGNER (*Biochem. Z.*, 1921, **125**, 253—256).—A description of a slight modification of Pregl's micro-Kjeldahl method of analysis. H. K.

Nesslerisation of Ammonia Solutions. CLARENCE E. MAY and HARRY P. ROSS (*J. Amer. Chem. Soc.*, 1921, **43**, 2574—2575).—In the estimation of ammonia in urine by the Folin-Bell method (A., 1917, ii, 268) and of urea in urine by the Folin-Youngburg method (A., 1919, ii, 304), the authors were troubled by the formation of clouds and precipitates during the time (twenty minutes) which the solution is kept after the addition of the reagent. An investigation of the reactions shows that such disturbing occurrences may be avoided if the following points are observed. Distilled water only must be used for dilutions; the flask must be rinsed with nitric acid before each determination to remove the mercury film which may have been formed in a previous experiment; the Nessler solution should be the one recommended by Folin and Wu (A., 1919, ii, 308); the whole of the Nessler solution must be added rapidly; after the addition, the solution must not be shaken or stirred and must be left unmoved for at least twenty minutes and any dilution must be made only after this time has elapsed; the solution to be Nesslerised should not contain more than 1.0 mg. of ammonia nitrogen in 150 c.c. On Nesslerisation and dilution to 200 c.c., the brown colour is very intense, and with such concentrated solutions part of the product tends to deposit on the walls of the flask and interfere with the colorimetric work. J. F. S.

The Volumetric Estimation of Hydroxylamine and Hydrazine. ALBIN KURTENACKER and JOSEF WAGNER (*Z. anorg. Chem.*, 1921, **120**, 261—266).—It was shown by Rupp and Mäder (A., 1913, ii, 618) that hydroxylamine can be oxidised quantitatively by a bromate-bromide mixture in sulphuric acid solution to nitric acid, according to the equation $\text{NH}_2\cdot\text{OH} + 6\text{Br} + 2\text{H}_2\text{O} = \text{HNO}_3 + 6\text{HBr}$. As a method of analysis, however, the reaction has serious limitations, since, unless only a very small quantity of hydroxylamine is taken and a large excess of bromine used, oxidation is incomplete and nitrous acid is formed. It is found, however, that if bromate alone is used in strong hydrochloric acid solution, nascent chlorine being then the oxidising agent, complete oxidation is assured, and the reaction can be used for the estimation of hydroxylamine. The hydroxylamine solution (containing about 1.14 gram of $\text{NH}_2\cdot\text{OH}\cdot\text{HCl}$ per litre) is mixed with excess of

0.1*N*-potassium bromate solution and acidified with hydrochloric acid. After a quarter of an hour (the reaction is not instantaneous), potassium iodide solution is added and the liberated iodine is titrated with thiosulphate. Sulphuric acid cannot be used instead of hydrochloric, and bromide must not be present.

Hydrazine is oxidised by bromate or a bromide-bromate mixture in hydrochloric acid solution instantaneously to nitrogen. The estimation can be carried out exactly as for hydroxylamine, estimating excess of bromate by means of iodide and thiosulphate, or a direct bromate titration can be made using indigo as indicator. The hydrazine solution is mixed with potassium bromide and hydrochloric acid and titrated with 0.1*N*-bromate solution at about 60°. Towards the end of the titration, a few drops of indigo solution are added and the titration is continued until the colour becomes yellow.

Hydroxylamine and hydrazine may be estimated together. A sample is first titrated as for hydroxylamine, and the bromate equivalent for the sum of the two found. A second sample is then oxidised with bromate in an atmosphere of carbon dioxide and the nitrogen evolved is collected and measured. This gives the amount of hydrazine present and that of the hydroxylamine can be calculated.

E. H. R.

The Action of Nitrous Acid on Iodides in the Presence of Oxygen. MAURICE LOMBARD (*Bull. Soc. chim.*, 1922, [iv], 31, 161–169).—When nitrous acid acts on potassium iodide in the presence of oxygen, the nitrous acid is regenerated as fast as it disappears. Without taking slight losses into account, two causes limit the phenomenon. One of these causes is independent of the analyst, and is small but relatively constant. It is the production of a small amount of nitrogen. The other cause, which is of variable importance, depends almost entirely on the method of working. It is the production of nitrate (which may be nil); and it is this which, coupled with the losses by diffusion, leads to such variable results. Thus the estimation of nitrites by the liberation of iodine is impossible in the presence of oxygen. Comparable results might be obtained by working under carefully controlled conditions which would, however, be difficult to realise, and different analysts would probably obtain widely differing results.

W. G.

Estimation of Oxides of Nitrogen [in Air]. V. C. ALLISON, W. L. PARKER, and G. W. JONES (*U.S. Bureau of Mines, Tech. Paper* 249).—The phenoldisulphonic acid method for the estimation of nitrates in water analysis is adapted to the estimation of small quantities of oxides of nitrogen in air. The sample is taken in an evacuated tube of about 250 c.c. capacity, and after the usual analysis has been made for carbon dioxide, carbon monoxide, oxygen, etc., 5 c.c. of 10% sodium hydroxide solution and 5 c.c. of hydrogen peroxide are introduced into the tube, which is then closed with a rubber stopper and rotated to coat the inside with a film of liquid, and is then left for thirty minutes. The contents are then washed through a filter-paper into a 150 c.c. beaker and

evaporated just to dryness. The residue is treated with 2 c.c. of the phenoldisulphonic acid reagent, diluted to 10 c.c., filtered into a Nessler tube, 15 c.c. of ammonia are added, and the whole made up to 100 c.c. and compared with standards similarly prepared from a standard potassium nitrate solution. The method is sensitive to 10 parts of oxides of nitrogen in 1,000,000 parts of air with an accuracy of about 5 parts per million. G. F. M.

The Argentometric Titration of Phosphoric Acid. I. M. KOLTHOFF (*Pharm. Weekblad*, 1922, 59, 205—215).—The solubility product of silver phosphate in water is of the order 1×10^{-21} ; accurate determinations are impossible, since decomposition occurs, the salt becoming black. Accurate results are easily obtained in estimating phosphoric acid by means of excess of silver nitrate if the solution is made neutral to phenol-red by addition of 0.1N-sodium hydroxide; phenolphthalein is less suitable. In place of sodium hydroxide, sodium acetate may be added; about 2 grams are required for 10 c.c. of 0.1 molar phosphate solution, and in this case ammonium, calcium, and magnesium salts do not interfere.

In estimating phosphoric acid in urine, the ammonium magnesium salt is precipitated, washed and dissolved in nitric acid, the solution being neutralised with sodium hydroxide, using dimethyl-yellow as indicator, and titrated with silver nitrate, the excess of which is estimated by Volhard's method. S. I. L.

Errors caused by Nitrates and Nitrites in the Estimation of Arsenic by the Distillation Method and a Means for their Prevention. J. J. T. GRAHAM and C. M. SMITH (*J. Ind. Eng. Chem.*, 1922, 14, 207—209).—In the presence of nitrates or nitrites the distillation method for the estimation of arsenic as usually carried out, using cuprous chloride or cuprous chloride and ferrous sulphate as the reducing agents, gives low results owing to some volatile substance, probably nitrosyl chloride, carried over with the arsenic trichloride into the distillate oxidising it to quinquevalent arsenic. The extent of the oxidation depends largely on the length of time the distillate is kept before titration. The error may be avoided by using hydrazine sulphate in conjunction preferably with sodium bromide as the reducing agent, whereby the nitrates, etc., are reduced to nitrogen. For a sample containing the equivalent of not more than 0.6 gram of As_2O_5 , 50 c.c. of a solution containing 2% each of hydrazine sulphate and sodium bromide in dilute (1 : 4) hydrochloric acid will be required for the analysis. The mixture is boiled for two to three minutes, 100 c.c. of concentrated hydrochloric acid are added, and the distillation is proceeded with in the usual way. G. F. M.

The Separation of Arsenic from Tungsten, Vanadium, and Molybdenum by Means of Methyl Alcohol in a Current of Air. L. MOSER and J. EHRLICH (*Ber.*, 1922, 55, [B], 430—437).—It has been shown previously (A., 1912, ii, 866) that trivalent arsenic can be separated quantitatively from antimony and other metals at the temperature of boiling water by volatilising it partly as

methyl arsenite and partly as arsenic trichloride in a current of air. In the presence of tungstic acid, however, the removal of arsenic is incomplete, owing to the adsorption of a portion of the arsenic trichloride by colloidal tungstic acid. The difficulty can be removed by bringing the latter into highly disperse solution, which is readily effected by means of pyrogallol; the procedure is described fully in the original. Accurate results are obtained thereby in the estimation of arsenic, but the method suffers under the disadvantage that the pyrogallol must be destroyed before the tungsten can be estimated in the residue. The action of a number of other substances (oxalic, tartaric, and citric acids) is considered and the following process is recommended. The solution containing the tungstate and arsenious acid (arsenic acid must be reduced by one of the customary methods) is evaporated to small bulk and treated with glacial acetic acid (20 c.c.) and concentrated hydrochloric acid (120—150 c.c.); after addition of methyl alcohol (30 c.c.), distillation is effected as described previously in a current of air. Arsenic is estimated, preferably iodometrically, in the distillate; the residue in the distillation flask is evaporated completely to dryness on the water-bath, dissolved in dilute sodium hydroxide solution, and the tungstic acid precipitated as mercurous tungstate.

The separation of arsenic from molybdenum and vanadium is effected without difficulty by the ester method; it is only necessary to make certain that a sufficient amount of the reducing agent is added (even when the arsenic is present in the tervalent state), since molybdic and vanadic acids themselves attack the latter.

H. W.

The Theory of the Distillation of Arsenic and a New Separation of Arsenic from all Metals in a Current of Air. L. MOSER and J. EHRLICH (*Ber.*, 1922, **55**, [B], 437—447; cf. Moser and Perjatel, A., 1912, ii, 866; Moser and Ehrlich, preceding abstract).—A study of the rate of distillation of arsenic chloride from a solution of arsenious oxide in concentrated hydrochloric acid shows that the process is influenced greatly by the hydrolysis of the chloride and that this effect becomes more marked as the distillation proceeds towards completion. The difficulty has been overcome largely by suitable addition of potassium bromide to which a catalytic action has been commonly ascribed. Its function, however, is shown to depend on its ability to repress hydrolysis of arsenic chloride, since it may be regarded as attracting the water from the mixture for purposes of solution and thus rendering the solutions of arsenic chloride in hydrochloric acid more concentrated with regard to the latter. The effect is exhibited by a number of other substances, for example, barium chloride, barium acetate, sodium pyroborate, sodium benzoate, sodium nitroprusside, crystalline lactose, etc., which are freely soluble in water, but insoluble or very sparingly soluble in concentrated hydrochloric acid.

The following method of estimating arsenic is recommended.

It does not involve the use of methyl alcohol. It requires no supervision and is complete within about forty minutes (or thirty minutes after addition of potassium bromide). Since the liquid never comes to its boiling point, it is impossible for compounds of antimony to distil. The apparatus consists of a wide-mouthed flask of 300 c.c. capacity provided with a rubber stopper carrying an inlet tube for air, a stoppered dropping funnel, and a bulb tube connected with a long glass tube dipping into water (250 c.c.) contained in a beaker which is cooled by running water. The arsenious oxide (0.15–0.25 gram) is dissolved in concentrated hydrochloric acid (*d* 1.19, 50 c.c.) in the flask which is immediately immersed up to the neck in boiling water, whilst a brisk current of air is passed through the solution. At intervals of ten minutes, further additions of concentrated hydrochloric acid (20 c.c.) are made. After forty to sixty minutes the distillation is interrupted and the arsenic titrated in the distillate with *N*/10-potassium bromate solution. The procedure is similar when potassium bromide (about 1.5 grams) is used, but two or at most three additions of hydrochloric acid only are necessary. Arsenic acid must be reduced in the usual manner, for example, with ferrous sulphate, hydrazine sulphate, or even with potassium bromide alone.

H. W.

Microchemical Estimation of Carbon and Hydrogen.

FRITZ WREDE (*Ber.*, 1922, **55**, [B], 557–563).—A valuable detailed discussion, unsuitable for abstraction, of apparatus, absorbent and oxidising materials, and procedure necessary for the microchemical estimation of carbon and hydrogen in organic compounds by Pregl's method.

J. K.

Estimation of the Carbon Dioxide Content of Air, with Special Reference to the "Aeronom." HANS RAUCH (*Z. Hyg. Infektionskrankh.*, 1920, **91**, 1–26).—A critical comparison was made between various methods for the estimation of carbon dioxide as used in analysing the air of schools, dwellings, etc. Results obtained with the "aeronom," an instrument in which the difference of pressure, measured with an oil manometer, of an enclosed volume of air before and after its content of carbon dioxide has been absorbed with sodium hydroxide, differ by as much as 20% when compared with the more exact Pettenkofer's baryta method. These larger errors were found also when the carbon dioxide was absorbed by sodium carbonate or sodium hydroxide as in the methods of Lung-Zeckerdorf and Wolput. The author concludes that of the methods studied in determining the ventilating conditions in rooms, Pettenkofer's method is preferable.

CHEMICAL ABSTRACTS.

Estimation of Carbon Dioxide in Mineral Carbonates.

L. A. SAYCE and A. CRAWFORD (*J. Soc. Chem. Ind.*, 1922, **41**, 57–58T).—The ignition method in a Teclu furnace until the substance shows no further loss in weight gives consistent results where the decomposition temperature is low enough for it to be

applied without complications arising, as, for example, reduction to metallic lead with cerussite, and oxidation of the ferrous oxide to an unknown extent with chalybite. The Schrötter method is unsuitable for estimating the carbonates of metals having comparatively insoluble sulphates. Hydrochloric acid can be used successfully for the decomposition, but this introduces the danger of loss of acid by volatilisation. Armstrong's simple modification of the Schrötter apparatus is capable of fair accuracy. Garrett's apparatus, consisting of a stout test-tube to the top of which is attached a Y-tube, one branch of which bears a tap funnel containing dilute acid, and the other a combined condenser and drying tube leading to potash bulbs or soda-lime tubes, gave good results with witherite, but for some unexplained reason very inconsistent results were obtained with calcite. Collin's calcimeter, by reason of the ease of operation, and the short time needed for an estimation seems well adapted for dealing with readily soluble carbonates when an accuracy of 0.1 or 0.2% is sufficient. G. F. M.

The Volumetric and Gravimetric Estimation of Zinc. STEFAN URBASCH (*Chem. Ztg.*, 1922, **46**, 6—7, 29—30, 53—55, 97—99, 101—103, 125—127, 133—134, 138—139).—The separation of zinc from the common metals and its estimation by means of potassium ferrocyanide and sodium sulphide and as zinc oxide have been studied in detail. In all cases the ore is dissolved in aqua regia, the solution evaporated with sulphuric acid, the heavy metals removed with hydrogen sulphide and the iron and aluminium with ammonia in the presence of ammonium chloride if the ferrocyanide or gravimetric method is to be used, or of magnesium chloride if the sulphide titration is adopted. The ferrocyanide titration is carried out in a bulk of 150 c.c. containing 2—3 drops of hydrochloric acid and 3 c.c. of a 0.03% ferric chloride solution. The ferrocyanide is added to the boiling zinc solution until the blue colour just fades to white, a standard zinc chloride solution is then added, drop by drop, until the blue colour just reappears, and this amount of zinc is deducted from that found in the first titration. In the sulphide method, ammonia and ammonium salts should be kept as low as possible. The separation of cadmium from zinc by hydrogen sulphide is not complete in one operation if much zinc is present, but a satisfactory separation may be obtained by boiling the solution of the mixed metals with aluminium foil and finally adding hydrogen sulphide water to prevent resolution of the cadmium. The separation of zinc from nickel and cobalt by the "salting out" method is discussed with regard to the necessary acidity of the solution; the author recommends saturating a solution containing less than 0.15 gram of zinc and about 1 c.c. of normal acid per 100 c.c. with hydrogen sulphide at 50°. [*Cf. J. Soc. Chem. Ind.*, 1922, 218A.] A. R. P.

The Detection of Small Quantities of Lead in Urine. O. SCHUMM (*Z. physiol. Chem.*, 1922, **118**, 189—214).—Copper sulphate is added to the urine and the lead precipitated with the copper as the sulphides by hydrogen sulphide; by then separating the

mixture by electrolysis, it is possible to detect small quantities of lead of the order of a few decimilligrams in a litre and a half.

S. S. Z.

Studies on Thallium Compounds. I. Analytical. ARTHUR JOHN BERRY (T., 1922, **121**, 394—399).

A New Iodometric Method for the Estimation of Copper. RUDOLF LANG (*Z. anorg. Chem.*, 1921, **120**, 181—202).—The usual iodometric method for estimating copper depends on the reduction of a cupric salt by an iodide to cuprous iodide followed by titration of the free iodine formed. The reaction $\text{Cu}^{++} + 2\text{I}' \rightleftharpoons \text{CuI} + \text{I}$ is, however, reversible, and in the present paper methods are developed for estimating copper which consist in oxidising a cuprous salt with a known quantity of iodine and titrating the excess. The most suitable salt for oxidation is cuprous thiocyanate, the reaction being carried out in presence of ammonium oxalate or tartrate. The reaction is complicated, however, by the possibility of a reaction between thiocyanate and iodine such as $\text{KCNS} + 8\text{I} + 4\text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{ICN} + \text{KI} + 6\text{HI}$. A lengthy investigation was carried out to study the extent to which this reaction proceeds in presence of thiocyanates of potassium, sodium, and ammonium, oxalic acid, ammonium oxalate, ammonium sulphate, nitrate, and chloride in presence and absence of copper salts, and it was found that the reaction could be altogether inhibited in presence of oxalic acid and the ammonium salts of strong acids, including ammonium thiocyanate in high concentration. The following method was finally adopted for the estimation of copper. A solution of cupric salt, weakly acidified with a mineral-acid, and containing at most 0.28 gram of copper is reduced with excess of sulphurous acid and diluted to 0.1*N*. Ammonium thiocyanate solution is added to precipitate the copper as cuprous thiocyanate and the solution is boiled to expel sulphur dioxide. After cooling, a mixture of 5 volumes of ammonium oxalate solution containing 45 grams of hydrated salt per litre and 7 volumes of oxalic acid solution containing 120 grams of hydrated acid per litre is added, and the whole is diluted to 400 c.c. Next 0.1*N*-iodine solution is run in until a clear solution is obtained, the mixture being well shaken, and excess of iodine is titrated with thiosulphate solution.

The cupric salt can be reduced with cyanide instead of sulphurous acid, the advantage of this method being that the reduction is selective for copper and that the reducing agent need not be removed. Conditions were determined experimentally under which reaction between cyanide and iodine is prevented, and it was found necessary, after reduction, to acidify before adding iodine since only cyanogen ions, not hydrocyanic acid, reduce iodine. The following method was finally adopted. The cupric salt solution containing at most 0.28 gram of copper is made ammoniacal in a long-necked flask and reduced with 0.5*N*-potassium cyanide solution. After addition of 1 gram of ammonium thiocyanate, the solution is acidified with concentrated oxalic acid solution, keeping

cold, so that all the copper is precipitated as thiocyanate. The oxidation with iodine and titration are then carried out as above.

In place of the expensive potassium iodide solution of iodine, a potassium cyanide solution can be used, prepared by dissolving 3 grams of potassium cyanide in a little water, dissolving in this 12.7 grams of iodine, and making up to a litre. This solution is quite stable.

The above methods are applicable in presence of all the commoner metals. Notes are given of slight precautions and modifications necessary in presence of silver, mercury, lead, bismuth, arsenic, antimony, cobalt, manganese, iron, barium, strontium, calcium, and magnesium.

E. H. R.

A Rapid Iodometric Estimation of Copper and Iron in Mixtures of their Salts. IAN WILLIAM WARK (T., 1922, 121, 358—363).

Estimation of Metallic Aluminium and Aluminium Oxide in Commercial Metal. H. V. CHURCHILL (*J. Ind. Eng. Chem.*, 1922, 14, 81); JULIAN H. CAPPS (*ibid.*, 81—82).—The first author criticises a recent paper by Capps (A., 1921, ii, 657), whose results indicate an atomic weight of 26.81 for aluminium, and concludes that the method described is untrustworthy. Capps replies, admitting an error pointed out by Churchill, but considers that his figures after recalculation still support his contention that the accepted atomic weight for aluminium is wrong.

W. P. S.

The Analysis of Aluminium Alloys. ANTON BRENNER (*Chem. Ztg.*, 1922, 46, 188).—The solution of aluminium and zinc hydroxides in alkali hydroxide solution is treated with sodium sulphide, the precipitate is collected on a filter, washed with hot water, and dissolved in dilute hydrochloric acid. The cold solution is treated with sodium carbonate and the precipitated zinc carbonate collected, washed, ignited, and weighed as zinc oxide. The method is more rapid than that involving separation of the zinc sulphide from organic acid solutions.

A. R. P.

The Separation of the Oxides of Iron and Aluminium from Admixture with Calcium Oxide by the Nitrate Method. CHARRIOU (*Compt. rend.*, 1922, 174, 751—754).—In St. Claire Deville's method for the separation of the oxides of iron and aluminium from calcium oxide by means of ammonium nitrate, it is preferable to carry out the drying, after the precipitation of the hydroxides with ammonia, at a temperature not exceeding 150° and in the presence of ammonium nitrate. The residue is then extracted three times with a boiling 10% solution of ammonium nitrate and subsequently washed with boiling water. Under these conditions the separation is complete.

W. G.

A New Quantitative Method for the Estimation of Iron in the Blood. ANSON L. BROWN (*J. Amer. Chem. Soc.*, 1922, 44, 423—425).—To 0.5 c.c. of blood, laked in 4 c.c. of water, 1 c.c. of concentrated hydrochloric acid and 0.01 gram of potassium chlorate

are added, and the mixture is heated in a boiling water-bath until it becomes white or light yellow and the whole of the proteins are precipitated. The mixture is allowed to cool and is filtered, and the residue is washed with water until 15 c.c. of filtrate are obtained. The iron is estimated colorimetrically in an aliquot portion of the filtrate against a standard iron solution, using potassium thiocyanate as indicator.

W. G.

Separation of Germanium and Arsenic. JOHN H. MÜLLER (*J. Amer. Chem. Soc.*, 1921, **43**, 2549—2552).—A method of separating minute traces of arsenic from germanium is described. The method consists in adding a large excess of hydrofluoric acid to the mixed oxides and precipitating cold with hydrogen sulphide. By these means arsenic is precipitated quantitatively. Hydrogen sulphide is without action on solutions of fluorogermanic acid and its salts. The separation is sufficiently accurate to estimate as little as 0.01% of arsenic in germanium compounds. The method is especially useful in connexion with the preparation of pure germanium compounds, as the fractional crystallisation of the double fluoride can thus be avoided and the operation carried out in small volumes of solution. Germanium dioxide is non-toxic, and solutions of it when injected subcutaneously show a marked erythropoietic action.

J. F. S.

Co-precipitation of Vanadic Acid with Ammonium Phosphomolybdate. J. R. CAIN and J. C. HOSTETTER (*J. Amer. Chem. Soc.*, 1921, **43**, 2552—2562).—The authors have investigated the conditions under which the simultaneous precipitation of vanadic acid and ammonium phosphomolybdate is best carried out in connexion with the method of estimation of vanadium in steel (A., 1912, ii, 1101). The ratio of vanadium to phosphorus in the precipitate has been determined for mixtures in which the phosphorus is constant and the vanadium varies, and for mixtures in which the vanadium is constant and the phosphorus varies. The influence of dilution, temperature, and acidity of the solutions has also been investigated. The results show that the co-precipitation of vanadic acid with ammonium phosphomolybdate may be explained as a phenomenon resulting from a partition of the vanadic acid in some undissociated form between the solution and the solid phase. The maximum absorption by the solid phase occurs at a temperature of 40—50° and in a nitric acid concentration of 4*N*. The effect of dilution in lowering the amount of occlusion is a direct result of the partition law and can be minimised by the presence of ammonium nitrate, the latter probably tending to repress the dissociation of the vanadium complex which is occluded. The ammonium vanadophosphomolybdates are probably a series of solid solutions the end members of which may be ammonium phosphomolybdate and ammonium phosphovanadate.

J. F. S.

Estimation of Methyl Alcohol. KARL H. A. MELANDER (*Svensk. Pappers Tid.*, 1921, **24**, 277—278).—A mixture of 22 grams

of iodine and 5 c.c. of the solution containing about 2% of methyl alcohol is heated for half an hour at 70° in a slow current of hydrogen, the flask having previously been connected with a condenser, a wash-bottle containing a little red phosphorus in water at 50°, and an absorption apparatus containing a few c.c. of pyridine. For a further period of half an hour a higher temperature is employed, and the current of hydrogen increased. The pyridine solution is concentrated on a water-bath, dissolved in water, and titrated with 0.1N-silver nitrate solution.

CHEMICAL ABSTRACTS.

Vapour Pressures of Dilute Alcohol Solutions. R. THOMAS (*J. Soc. Chem. Ind.*, 1922, **41**, 33—34T).—A rapid method of determining the partial pressures of alcohol and water in aqueous solutions of alcohol is described. This method also constitutes a method of analysing air containing water and alcohol vapour. It depends on the facts that water is retained by a layer of calcium carbide which has no action on alcohol, and that alcohol is completely absorbed by a layer of ignited alumina or by passing it through 98% sulphuric acid. The process is carried out by passing dry air, free from carbon dioxide, through a bubbler containing the alcohol solution at a rate of 4—5 litres an hour and thence over calcium carbide contained in a U-tube and finally through 98% sulphuric acid or over ignited alumina in a U-tube. The loss of weight of the alcohol bubbler gives the total weight of vapour, and the increase in weight of the sulphuric acid or alumina gives the weight of alcohol. It is essential that fresh carbide be used in each experiment, for calcium hydroxide would retain some of the alcohol. It is shown for solutions containing 5% and 10% of alcohol that the partial pressure of the alcohol is approximately proportional to its concentration. From the data obtained, a table has been constructed showing the ratio of the concentration of alcohol in the gaseous phase to its concentration in the liquid phase for the temperature range 15—26°. J. F. S.

Estimation of Glycerol in the Presence of Sugars. L. F. HOYT and H. V. PEMBERTON (*J. Ind. Eng. Chem.*, 1922, **14**, 54—56).—A method is described for the estimation of glycerol in transparent soaps, which almost invariably contain added sucrose. The soap is dissolved in water, the solution acidified with sulphuric acid, and boiled to remove any alcohol which may be present. The mixture is filtered to separate insoluble fatty acids, the filtrate treated with a small quantity of silver sulphate, diluted to a definite volume, and again filtered. A portion of this filtrate is oxidised in the usual way with potassium dichromate-sulphuric acid mixture, using a larger excess of the oxidising mixture than is customary in glycerol analysis; this estimation gives the sum of the glycerol and sugar, and the latter is then estimated separately in another portion of the filtrate. W. P. S.

Sensitive Test for Phenols. JAMES MOIR (*J. S. African Chem. Inst.*, 1922, **5**, 8—9).—Five c.c. of *p*-nitroaniline hydrochloride

solution (1.5 grams of *p*-nitroaniline dissolved in a mixture of 40 c.c. of hydrochloric acid and 500 c.c. of water) are treated with dilute sodium nitrite solution until decolorised, and the mixture is then added to the solution to be tested; an orange-coloured precipitate is formed if much phenol is present. After one minute, an excess of sodium hydroxide is added; a coloration develops varying in depth from salmon-pink to ruby-red, according to the quantity of phenol present. The salmon-pink coloured solution exhibits a broad absorption band at λ 494 and this serves to distinguish phenol from the cresols, etc. The test will detect 1 part of phenol in 1,000,000 parts of solution. W. P. S.

Proteinogenous Amines. XIV. A Microchemical Colorimetric Method for Estimating Tyrosine, Tyramine, and other Phenols. MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1922, **50**, 235—270).—The colour reaction given by phenol, *o*-, *m*-, and *p*-cresols, and *p*-hydroxyphenylacetic, *p*-hydroxyphenylpropionic and *p*-hydroxyphenyl-lactic acids with sodium *p*-diazobenzene sulphonate may be used for the colorimetric estimation of these substances. The details of the method are practically identical with those previously described for the estimation of iminazole derivatives (A., 1920, ii, 67). Tyrosine and tyramine give with a solution of diazobenzenesulphonic acid in sodium carbonate a pink coloration which rapidly changes to yellow. Addition of sodium hydroxide produces an intensification of the yellow and a restoration, to a small extent, of the pink coloration, but at no stage is the intensity proportional to the concentration of the phenol. If, however, sodium hydroxide and then hydroxylamine hydrochloride are added to the solution, an intense bluish-red colour is obtained which is proportional to the amount of tyrosine or tyramine present. The coloration so produced may consequently be employed for the estimation of small quantities of these two compounds. Ammonium salts, leucine, glycine, hydrogen peroxide, formaldehyde, acetaldehyde, acetone, acetoacetic acid, dextrose, and alcohols interfere with the colour. An explanation based on a tautomeric change of the keto-enol type is tentatively advanced to account for the colour changes described in the case of tyrosine and tyramine. E. S.

Proteinogenous Amines. XV. A Quantitative Method for the Separation and Estimation of Phenols including Phenol, *o*-, *m*-, and *p*-Cresols, and *p*-Hydroxyphenylacetic, *p*-Hydroxyphenylpropionic and *p*-Hydroxyphenyl-lactic Acids, Tyrosine, and Tyramine. MILTON T. HANKE and KARL K. KOESSLER (*J. Biol. Chem.*, 1922, **50**, 271—288).—The method of separation described was designed to render possible the application of the author's method for the estimation of certain phenolic substances (preceding abstract) to mixtures of these substances. It is intended primarily for use in bacterial metabolism studies on tyrosine and is not applicable to more complex liquids such as urine or blood. The liquid containing the mixture of phenols is acidified and distilled, whereby phenol and the cresols pass over.

Non-aminophenolic acids are removed from the residual liquid by extraction with ether, after which it is made alkaline with sodium carbonate and extracted with amyl alcohol. Tyramine is thus removed, whilst tyrosine remains in the alkaline solution. Separation is thus effected into four fractions. If, as will normally be the case in bacterial metabolism experiments, only one member of each fraction is present, the estimation is proceeded with after appropriate treatment of the various solutions. The method fails, however, in those cases where more than one member of each fraction is present since further separation is impossible.

E. S.

Estimation of Sugar in Small Quantities of Blood by the Pavy-Sahli Method. SVEND HUBERT REIST (*Schweiz. med. Woch.*, **51**, 419—423; from *Chem. Zentr.*, 1921, iv, 1056).—0.1 c.c. of blood is washed into a test-tube with 3 c.c. of alcohol. The mixture is shaken for half an hour, filtered through hardened filter-paper, and the residue washed twice with 2 c.c. of alcohol. The alcohol is then removed over a water-bath and 0.3 c.c. of Pavy's solutions and 1.8 c.c. of water are added. The liquid is heated to boiling and while boiling titrated with standard (approximately 0.1%) dextrose solution.

G. W. R.

Estimation of Lævulose (Fructose) in Straw. S. H. COLLINS (*J. Soc. Chem. Ind.*, 1922, **41**, 56—57r).—The colouring matters present in this case bear a high ratio to the sugar and attempts to obtain concentrated solutions sufficiently translucent for the polarimeter failed. It was found in practice that a solution obtained by continuous extraction, of which 10 parts of liquid represented 1 part of straw, was as dark as could be used even with a 200 mm. tube and a quartz wedge saccharimeter illuminated by a 100 c.p. electric lamp. By means of hot and cold water circulating through the jacketed polarimeter tube, temperatures of about 70° and 10°, constant to a fraction of a degree, could be obtained, and ten readings were taken in order to reduce chance errors to unimportance. A serious error was found to be due to the deflexion of the zero by temperature alterations. This was traced to the end glasses of the polarimeter tube and was overcome by annealing them for three hours at 300°. The least trace of alkalinity must be avoided, otherwise the lævulose solutions become almost black at the higher temperature. Faint acidity is not of so much consequence. With straw containing 5—7% of lævulose the error in the estimation is about 0.05% with carefully annealed end glasses. The results of the investigation have shown that with straws containing much sugar three-fourths of the total is lævulose, but when the total sugar is low in amount, lævulose is absent.

G. F. M.

Micro-estimation of Lactose by means of Potassium Permanganate. Application to Milk. G. FONTÈS and L. THIVOLLE (*Bull. Soc. Chim. Biol.*, 1922, **4**, 23—42).—The author's method for the estimation of dextrose in blood (A., 1921, ii, 563)

can, with slight modifications, be used for the estimation of lactose in milk. E. S.

A Simpler Method of Determining Acetyl Values. LEON W. COOK (*J. Amer. Chem. Soc.*, 1922, **44**, 392—394).—A modification is given of André's formula (cf. A., 1921, ii, 419) for calculating the acetyl value of an oil from its saponification values before and after acetylation. The new formula is $A = (S' - S) / (1 - 0.00075S)$, where A is the acetyl value, S the saponification value before acetylation, and S' the value after acetylation. Similarly, the percentage of alcohol in the original sample may be calculated by the formula: percentage of alcohol = $M(S' - S) / (560 - 0.42S')$ provided that the molecular weight, M , of the alcohol is known. W. G.

The Estimation of Fatty Acids Based on their Volatility in Steam. W. ARNOLD (*Z. Unters. Nahr. Genussm.*, 1921, **42**, 345—372).—From a large number of determinations of the Reichert-Meissl and Polenske values of pure fatty acids, using the Polenske apparatus and weights of fatty acid varying from 0.01 gram to 0.05 gram, it appears that butyric and hexoic acids only give a Reichert-Meissl value; octoic and decoic acids give both Reichert-Meissl and Polenske values, the Reichert-Meissl value of decoic acid being distinct but very small. Acids from lauric upwards only give Polenske values. Of the insoluble acids decoic and lauric are easily volatile, palmitic and stearic volatile with difficulty, myristic standing midway between the two groups. In the case of palmitic and stearic acids, the amount that passes over is so small that the Polenske value is practically independent of the quantity of acid originally present. With myristic acid, this is only the case if more than 0.06 gram is present. Lauric acid gives a maximum Polenske value with 0.3 gram present. In the case of the easily volatile acids, there is a rough proportionality between the Reichert-Meissl and Polenske values and the weight of acid present. The later fractions of the higher acids are only very slowly volatile in steam, but even fractions of a milligram are easily visible in the condensate. The fact that the Polenske value of the higher fatty acids is independent of the weight present is useful in the analysis of mixtures of fatty acids. The work of Dons (A., 1908, ii, 238; 1909, ii, 75) on the estimation of decoic, lauric, and myristic acids in butter by distillation of the fatty acids in steam is described. If 1 gram of mixed fatty acids is distilled in 100 c.c. of steam (measured as water), the partition coefficient of the volatile acids between distillate and condensate is given by $K = (m_1 \times 100) / m_2$, where m_1 is the weight of acids remaining in the flask and m_2 the weight distilling over. The partition of the different acids is unaffected by the other components of the mixture and depends on their volatility under the conditions of distillation and on the proportion present in the mixture. Dons found that if c_1 is the quantity reckoned as c.c. $N/10$ alkali hydroxide volatilising with the first 100 c.c. of water, $c_1 = xr$, where r is the "volatility" and is equal to 0.244, 0.060, 0.016 for decoic, lauric, and myristic acids respectively, and x

equals the percentage of the respective acid in the mixture. The partition coefficient is given by $K = (100 \times 1 - r)/r$. For decoic, lauric, and myristic acids K has the values 138.1, 733.3, and 2640, respectively. The general formula for r is $r = l_2/(Kl_1 + l_2)$, where l_1 is the weight of the acid phase and l_2 that of the condensed steam. From this it follows that the volatility of a fatty acid becomes greater with decrease in l_1 . This is borne out by Arnold's experiments. If a series of distillations of a given weight of fatty acid is undertaken, using each time 100 c.c. of aqueous condensate, the weight of a given acid distilling over at the n th distillation is given by $c_n = c_1(1 - r)^{n-1}$.

In practice, Dons's method is applied as follows. Using 0.5 gram of fatty acids, the Polenske value (p_{16}) of the sixteenth distillation is determined. It is considered that decoic and lauric acids have by this time been completely eliminated from the mixture, so that this value is due only to myristic and the higher acids. The latter have a constant figure of 0.2. Hence c_{16} (myristic acid) = $p_{16} - 0.2$. Hence c_1 (myristic acid) = $c_{16}/(1 - r)^{15}$, where $r = 0.0704$. The percentage of myristic acid is given by $c_1/0.016$. Using 1 gram of fatty acids, 700 c.c. of distillate are then collected and the sum of the Reichert-Meissl and Polenske values for the first six distillations, and the Polenske value (p_7) for the seventh distillation obtained. The seventh distillate is free from decoic acid, as it no longer gives a Reichert-Meissl value; $p_7 - 0.2$ is therefore due entirely to lauric and myristic acids, c_1 for myristic acid is known, so $c_7 = c_1(1 - r)^6$. Hence the lauric acid in the seventh distillate is given by $p_7 - 0.2 - c_7$ and from this c_1 (lauric) and the percentage of lauric acid in the mixture can be calculated. The percentage of decoic acid can be obtained in a similar manner from the results of the first six distillations. Dons's method is interesting from a theoretical point of view, but cannot be considered established as a practical method of analysing fatty acid mixtures.

H. C. R.

A Micro-extraction Apparatus. FRITZ LAQUER (*Z. physiol. Chem.*, 1922, 118, 215—217).—An adaptation of an extraction apparatus for the detection of small quantities of lactic acid of the order 2—10 mg. in tissues.

S. S. Z.

Estimation of Oxalic Acid in Urine. E. MISLOWITZER (*Biochem. Z.*, 1921, 126, 77—81).—A comparison has been made of the old standard method of Salkowski and the new calcium acetate process of Bau (A., 1921, ii, 356) for the estimation of oxalic acid in urine. Bau's process was found inferior and especially so if more ether be used for the extraction of the oxalic acid and the extraction be carried out mechanically.

H. K.

The Relation between the Refractive Index and the Chemical Characteristics of Oils and Fats (Glycerides). G. F. PICKERING and G. E. COWLISHAW (*J. Soc. Chem. Ind.*, 1922, 41, 74—77T).—An attempt has been made to discover a quantitative relation between the refractive index and the molecular weight, free fatty

acid content, and iodine value of the following oils : linseed, soja bean, cotton-seed, ground nut, palm-kernel, and coco-nut. The refractive index of each of these oils can be calculated with a high degree of accuracy from the formula $n_D^{40} = 1.4643 - 0.000066(S.V.) - 0.0096(A.V./S.V.) + 0.000117(I.V.)$ where *S.V.*, *A.V.*, and *I.V.* are the saponification, acid, and iodine values respectively. The equation has a useful application in the commercial analysis of the above oils.

E. H. R.

Use of the " Silver Method " in the Estimation of Acetaldehyde. Its Application in the Estimation of other Aldehydes. A Convenient Method of Accumulation of Aldehyde and other Volatile Substances from Body Fluids. ROBERT FRICKE (*Z. physiol. Chem.*, 1922, **118**, 241—246).—Further details regarding the method described by Stepp and Fricke (this vol., ii, 236). Acetaldehyde can be removed from body-fluids by steam distillation.

S. S. Z.

The Detection of Aldol in the Urine of Diabetic Patients. ROBERT FRICKE (*Z. physiol. Chem.*, 1922, **118**, 218—223).—By distilling acid urine from diabetic patients small quantities of crotonaldehyde have been demonstrated in the distillate; possibly this is derived from the aldol present in the urine. The "dime-don" method of precipitation was employed.

S. S. Z.

Micro-estimation of Total Acetone in Urine. HEINRICH LAX (*Biochem. Z.*, 1921, **125**, 262—264).—An apparatus is pictured and a method described, suitable for clinical use, for the estimation of acetone in 2 c.c. of urine in ten minutes. Twenty-five c.c. of water, 2 c.c. of urine, and 3 drops of 80% acetic acid are distilled for four minutes into a second flask containing 2 c.c. of water and 2 drops of concentrated hydrochloric acid. The ammonia is thus retained and the acetone passes on and is absorbed by 30 c.c. of water kept at 0°. Ten c.c. of *N*/20-iodine solution are added and 1 c.c. of 33% sodium hydroxide solution and after three minutes the excess of iodine after acidification is titrated with sodium thiosulphate.

H. K.

Estimation of Monobromocamphor. ELGAR O. EATON (*J. Ind. Eng. Chem.*, 1922, **14**, 24).—A weighed quantity of about 0.2 gram of monobromocamphor is dissolved in alcohol, 50 c.c. of *N*/2 alcoholic potash solution, and 25 c.c. of 0.4% alcoholic silver nitrate solution are added and the mixture is boiled under a reflux apparatus for ninety minutes; during the boiling, further quantities (25 c.c. in all) of the alcoholic silver nitrate solution are added through the reflux apparatus. After cooling, the mixture is diluted with water to 200 c.c., the solution decanted into a beaker, and the insoluble portion washed by decantation. This dilute alcohol solution is boiled for five minutes with the addition of 1 gram of zinc dust, filtered, the filtrate acidified with nitric acid, and treated with an excess of silver nitrate solution; the silver bromide formed is collected and weighed. The weight of silver bromide found

multiplied by 1.23 gives the corresponding amount of monobromocamphor. Potassium bromide is formed in the first part of the process, and not silver bromide.
W. P. S.

Extraction and Characterisation of Alkaloids. W. C. COLLEDGE (*J. S. African Chem. Inst.*, 1922, 5, 5—8).—A description of methods of purifying extracted alkaloids, methods of testing, general alkaloidal reagents, certain colour reactions, etc. Physiological tests may be applied when any doubt exists as to the nature of a supposed alkaloid.
W. P. S.

Extraction of Alkaloids from Viscera. W. C. COLLEDGE (*J. S. African Chem. Inst.*, 1922, 5, 3—5).—The Stas-Otto method is recommended; substances produced by putrefactive changes and extracted together with the alkaloids do not interfere with the identification of the latter, but if desired, the alkaloidal residue may be purified by dissolving it in a mixture of benzene and amyl alcohol, shaking the solution with dilute hydrochloric acid, separating the acid aqueous layer, extracting this with light petroleum, and then rendering the solution alkaline and extracting it with ether. For the detection of morphine, the alkaloidal residue is dissolved in acetic acid, the solution treated with lead acetate to precipitate meconic acid, and the morphine is extracted subsequently from the ammoniacal solution by means of amyl alcohol. In some cases, dialysis of the original material (stomach contents, etc.) affords a means of separating certain alkaloids such as strychnine and morphine.
W. P. S.

Iodic Acid as a Microchemical Reagent for the Detection of Organic Bases. L. ROSENTHALER (*Schweitz. Apoth. Zeit.*, 1921, 59, 477—479; from *Chem. Zentr.*, 1921, iv, 1055—1056).—The precipitates obtained with iodic acid and solutions of organic bases have in many cases characteristic forms, suitable for use in microchemical work. Strychnine, cinchonine, morphine, codeine, hydrastinine, pyridine, quinoline, and aniline give characteristic crystalline precipitates. Other alkaloids and organic bases may be distinguished by colorations.
G. W. R.

Identification of Alkaloids under the Microscope from the Form of their Picrate Crystals. BURT E. NELSON and HELEN A. LEONARD (*J. Amer. Chem. Soc.*, 1922, 44, 369—373).—The more commonly occurring vegetable alkaloids may be tentatively identified under the microscope by the form or habit of their picrate crystals prepared under standard conditions. A chart is given showing the crystalline structure of the picrates of twenty-five of the alkaloids. For the test, the aqueous solution of the separated alkaloid is slightly acidified with hydrochloric acid and a slight excess of a saturated solution of picric acid is added. The precipitated picrate is washed in a centrifuge and recrystallised from the smallest possible amount of warm 95% alcohol. The crystals are separated centrifugally and examined under a microscope without a cover-slip.
W. G.

Estimation of Carnosine in Muscle Extract. GEORGE HUNTER (*Biochem. J.*, 1921, **15**, 689—694).—Consistent results can be obtained in the estimation of carnosine in muscle by the diazo-method of Koessler and Hanke (*A.*, 1920, ii, 67). Details are given of the method recommended by the author for preparing the protein-free extract, together with a few analytical results. Ox muscle is found to contain from 0.4% to 0.6% of carnosine.
W. O. K.

Pyrimidines. XCII. New Methods of Identifying the Pyrimidine, Thymine. TREAT B. JOHNSON and OSKAR BAUDISCH (*J. Amer. Chem. Soc.*, 1921, **43**, 2670—2674).—The thymine molecule is completely destroyed at the ordinary temperature when subjected in aqueous solution to the oxidising action of the system, ferrous sulphate plus sodium hydrogen carbonate plus air. The products formed are pyruvic acid, acetylcarbinol, urea, and formic acid. The urea may be identified by its xanthrydrol derivative and the formic acid by its reducing action. The pyruvic acid is best identified by its interaction with *o*-nitrobenzaldehyde in alkaline solution to form indigotin. For the detection of acetylcarbinol Baudisch's specific reaction (cf. *A.*, 1918, ii, 412) with *o*-amino-benzaldehyde is best used. Uracil and cytosine are also oxidised by the above reagent, but in neither case is any pyruvic acid obtained and hence the detection of this acid among the products of the oxidation is sufficient proof of the presence of thymine in the original material.
W. G.

Colorimetric Estimation of Uric Acid. Estimation of 0.03 to 0.5 mg. quantities by a New Method. J. LUCIEN MORRIS and A. GARRARD MACLEOD (*J. Biol. Chem.*, 1922, **50**, 55—63).—The phosphotungstic acid reagent used by Folin and Denis (*A.*, 1913, ii, 162) is replaced by an arsenotungstic acid reagent, which produces a greater depth of colour. Uric acid is precipitated from urine or deproteinised blood by the addition of zinc chloride and sodium carbonate (cf. *A.*, 1916, ii, 456). After separation by centrifuging, it is dissolved in hydrochloric acid and the colour developed in the presence of sodium cyanide by the addition of the arsenotungstic acid reagent compared with a standard. The formation of precipitates is avoided by the use of sodium cyanide as the only alkali.
E. S.

A Modification of Folin's Colorimetric Method for the Estimation of Uric Acid. HENRY JACKSON, jun., and WALTER W. PALMER (*J. Biol. Chem.*, 1922, **50**, 89—101).—The estimation is made by the method of Folin and Denis (*A.*, 1913, ii, 162), using a modified phosphotungstic acid reagent. The addition of sodium carbonate is omitted, the necessary alkalinity being furnished by the use of sodium cyanide. By these modifications a greater intensity of colour is obtained and the formation of precipitates avoided.
E. S.

General and Physical Chemistry.

A Modified Form of Double Slit Spectrophotometer.

A. L. NARAYAN and G. SUBRAHMANYAM (*Phil. Mag.*, 1922, [vi], 43, 662—663).—This consists essentially of an electromagnetically maintained pendulum carrying a double slit, which is mounted in front of the collimator slit of the spectrograph. This form of spectrophotometer is free from the defects of Vierordt's type, giving a better method of regulating the brightness of the spectrum. It also possesses many of the advantages of the sector photometer.

W. E. G.

Molecular Refraction of some Molten Salts.

G. MEYER and ADOLF HECK (*Z. physikal. Chem.*, 1922, 100, 316—333; cf. this vol., ii, 241).—The index of refraction of molten sodium nitrate, potassium nitrate, sodium hydroxide, and potassium hydroxide has been determined by the method of autocollimation at a series of temperatures between 320° and 440°. The following values of the refractive index are recorded: sodium nitrate, $643.9\mu\mu$, $n=1.479-1.75 \times 10^{-4}t$; $589.3\mu\mu$, $n=1.499-2.12 \times 10^{-4}t$; $579.1\mu\mu$, $n=1.487-1.75 \times 10^{-4}t$; $546.1\mu\mu$, $n=1.483-1.50 \times 10^{-4}t$; potassium nitrate, $643.9\mu\mu$, $n=1.525-3.12 \times 10^{-4}t$; $589.3\mu\mu$, $n=1.664-4.00 \times 10^{-4}t$; $579.1\mu\mu$, $n=1.556-5.75 \times 10^{-4}t$; $546.1\mu\mu$, $n=1.538-3.12 \times 10^{-4}t$; sodium hydroxide, $643.9\mu\mu$, $n=1.467-1.25 \times 10^{-4}t$; $589.3\mu\mu$, $n=1.458-8.75 \times 10^{-5}t$; $585.7\mu\mu$, $n=1.460-8.75 \times 10^{-5}t$; $558.9\mu\mu$, $n=1.471-1.12 \times 10^{-4}t$; potassium hydroxide, $643.9\mu\mu$, $n=1.453-1.0 \times 10^{-4}t$; $589.3\mu\mu$, $n=1.479-1.5 \times 10^{-4}t$; $585.7\mu\mu$, $n=1.479-1.33 \times 10^{-4}t$; $558.9\mu\mu$, $n=1.475-1.33 \times 10^{-4}t$. The density of molten sodium hydroxide and potassium hydroxide has been determined and the following values have been found: sodium hydroxide, 340°, 1.89; 400°, 1.86; 440°, 1.84; potassium hydroxide, 380°, 1.87; 420°, 1.83, and 440°, 1.81. The molecular refractivity calculated according to the formula $(n^2-1) \cdot M / (n^2+2) \cdot d$ is in all cases in keeping with the theoretical value. In the case of sodium nitrate, the degree of dissociation has been calculated from the molecular refraction and shown to be 64.7%.

J. F. S.

A New Band Spectrum of Oxygen.

C. RUNGE (*Physica*, 1921, 1, 254—261).—A direct current, high voltage arc was operated in a cylinder through which a stream of oxygen was passed, and a group of bands photographed in the region λ 2200—4900 Å. Although closely crowded towards the ends of the region, the separate lines could be observed from λ 2980 to λ 3900. The vibration frequencies are given by an expression of the form $a+bn+cn^2$; for the first series, n is a whole number, and for the related series, negative fractional numbers differing by whole numbers. Formulæ representing seven bands are given.

CHEMICAL ABSTRACTS.

Structure of the Band Spectrum of Helium. W. E. CURTIS (*Proc. Roy. Soc.*, 1922, [A], **101**, 38—64). An investigation of the structure of the red band near λ 6400, the green band near λ 5730, and a blue band near λ 4550 in the helium spectrum. The principal features of the structure are shown to be accounted for by the quantum theory of band spectra, which are considered to originate in the passage of molecules between stationary states characterised by constant values of angular momentum, such passage being possibly accompanied by a change in the configuration of the molecule, as assumed by Schwarzschild. A brief résumé of the theory is given. In each of the three bands a new type of series is found, which, although closely related to the others, has not yet received a theoretical explanation. Certain other departures from the theory are also noted. It is concluded that the spectrum is due to an unstable helium molecule having a moment of inertia equal to about 1.8×10^{-40} gram cm². J. S. G. T.

The Spectra of Helium, Hydrogen, and Carbon in the Extreme Ultra-violet. J. C. McLENNAN and P. A. PETRIE (*Trans. Roy. Soc. Canada*, 1921, **15**, iii, 15—25).—In identifying the wave-lengths obtained in vacuum grating spectra of helium, and possibly of hydrogen, regard must be paid to the possibility of certain of the recorded wave-lengths originating in carbon or mercury introduced into the discharge tube. The authors support the contention of Millikan (*Astrophys. J.*, 1920, **52**, 47) that certain of the lines obtained by Lyman (*A.*, 1920, ii, 207) in the Schumann spectrum of helium are due to carbon. In particular, the wave-lengths $\lambda\lambda$ 1931, 1657, and 1561 Å., together with others of less intensity, originate in the atoms of carbon. The series of wave-lengths the frequencies of which are given by $\nu = 4N(1/2^2 - 1/n^2)$ exists for the spark spectrum in helium. J. S. G. T.

The Corpuscular Spectra of the Elements. MAURICE DE BROGLIE (*Compt. rend.*, 1922, **174**, 939—941; cf. *A.*, 1921, ii, 232, 292, 615).—The spectra of the four elements silver, tin, gold, and uranium are given, showing the position of the lines which appear on the photographic plate. To identify the origin of the rays, a selective screen which will absorb certain radiations more strongly than others may be interposed between the source of the X-rays and the apparatus. Thus a screen containing the oxides of the rarer earths causes the almost complete disappearance of the β - and γ -rays of the K spectrum of tungsten. W. G.

A New Method of Absorption Spectroscopy. WALTER GERLACH and ERICH KOCH (*Ber.*, 1922, **55**, [B], 695—697).—The sources of light usual in spectroscopy suffer under the drawback that they are either insufficiently intense or not so constant as is desirable. The defect can be overcome by using as source of light a wire which suffers disintegration by a high-tension condenser discharge. A battery of Leyden jars (capacity about 30,000 cm.) is connected with a spark gap of constant dimensions and the iron wire which is to be disintegrated (about 2 cm. long and 0.031 mm.

diameter). The battery is slowly charged from a small machine until an arc is struck across the gap, when the wire is disintegrated with a blinding light and the current is broken; a single discharge is invariably sufficient for spectroscopic purposes. The constant brightness of the source of light is guaranteed by the constant energy expended in producing it, which depends only on the dimensions of the spark gap and the thickness of the wire.

The disposition of the apparatus and the methods for its adjustment are fully described and figured in the original. H. W.

The Absorption Spectrum of Liquid and Gaseous Oxygen.

W. W. SHAVER (*Trans. Roy. Soc. Canada*, 1921, **15**, iii, 7—14).—The absorption spectra of oxygen, liquid and gaseous, were determined by means of a quartz spectrograph, employing a spark between aluminium electrodes under water as the light source. In the visible region, eight absorption bands were observed in the case of liquid oxygen, and seven with gaseous oxygen. The mean wave-lengths of the bands in the former case were 6285, 5800, 5350, 4816, 4458, 3828, 3631, and 3461 Å. In the case of gaseous oxygen at 140 atmospheres pressure, the band at 4458 Å. was absent. At 107 atmospheres pressure, the bands at 6285, 5800, and 4816 Å. alone were observed. In the ultra-violet, four broad bands, about 30 Å. wide, were observed in the case of both liquid and gaseous oxygen. In the former case, the centres of the bands were located at 2795, 2731, 2681, and 2631 Å., and each band consisted of a fine set of symmetrical triplet bands. In the gaseous spectrum, the similar bands observed were slightly displaced towards the ultra-violet. It was shown that the bands were not due to the presence of nitrogen or ozone.

J. S. G. T.

An Absorption Band Spectrum for Water in the Region of Wave-lengths of Several Decimetres. RICHARD WEICHMANN (*Ann. Physik*, [iv], **66**, 501—545).—A more detailed account of work previously published (this vol., ii, 5).

Studies in Catalysis. XV. Absorption Spectra of Triethylsulphonium Bromide in Various Solvents, in the Short Infra-red Region. HENRY AUSTIN TAYLOR and WILLIAM CUDMORE McCULLAGH LEWIS (*T.*, 1922, **121**, 665—675).

Absorption Spectrum of Benzene Vapour and the Fundamental Magnitudes of the Benzene Molecule. VICTOR HENRI (*Compt. rend.*, 1922, **174**, 809—812).—The ultra-violet absorption spectrum of benzene vapour is composed of four series of superposed bands, which obey the formulæ, $1/\lambda = 37703 + 921 \cdot 4n - (159p + 2p^2) + 2(m^2 - q^2)$; $1/\lambda = 37494 + 921 \cdot 4n - (159p + 2p^2) + 2(m^2 - q^2)$; $1/\lambda = 37613 + 921 \cdot 4n - (159p + 2p^2) + 2(m^2 - q^2)$; $1/\lambda = 37426 + 921 \cdot 4n - 166p + 2(m^2 - q^2)$, where n has the values 0 to 7, p the values 0 to 6, and $q = m$ or $q = m \pm 1$ and $m = 1, 2 \dots 10$. Eight groups of bands correspond with the eight values of n . The positions of the heads of the bands in each group correspond with the different values of p , and the values of m give the fine structure of

each band. The intensity of the bands diminishes rapidly as p increases. The constants 921.4 and 159 represent the number of vibrations of the atomic nuclei or of the groups of atoms in the molecule. Hence the infra-red absorption spectrum is given by $1/\lambda = 921.4n - 159p$, and this is confirmed by the results of Coblenz and Puccianti. The moment of inertia of the benzene molecule is deduced as being 1.45×10^{-38} . From this the distance between the carbon atoms is calculated as being 1.85×10^{-8} cm. and the diameter of the molecule as 2.6×10^{-8} . Thus the benzene molecule is a very symmetrical edifice the movements of which obey the simple laws deduced for diatomic molecules, and it may be considered as being formed of two halves, $C_3H_3-C_3H_3$, which vibrate with respect to one another. W. G.

Ultra-violet Absorption Spectrum of Phenol in Different Solvents. F. W. KLINGSTEDT (*Compt. rend.*, 1922, 174, 812—815).—A quantitative study of the ultra-violet absorption spectrum of phenol in different solvents shows that the spectrum of phenol dissolved in pentane or hexane, which the author calls the normal spectrum, comprises two regions in the ultra-violet. In the first, between $\lambda = 2860$ and 2400 there are three intense narrow bands, and in the second, between $\lambda = 2325$ and the extreme ultra-violet there are two broad bands. The absorption spectrum changes with the nature of the solvent, and from this point of view the solvents may be divided into two groups. The solvents of the first group, such as carbon tetrachloride, chloroform, ether, do not modify the general aspect of the absorption spectrum, only producing a displacement and a broadening of the bands. The solvents of the second group, such as methyl or ethyl alcohol or water, completely modify the absorption spectrum of phenol. In these solvents there is only a single very broad and uniform band. The absorption spectrum of pure liquid and solid phenol occupies a position intermediate between the two preceding types. W. G.

Fundamental Laws of Photochemistry. II. Influence of Cooling on the Absorption of Light by Dyes. P. LASAREV (*Z. physikal. Chem.*, 1922, 100, 266—270; cf. this vol., ii, 103).—The absorption of light of wave-lengths $\lambda = 514, 543, 559, 576, 595, 617$, and 644 by layers of collodion containing cyanin and pinacyanol has been measured at ordinary temperatures and at the temperature of liquid air. In the case of cyanin, it is shown that the simple absorption band becomes narrower, whilst in the case of pinacyanol the single band is resolved into two absorption bands at the temperature of liquid air. J. F. S.

Application of Photo-electric Cells to the Measurement of the Light Absorption in Solutions. II. H. VON HALBAN and K. SIEDENTOPF (*Z. physikal. Chem.*, 1922, 100, 208—230; cf. A., 1921, ii, 145).—An arrangement for measuring the absorption of light by solutions is described, which depends on the use of photo-electric cells and in which variations in the intensity of illumination of a mercury lamp are eliminated by compensation

with two photo-electric cells. The cells are used only as a zero instrument. A rotating sector and a grey wedge are used to measure the weakening of the light. The greatest variation of an individual measurement of the absolute value of the extinction coefficient from the mean value does not exceed 0.5%. Measurements with the wedge permit of the identity of two objects in respect of their light absorption being established to 0.1% and differences can also be determined with the same accuracy. Measurements are recorded for solutions of potassium chromate in potassium hydroxide, equimolecular quantities of potassium chromate and copper sulphate in ammonia, azobenzene in alcohol, and anthracene in alcohol for the mercury lines 579 $\mu\mu$ and 254 $\mu\mu$. J. F. S.

Colour and Chemical Constitution. XIII. Calculation of the Colour of Monocyclic Dyes. JAMES MOIR (*Trans. Roy. Soc. Sth. Africa*, 1921, 10, 35—39; cf. A., 1921, ii, 475).—Dyes which contain only one active colour ring do not fit into the scheme previously described (A., 1921, ii, 6) for those containing two such rings, but their colours are deducible by a similar factorial scheme, based on *p*-hydroxybenzyl alcohol (for which, and probably also for *p*-cresol, in faintly alkaline aqueous solution, $\lambda=290$). The factors in parenthesis are employed in conjunction with this value: replacement of carbinol hydrogen by phenyl (1.135); conversion of phenyl carbinol into a phthalein (1.060); replacement of ring hydroxyl- by amino-group (1.140); replacement of amino-hydrogen atoms by methyl (1.035). Values are thus predicted for certain compounds for which measurements are at present lacking. It appears that colour cannot be traced to lower terms than the presence of one benzene ring, with one ionisable group, usually with another active atom, and that the physical cause of colour is the periodic motion of an electron round a molecule. Although the sinuous orbit previously conceived (A., 1921, ii, 475) is now considered not to be very likely, the tautomeric pauses then assumed are a probable feature of the orbit. It is suggested that the colours of dyes containing two active colour rings (*loc. cit.*) may be based on 4:4'-dihydroxybenzhydrol ($\lambda=539$). The pink colours attributed to phenylphenolphthalein and to its analogue from salicylic acid (A., 1917, ii, 349; 1919, ii, 78) were due to impurity. J. K.

Constitution and Colour. VIII. F. KEHRMANN (*Helv. Chim. Acta*, 1922, 5, 158—163; cf. A., 1921, ii, 476).—The effect of salt formation on the colour of basic nitrogen compounds is to lighten it if the unsaturated condition is destroyed, and to intensify it if the unsaturated condition persists (for example, in the cases of auramine base, azo-compounds, azomethines, and members of the quinoline, pyridine, acridine, phenazine, etc., series). If no change occurs in the degree of saturation (for example, ammonium, imonium, cyclonium, and diazonium compounds), the colour is also unchanged. Similar generalisations apply to basic sulphur and oxygen compounds, with the reservation that knowledge of the colour changes accompanying destruction of the unsaturated con-

dition in these cases is at present insufficiently specific. The behaviour of the group, $\cdot\text{CH}:\text{CH}\cdot$, is apparently analogous to that of the azo-group, since intensely coloured sulphates of diphenylcyclopentadiene (Borsche and Menz, A., 1908, i, 147) and of unsaturated ketones (Kehrmann and Effront, A., 1921, i, 348) have been described. The effect of salt formation on the colour of iodonium compounds is so far unknown. The above rules also apply to all those cases of salt formation from pseudo-bases (for example, carbinol bases) in which the nature of the changes is properly understood. J. K.

Fluorescence and Photochemistry. R. W. WOOD (*Phil. Mag.*, 1922, [vi], 43, 757—765).—The theory of Perrin (cf. A., 1918, ii, 418) is tested by exposing aqueous solutions of eosin, rhodamine, and fluorescein to a very intense beam of sunlight. The products, "photo compounds," are usually coloured, non-fluorescent substances, which are bleached by further action of the light. Their absorption bands have a totally different form from those of the original substances. Rhodamine is almost non-fluorescent at 100° , but decomposes under the action of light as rapidly as at ordinary temperatures. This is contrary to Perrin's theory. The relation between the rate of breakdown of eosin and the intensity of the light is at variance with the Bunsen-Roscoe law, whereas unstable non-fluorescent substances behave normally. The proportionality between the emission of fluorescence and the intensity of the exciting light holds over a wide range of intensity. W. E. G.

The Quantitative Determination of the Fluorescent Powers (the Spectro-fluorescometry) of Cellulose, Sugars, and other Substances. SAMUEL JUDD LEWIS (*J. Soc. Dyers and Col.*, 1922, 38, 68—76, 99—108).—An instrument has been designed by which the fluorescent powers of different substances can be quantitatively compared. It consists of a Hilger quartz spectrograph with the back of its camera modified so as to accommodate the lens of an auxiliary camera of the ordinary type directed towards the position usually occupied by the photographic plate of the spectrograph. The usual spectrum falls on to the paper, fabric, or other substance placed in the position of the photographic plate of the spectrograph. The auxiliary camera is directed on to the ultra-violet region only, and since the lens is of glass, any light transmitted by it must consist of visible light produced from the ultra-violet light by the fluorescent substance under examination. As a standard for comparison, Whatman No. 44 filter-papers were used and quantitative comparison was obtained by comparing the times required by the standard and the substance under examination to produce equal photographic effects in a given part of the spectrum. Great difficulties were met in obtaining suitably sensitive photographic plates, and it is suggested that the properties of gelatin may vary with the season of the year at which it is prepared. This method of investigation was applied to determine the fluorescent properties of many different textiles and woods, of papers made from pure cotton, flax, hemp, esparto, and ramie, of cellulose

derivatives, and of a number of carbohydrates, including several sugars, starch, and dextrin. The results are presented in the form of curves in which the fluorescence, expressed as a percentage of that of the arbitrary standard, is plotted against the wave-length of the incident light. Cellulose acetate was the most strongly fluorescent of the cellulose derivatives examined, the maximum strength being at λ 2500—2800, where it was seven times that of the standard. Cellulose nitrate is almost devoid of fluorescent properties. The sugars examined included xylose, dextrose, galactose, lævulose, sucrose, maltose, and lactose, and indications were found of some relation between structure and fluorescent power. There is some evidence to suggest that the cellulose complex may contain groups more nearly related to dextrose than to *d*-fructose.

E. H. R.

The Spectra Structure of the Luminescence excited by the Hydrogen Flame. HORACE L. HOWES (*Physical Rev.*, 1921, 17, 469—474).—An investigation, with determinations of wave-lengths, of the spectra of the luminescence of air-slaked lime, and of certain phosphorescent sulphides ("strontium sulphide-bismuth sodium sulphate," "strontium sulphide-bismuth potassium phosphate," and a calcium sulphide compound containing both bismuth and fluorine as active elements), when partly bathed in a hydrogen flame, but at a temperature below red heat.

A. A. E.

Scattering of Light by Dust Free Liquids. II. W. H. MARTIN and S. LEHRMAN (*J. Physical Chem.*, 1922, 26, 75—88).—A continuation of previously published work (A., 1920, ii, 573). In the present paper, the relative intensity and polarisation of the light scattered by dust-free benzene, toluene, xylene, chlorobenzene; methyl alcohol, ethyl alcohol, *n*-propyl alcohol, *isobutyl* alcohol, *isoamyl* alcohol, water, and mixtures of carbon disulphide with ether, benzene with hexane, and hexane with *cyclohexane* have been measured with an accuracy greater than that obtained in earlier work. The increased accuracy was made possible by the use of cross-shaped containers with sealed in, flat, glass end plates in place of the bulbs used previously. Measurements of the light scattered by two-component liquid solutions show that the relative intensity of the scattered light is always somewhat greater than that calculated on the assumption that the scattered light is an additive property for the two liquids. Liquids which polarise the scattered light very far from completely show, on dilution, much more nearly complete polarisation. Measurements of the ratio of the intensity of incident light to that of scattered light have been made for liquids. The results show that ether and water scatter about one-tenth as much light as do the same weights of these liquids in the gaseous state. For benzene and its homologues, the ratio is about one-fifth. Measurements of the intensity of the scattered light for various wave-lengths show that this value varies inversely as the fourth power of the wave-length.

J. F. S.

Radiation and Chemical Action. T. W. J. TAYLOR (*Nature*, 1921, **108**, 210; cf. following abstract).—An experimental refutation of Lewis's explanation that the velocity of inversion of sucrose by dilute acid is not increased by sunlight because the activating rays lie in the region of 1μ , and at this wave-length water would absorb the radiation almost totally in the first thin layer, so that the bulk of the liquid would remain unaffected (cf. Lindemann, A., 1920, ii, 743). A solution of sucrose containing hydrogen chloride was forced upwards in bright sunlight through extremely fine capillary jets; the liquid formed fine columns about 8 cm. high, which then broke up into clouds of small drops (about 0.015 cm. in diameter), the drops rising a further 40 cm. After falling during an average time of 0.68 second, the drops were collected. The rotation was only 0.24° less than that of an unexposed control portion of the solution. Even assuming that the radiation density at 1μ had been reduced, by absorption, inside each drop to 10^{-8} of its value, which is considered to be unlikely, a difference in polarimeter readings of about 13° would have been anticipated. A. A. E.

Radiation and Chemical Action. W. C. McC. LEWIS (*Nature*, 1921, **108**, 241; cf. preceding abstract).—An alternative reply to Lindemann's criticism (A., 1920, ii, 743) of the radiation hypothesis of chemical reactions, based on the relatively small absorption capacity of the reactant solutes (cf. Lewis and McKeown, A., 1921, ii, 623). A clear distinction must be drawn between photochemical and thermal conditions, the former involving an absorption coefficient term. It is argued mathematically that the photochemical fractional decomposition and the thermal value (about 0.01 of the magnitude of the former) would be inappreciably small in Taylor's experiments. Further, Taylor carried out no determination of the amount of radiation absorbed by the sugar in the solution; if this were small, no chemical change in excess of the thermal change would be anticipated. A. A. E.

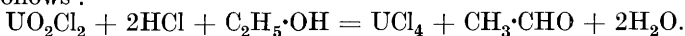
Dependence of Velocity of Reaction on the Concentration in Photochemical Processes. M. VOLMER and K. RIGGERT (*Z. physikal. Chem.*, 1922, **100**, 502—511).—The velocity of the dissociation of anthracene in hexane solution into a positive residue and an electron has been determined with the object of testing Luther and Weigert's (A., 1905, ii, 785) expression for the dependence of the velocity of photo-decomposition on the concentration. The expression has the form $v = dC/dt = kJ_0(1 - e^{-\epsilon Cd})/d$, where C is the concentration, ϵ the extinction coefficient, d the thickness of the illuminated layer, J_0 the intensity of the light, and k a constant. The amount of change was measured by the saturation current. It is shown that the current experimentally observed and that calculated from the above-mentioned equation are in excellent agreement, thus proving the correctness of the formula. J. F. S.

Theory of Induced Reactions. CHR. WINTHER (*Z. physikal. Chem.*, 1922, **100**, 566—571).—A theory of induced reactions is

put forward which is based on the conversion of oxygen into ozone in the presence of zinc oxide by ultra-violet light and other induced reactions. In the case mentioned, it is assumed that the light is absorbed by the zinc oxide and the light energy is given out again in the form of very short wave-length radiation which is photochemically absorbed by the oxygen. J. F. S.

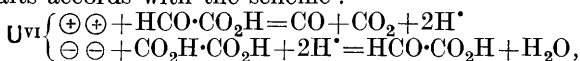
The Action of Light on Silver Bromide. ERNST JOHANNES HARTUNG (T., 1922, 121, 682—691).

Action of Light on Uranium Salts. J. ALOY and E. RODIER (*Bull. Soc. chim.*, 1922, iv, 31, 246—249).—Under the influence of light, uranyl salts are converted into uranous salts in the presence of the acid entering into the constitution of the salt and a readily oxidisable substance such as alcohol. The reaction which occurs is as follows :

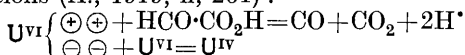


Two molecules of acid are necessary for each molecule of uranyl salt. In this way, the fluoride, chloride, bromide, iodide, and sulphate have been prepared, and an aqueous solution of the nitrate. If an insufficient amount of acid is present, basic salts are obtained. If the reaction is allowed to proceed further, a black precipitate of uranous hydroxide is obtained. W. G.

Photolysis of Uranyl Oxalate and Uranyl Acetate. EMIL BAUR and A. REBMANN (*Helv. Chim. Acta*, 1922, 5, 221—239).—If photolysis consists of two processes respectively akin to anodic oxidation and cathodic reduction, the presence of a suitable third substance should affect the quantitative, and possibly the qualitative, results of the process. Thus, the photolysis of oxalic acid by uranyl salts accords with the scheme :



which is supported by the decomposition of glyoxylic acid under similar conditions (A., 1919, ii, 264) :



In the latter reaction, no evidence could be obtained of the formation of glycollic acid, or of formaldehyde, derived from its decomposition in the photolysis of uranyl oxalate. On the other hand, the influences of mercuric chloride, potassium iodide, ferrous sulphate, quinol, uranyl chloride, and sodium uranyl oxalate respectively in increasing the proportion of carbon dioxide formed in comparison with carbon monoxide are explicable in accordance with the theory. Sodium sulphite has no effect (compare Hatt, A., 1918, ii, 143; Trümpler, A., 1916, ii, 9), and formic acid only gives rise to excess of carbon dioxide in the later stages of the reaction, probably because the formate- takes place independently of the oxalate-photolysis. The gas produced in the photolysis of uranyl acetate (A., 1918, ii, 143), and considered to be hydrogen, is now shown to have been carbon monoxide originating from glyoxylic acid, frequently present as an impurity in acetic acid. Two reactions occur

during the photolysis of uranyl acetate: (1) true photocatalytic decomposition into methane and carbon dioxide (Fay, A., 1896, i, 464), (2) non-catalytic oxidation of acetate-ions to ethane and carbon dioxide by uranyl salts, which only occurs in acetic acid solution with a sufficient concentration of acetate-ions. The photolysis is favoured by the presence of free acetic acid, but restricted by chloridions and mercuric-ions to some extent, almost entirely by ferric salts or formic acid. Such a reaction cannot be looked on as, for example, a unimolecular decomposition of the uranyl acetate complex by light, but as an action of the activated uranyl complex on surrounding molecules by interchange of electrons. In other words, it is always an oxidation-reduction process, and so closely related to electrolysis. Probably Fay's reaction is connected with Kolbe's electrolytic decomposition of acetates, acetyl peroxide and atomic hydrogen being the respective anodic and cathodic products, which then interact and form methane and carbon dioxide. Since the photolytic oxidation of acetic acid to ethane and carbon dioxide, and of glyoxylic acid to carbon monoxide and carbon dioxide, can be reproduced electrochemically only by the use of a considerable potential difference, it is concluded that the energy quantum absorbed by the uranyl complex must also have such a value as would suffice, not only for the production of oxygen, but also for the formation of peroxides. The formation of uranyl peroxide, observed by Usher and Priestley (A., 1906, ii, 881), is recalled in this connection. J. K.

Photolysis of Uranyl Oxalate. EMIL BAUR and HAGGENMACHER (*Z. physikal. Chem.*, 1922, 100, 36—41).—The action of sunlight on aqueous solutions of uranyl sulphate and oxalic acid has been investigated. The products of the reaction are found to be formic acid, carbon dioxide, and carbon monoxide. The amount of formic acid formed is very small, and it is held that it must remain small because it is used up as fast as it is produced in reducing the uranyl-ion to uranous-ion. The gas evolved contains a slight excess of carbon dioxide above that required for the simple stoichiometric relationship $\text{CO}_2:\text{CO}$. The formation of formic acid is regarded as a cathodic reduction of carbon dioxide, thus: $\text{CO}_2 + 2\text{H}^+ + \ominus\ominus = \text{H}\cdot\text{CO}_2\text{H}$. J. F. S.

Action of Ultra-violet Light on Gels. EDWARD O. HOLMES, jun., and WALTER A. PATRICK (*J. Physical Chem.*, 1922, 26, 25—41).—The action of ultra-violet light from an iron arc on silica gels, which had been impregnated with acetone, acetic acid, and nitric acid, respectively, and also on celluloid, has been investigated by a tensimetric method. The gel was placed in both bulbs of the tensimeter, and one was exposed to ultra-violet light whilst the other was kept in the dark and the difference in pressure measured. It is shown that the gels give off gaseous products, provided the liquid contained in the gel is decomposed photochemically into gaseous products which are not adsorbed by the gel. Thus increase of pressure was observed in the case of gels containing acetic acid and acetone, but not in the case of nitric acid, for the decomposition

products of nitric acid are strongly adsorbed by silicic acid gel. The gaseous products consist of a mixture of the vapour of the organic liquid itself along with those gases resulting from the photo-chemical decomposition of the liquid. Celluloid behaves in a similar manner under the influence of ultra-violet light. The mechanism of the liberation of the adsorbed liquid is explained as follows. In the gel there are a large number of pores partly filled with the adsorbed substance under great negative pressure and therefore having a very low vapour pressure. The negative pressure in the film is caused by the surface tension acting along the sides of the pores and round their circumference. The force of the surface tension is reduced by the action of ultra-violet light owing to its decomposition of the liquid of the film with the formation of gas bubbles, which prevent the film from completely wetting the surface of the pores, resulting in a decrease of the negative pressure and subsequently an increase in the vapour pressure of the adsorbed substance, and consequent evaporation of some of the liquid. The same mechanism explains the liberation of gases by celluloid under the influence of ultra-violet light, only here the case is complicated by the fact that light decomposes the structure of the gel itself (cellulose nitrate) as well as the solvent in the pores. Hence the reason for celluloid turning brown and becoming brittle under the action of light is evident.

J. F. S.

β -Ray Spectra and their Meaning. C. D. ELLIS (*Proc. Roy. Soc.*, 1922, [A], **101**, 1—17).—The shortest wave-length that has hitherto been measured by the crystal method is 0.07 Å.U., which is greater than the wave-lengths of γ -rays emitted by many radioactive substances. A method based on the quantum theory has been developed for the measurement of the wave-lengths of such rays, and has been applied to the cases of the γ -rays of radium-*B*, radium-*C*, and thorium-*D*. The method involves the measurement of the energies of the different lines in the natural β -ray spectrum of the element in question, and the energy of the corresponding line in the excited spectra of a substance of neighbouring atomic number. The numerical results obtained support the view that γ -rays are emitted from the nucleus. The quantum theory is probably applicable to the nucleus, and a part, at least, of the structure of the nucleus is expressible in terms of stationary states.

J. S. G. T.

Coloration and Luminescence produced by the Action of Becquerel Rays. STEFAN MEYER and KARL PRZIBRAM (*Z. physikal. Chem.*, 1922, **100**, 334—336).—A number of examples are recorded which show that the coloration, brought about in glass, quartz, and similar materials by exposure to radium rays, may be removed entirely or in part by prolonged heating at comparatively low temperatures. It is also shown that thermoluminescence is exhibited on heating such coloured material at comparatively low temperatures. Thus a piece of colourless glass which has been turned brown by the rays and has remained unchanged for years in daylight on heating at 100° for twenty-four hours became con-

siderably lighter in colour, after several days at 130—140° it showed a violet tinge, and at 150—200° for several days it was definitely violet. Violet coloured glass is more resistant. Quartz which had been coloured brown became colourless after several days' heating at 150—200°. Sapphire which was originally light blue and had become topaz coloured by exposure to radium rays, after heating at 60° for a day became yellow, after a further two days at 80—90° it was pale yellow with a blue tinge, and after several days at 150—200° it regained its blue colour. A piece of kunzite which had become green in colour when heated for nine hours at 90° showed a feeble thermoluminescence, which disappeared in three hours. By heating at 170—180°, thermoluminescence was again shown, and the green colour had become much paler in half an hour. The same piece of material was then slowly heated at 140° without luminescence appearing, but at 160° weak luminescence appeared which became stronger as the temperature was raised to 185°, and after two hours' heating at 190° the luminescence failed and the kunzite had regained its original lilac colour. J. F. S.

The Existence of the New Radioactive Element Uranium-V described by Piccard and Stahel. OTTO HAHN (*Physikal. Z.*, 1922, **23**, 146—150).—The decrease in activity of a number of uranium-X preparations has been determined to test the observations of Piccard and Stahel (*A.*, 1922, ii, 185). The observed activity was the sum of the exponentially decreasing activity of pure uranium-X and a constant α activity due to the presence of ionium. No evidence of the existence of uranium-V was found. W. E. G.

Existence of Isotopes of the Disintegration Products of Actinium and the Meitner Nuclear Model. MAXIMILIAN CAMILLO NEUBURGER (*Z. anorg. Chem.*, 1921, **120**, 150—158).—The actinium family shows many irregularities when compared with the radium and thorium families, which it is suggested are due to the existence of unknown isotopes. The production of isotopes by branching at radioactinium is probable since this element gives α -particles with two ranges. A scheme is given for the disintegration of radioactinium in which the disintegration process, $\alpha'-\beta-\alpha-\beta$, is assumed (cf. Meitner, *A.*, 1921, ii, 293). W. E. G.

Electrochemical Behaviour of Liquid Sodium Amalgams. THEODORE W. RICHARDS and JAMES BRYANT CONANT (*J. Amer. Chem. Soc.*, 1922, **44**, 601—611).—A number of improvements are described in the electrolytic preparation and the subsequent manipulation of pure liquid sodium amalgam, as well as in the apparatus for the measurement of the *E.M.F.* of sodium amalgam concentration cells with aqueous electrolytes. The *E.M.F.* of many concentration cells of liquid sodium amalgam has been measured at 25°, and a few cells also at 15° and 35°. The deviations of these potentials from the simple concentration law were found to be greater in sodium amalgam than with any other mercurial solution hitherto investigated in detail. The heats of transference

of sodium from one amalgam to another calculated by the Helmholtz equation are found to be unusually large. J. F. S.

Solid Thallium Amalgams and the Electrode Potential of Pure Thallium. THEODORE W. RICHARDS and CHARLES P. SMYTH (*J. Amer. Chem. Soc.*, 1922, **44**, 524—545).—Pure thallium in compact form is definitely shown to possess at 20° an electrode potential 2.1 millivolts higher than saturated thallium amalgam. When immersed in a *N*-solution of thalloses and connected with a normal calomel electrode, the total potential 0.6192 is indicated at 25°. The potential of pure thallium is not influenced by quenching the metal, which is so soft that no important strain can exist in it. α -Thallium is the only phase of the pure metal which is stable at ordinary temperatures. Finely divided electrolytic thallium sponge gives a potential 0.6 millivolt higher than the compact fused form. The difference is probably due to the fine state of division, and disappears on long keeping. The difference of potential shown by β -thallium, if it could exist at ordinary temperatures, would probably be nearly three times as great. Solid thallium amalgams may be made having potentials anywhere between that of pure thallium and the 2-phase amalgam. As mercury is added, the potential decreases at first, then remains constant, between 4% and 10% of mercury, and later decreases again until at about 15% of mercury the liquid phase becomes permanent at 20°. Crystals of solid amalgam separated centrifugally from the liquid containing more mercury showed as much as 20% of mercury, but some of this was undoubtedly adhering mother-liquor. The densities of solid thallium amalgams indicate an increase in volume of thallium on amalgamation. The corresponding curve shows a slight inflection at about 5% of mercury. The hardness of solid thallium amalgams increases with added mercury until about 5% is present, when it begins slowly to diminish. From these phenomena it is inferred that α -thallium dissolves mercury, increasing in hardness and volume up to about 5% of mercury. When more mercury is added, another solid phase of about the same hardness and volume, but containing more mercury, appears. These two phases appear to exist mixed together in equilibrium, over the range from about 5% of mercury to 10% at 20°. With more than about 10% of mercury the α -solid solution ceases to exist and the other phase continues to dissolve mercury in solid solution until it is saturated, with perhaps 15% of mercury. The other solid phase is probably a solid solution of mercury in β -thallium, which appears in definite crystalline form, making the amalgam friable after the admixture of α -thallium has been eliminated. β -Thallium can exist at ordinary temperatures only in the presence of much mercury, but it is always the form present in equilibrium with the liquid amalgam. Pure thallium melts at 303.5° and has a transition point at 235.3°. J. F. S.

Electromotive Behaviour of Aluminium. ROBERT MÜLLER and FRANZ HÖLZL (*Z. anorg. Chem.*, 1921, **121**, 103—109).—The potential of aluminium and amalgamated aluminium has been

measured in solutions of aluminium chloride, potassium chloride, hydrochloric acid, and sodium hydroxide of various concentrations and in mixtures of hydrochloric acid and aluminium chloride of various concentrations. The values of the potential are found to be in qualitative agreement with the Nernst theory. It is shown, from a comparison of the potentials of pure and amalgamated aluminium in acid and alkaline electrolytes, to be probable that the activation by means of mercury and the apparent anomaly of the potential of pure aluminium is occasioned by a protecting layer of hydroxide. In concentrated hydrochloric acid (6.8 *N*), pure aluminium is more electropositive than the amalgam; cf. Dhar (*ibid.*, 1921, 118, 75). J. F. S.

Acidifying Action of Hydroxy-organic Compounds on Boric Acid and Molybdic Acid. E. RIMBACH and P. LEY (*Z. physikal. Chem.*, 1922, 100, 393—407).—The authors have measured at 18° the hydrogen potential of solutions of boric acid, molybdic acid, glycolic acid, lactic acid, malic acid, citric acid, tartaric acid, propylene glycol, glycerol, mannitol, and dextrose and also mixtures of the two inorganic acids with various concentrations of each of the organic compounds. The hydrogen-ion concentration has been calculated in each case, and the increase in hydrogen-ion concentration occasioned by the mixing. The results are represented by curves and tabulated. The increase in the acidity is attributed to complex formation in which the hydroxyl group is operative. In the case of boric acid, tartaric acid produces a much greater increase than the monohydroxy-acids, whilst in the mixtures of molybdic acid the reverse is the case. Similar results are obtained with the non-acidic hydroxy-compounds. With molybdic acid, glycerol increases the acidity most, whilst mannitol has a smaller action than propylene glycol, but with boric acid, mannitol and dextrose have the most pronounced action, whilst propylene glycol has a greater action than glycerol. J. F. S.

Thermodynamic and Electrokinetic Potential Difference at the Surface of Two Liquids. H. FREUNDLICH and A. GYEMANT (*Z. physikal. Chem.*, 1922, 100, 182—196).—The thermodynamic potential, ϵ , and the electrokinetic potential, ζ , of the liquids phenol, guaiacol, benzonitrile, and aniline against aqueous solutions of a number of electrolytes have been measured. The ϵ -potential was measured by Beutner's method and the ζ -potential determined from the microscopic observations on the velocity of kataphoresis of the liquid drops. The two potentials are shown to be very largely independent of one another, a fact in keeping with the views of Freundlich (*Kolloid Z.*, 1921, 28, 240). The negatively charged drops are generally discharged and recharged oppositely by the kations, particularly strongly by multivalent kations such as calcium and aluminium, whereas such an effect does not occur in connexion with the ϵ -potential. A certain similarity of action is observed in the case of some organic ions; the kations of basic dyes and the alkaloids have a positive effect on

both potentials, whilst the anions of organic acids have a negative action. Exceptions and great variations in the dimensions of the action are, however, to be observed. The regularities previously published (*loc. cit.*) are confirmed. The partition relationship of the ions is determinative of the ϵ -potential, the organic liquid phase being more strongly positive or negative the more soluble the kation or anion is in the liquid. In the case of the ζ -potential, the adsorption and valency of the kations are responsible for the discharge and positive recharging of the drops; thus, for example, the kations of the basic dyes and the multivalent kations have a particularly strong action. All four liquids are negatively charged towards water in respect of their ζ -potential, even aniline, despite its strongly basic character. J. F. S.

Measurement of Overvoltage. HERMAN V. TARTAR and HARMON E. KEYES (*J. Amer. Chem. Soc.*, 1922, **44**, 557—567).—The conclusions of earlier investigators that overvoltage increases with time and current density and varies with the nature of the electrode surface have been confirmed. A comparison, based on the transition point for hydrogen-zinc deposition from solutions containing sulphuric acid and zinc sulphate, has been made by the two methods used for overvoltage measurement. The data obtained show that the commutator method gives erroneous results; when gas is being evolved at the experimental electrode, the error is large and varies with the speed of rotation of the commutator. The direct method has been found to give more consistent results and to be the more accurate method; the criticism that it is subject to variation due to electrode spacing and size and shape of the containing vessel is shown to be invalid. The existence of an appreciable transfer resistance at the surface of the electrodes examined is doubtful. While gas is being evolved, it is evidently not of the magnitude which has been stated. Evidence is advanced which indicates that the ordinary hydrogen overvoltage tables, obtained by using pure acid solutions as electrolyte, do not show the current densities necessary for the deposition from acid solutions of metals having a greater *E.M.F.* than hydrogen. J. F. S.

Low-voltage Standard Cells. J. OBLATA (*Proc. Phys. Math. Soc. Japan*, 1921, [iii], **3**, 136—149; cf. *ibid.*, 1921, [iii], **3**, 64).—The properties of various cell combinations were studied in order to obtain a satisfactory low-voltage standard. The following two were the most reproducible and constant: Cd amalgam | CdI₂ | PbI₂ | Pb amalgam, and Cd amalgam (10%) | CdSO₄.8/3H₂O | Cd amalgam (dilute). The *E.M.F.* of the former is 0.09838 at 20° and that of the latter is of the order of 0.01 volt, giving different values according to the concentration of the dilute amalgam. The temperature coefficients were determined between 15° and 30°. The heats of formation of cadmium chloride, iodide, and bromide were computed by applying the Gibbs-Helmholz equation. They were found to be 94090, 49340, and 74700 cals., respectively.

CHEMICAL ABSTRACTS.

Modifications of Kohlrausch's Method for the Measurement of the Conductivity of Electrolytes. MARCEL ABRIBAT (*Bull. Soc. chim.*, 1922, iv, **31**, 241—245).—The ordinary telephone receiver used for determining the zero point on the Wheatstone bridge is replaced by a galvanometer. In order to permit of this, the current passing through the galvanometer is converted from alternating to direct by means of a thermionic valve. The arrangement of the apparatus is sketched. To make the readings still more exact, an amplifier may be used.

W. G.

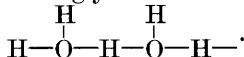
Questions Relating to the Constitution and Function of Electrolytes. W. MADELUNG (*Annalen*, 1922, **427**, 35—109).—A theoretical enquiry into the constitutional causes which determine the formation and stability of electrically charged atomic aggregates (ions) in crystals and in solution. The form of the paper does not admit of satisfactory abstraction, and the original should be consulted in order to obtain a just appreciation of the comprehensive character of the author's views.

Hantzsch's theory of ψ -isomerism is discussed and extended. The cyanogen compounds described in the preceding paper (cf. this vol., i, 438) are ψ -acids in their non-ionisable forms, and true acids in the forms corresponding with their salts: disodium cyanamide is $\text{Na}\cdot\text{N}:\text{C}:\text{N}\cdot\text{Na}$, sodium dicyanamide is $\text{Na}\cdot\text{N}:\text{C}:\text{N}\cdot\text{CN}$, and sodium cyanoform is $\text{Na}\cdot\text{N}:\text{C}:\text{C}(\text{CN})_2$. Corresponding with ψ -acids and ψ -bases, a class of ψ -salts can be recognised as falling within the same view of ψ -isomerism. Aluminium and stannic chlorides are not ionised as such; they are therefore ψ -salts. In general, the univalent and some bivalent metals tend to form salts, whilst most of the ter- and quadri-valent metals form ψ -salts. The sodium compound of acetyl acetone is an electrolyte and non-volatile, like sodium chloride, whilst the aluminium derivative is a non-electrolyte and is volatile, like aluminium chloride; both the sodium compounds are salts, and both the aluminium compounds ψ -salts. In order to form ions, the ter- and quadri-valent metals have to combine with other ions or molecules to form centrally orientated complexes: $[\text{Fe}(\text{H}_2\text{O})_6]^{+++}$, $[\text{Fe}(\text{CN})_6]^{---}$, $[\text{Cr}(\text{NH}_3)_6]^{+++}$, $[\text{SnCl}_6]^{--}$.

Ionisation therefore is largely a matter of the formation of centrally orientated complexes. In acids, it is assisted by the accumulation of a number of electro-negative peripheral groups around the nuclear atoms, for example, $[\text{Fe}(\text{CN})_6]^{---}$ and $[\text{SnCl}_6]^{--}$. In bases, the accumulation of hydrogen atoms either as such, as amino- or hydroxyl-groups, or as water or ammonia molecules, has a similar effect; cf. $[\text{NH}_4]^+$, $[\text{PH}_4]^+$, $[\text{Cr}(\text{NH}_3)_6]^{+++}$, etc. Even carbon may become the central atom of an ion if sufficiently loaded with electrically powerful groups; the ion of guanidine is represented by the formula $[\text{C}(\text{NH}_2)_3]^+$, which expresses its strongly basic character much better than the customary formula based on the integral valencies of the organic chemist. *tert.*-Butyl iodide, $(\text{CH}_3)_3\text{CI}$, is better termed trimethylcarbonium iodide, as it is ionised in solution in liquid sulphur dioxide, a remarkable instance

of the tendency of a large accumulation of hydrogen atoms to promote ion-formation; the ions $[\text{C}(\text{CH}_3)_3]^+$, $[\text{C}(\text{NH}_2)_3]^+$, and $[\text{CO}_3]^{--}$ are strictly analogous.

Apparently simple ions, H^+ , OH^- , NO_3^- are subject to the same laws regarding the tendency to centric orientation and the influence of the peripheral groups. Hydrogen- and hydroxyl-ions are invariably combined with at least one molecule of water: $[\text{OH}_3]^+$, $[\text{H}(\text{OH})_2]^+$, and often with more. By assuming a further degree of hydration, chains may be produced which are strongly reminiscent of the structure of the crystalline compound :



The electrical influence of peripheral groups is often felt, not only in the circumjacent atoms, but also in more remote parts of the molecule. This phenomenon is termed induction; it is fully discussed and illustrated by many examples in the original paper.

C. K. I.

[Theory of Strong Electrolytes.] SVANTE ARRHENIUS (*Z. physikal. Chem.*, 1922, **100**, 9—35).—A theoretical paper in which the author discusses the theory of strong electrolytes as put forward by Ghosh (T., 1918, **117**, 449, 627, 707; 1920, **117**, 823, 1390; this vol., ii, 125). The various calculations made by Ghosh in connexion with the dissociation of strong electrolytes and the more complete calculations of Partington (A., 1920, ii, 151) are considered, and in connexion with those of the former author it is shown that they are not always consistent, nor have they always the deep significance which Ghosh places on them. For example, in a comparison of the Arrhenius formula, $i=1+(n-1)\alpha$, with Ghosh's formula, $i=n(1+\frac{1}{3}\log_e \alpha)$, calculations are put forward by Ghosh which indicate the superiority of the second formula. The present author points out that in obtaining values from the second formula values which had been corrected for viscosity are used in the case of salts of the potassium chloride type, but not for those of the calcium chloride type, whilst with the former formula no correction was applied anywhere. The author concludes that could the Ghosh hypothesis be applied it would be a distinct advance on the previous hypotheses, but, unfortunately, it cannot be applied without great modifications.

J. F. S.

The λ -V Curves of Non-aqueous Solutions of Binary Electrolytes. P. WALDEN (*Z. physikal. Chem.*, 1922, **100**, 512—531).—A theoretical paper in which the influence of the viscosity, dielectric constant, and mobility on the form of the λ -V curves is discussed.

J. F. S.

Dissociation and Hydrolysis Equilibria in Solutions of Salts of Carbonic and Boric Acids. HEINRICH MENZEL (*Z. physikal. Chem.*, 1922, **100**, 276—317).—From electrometric measurements of mixtures of sodium carbonate and hydrogen carbonate in various concentrations at 18°, the second dissociation constant of carbonic acid has been determined and the value $K_2=6.2 \times 10^{-11}$ found, which agrees well with the value found by Auerbach and

Pick (*Arbt. Kais. Gesundh.*, 1911, **38**, 2). The hydrolysis of sodium carbonate has been calculated from the results, and the following values are recorded: $0.2M$, 1.12%, $0.1M$, 1.76%, $0.05M$, 3.0%, $0.02M$, 5.5%, $0.01M$, 8.3%, and $0.005M$, 10.65%. The dissociation constant for boric acid has been determined at 18° by *E.M.F.* measurements of solutions of borax and sodium metaborate, and the value $K_B = 5.7 \times 10^{-10}$ obtained. This value is much smaller than that recorded by Walker (*T.*, 1900, **77**, 17), but is in keeping with the values recorded by Lundberg and Lundén at other temperatures. Concentrated solutions of borax and metaborate show, in consequence of the formation of polyborate ions, a somewhat stronger alkalinity than would be expected from the dissociation and hydrolysis. The degree of hydrolysis of sodium metaborate has been determined, and the following values have been obtained: $0.4M$, 0.50%; $0.2M$, 0.57%; $0.1M$, 0.76%; $0.04M$, 1.22%; $0.02M$, 1.7%, and $0.01M$, 2.3%. The equilibrium sodium carbonate + borax \rightleftharpoons metaborate + bicarbonate has been experimentally examined in dilute solutions, and also in two cases for concentrated solutions where the polyborate formation was taken into account.

J. F. S.

Calculation of the Second Dissociation Constant of Dibasic Acids from the Hydrogen-ion Concentration. MARCEL DUBOUX (*J. Chim. physique*, 1921, **19**, 179—187).—Two methods are given for calculating the second degree of dissociation of dibasic acids, which are applicable to solutions containing 0.01—0.005 gram-mol. per litre. At these concentrations, the determination of the hydrogen-ion concentration presents no difficulties. It is shown that Noyes's formula can be rigorously applied only to solutions less concentrated than 0.001 gram-mol./litre. Making use of known hydrogen-ion concentrations, the following values have been calculated: tartaric acid, $K_2 = 32 \times 10^{-6}$ at 25° , $K_2 = 28.4 \times 10^{-6}$ at 76° ; malic acid, $K_2 = 4.1 \times 10^{-6}$ at 100° ; succinic acid, $K_2 = 2.5 \times 10^{-6}$ at 25° , and $K_2 = 1.5 \times 10^{-6}$ at 100° . J. F. S.

Behaviour of the Photo-haloids in a Direct Electric Current. C. TUBANDT and GERHARD ESCHENHAGEN (*Z. physikal. Chem.*, 1922, **100**, 489—501).—The effect of passing a direct electric current through photo-haloids has been investigated. It is shown that both the synthetic photo-haloids and those which have been formed by the action of light are simple electrolytic conductors; the presence of colloidal metals, whether adsorbed or mechanically mixed, does not affect the character of the electrical conductivity. Metallic silver may be separated electrolytically from strongly illuminated dry silver chloride, and also from synthetic photo-chlorides and bromides, but not from photo-iodides even when these are mixed with large quantities of colloidal silver. The colloidal silver in synthetic photo-haloids and also that in illuminated silver haloids is unaffected by a direct current, but the silver-ions, as in the case of pure silver haloids, wander uninfluenced by the silver particles toward the electrode; a displacement of the silver

particles is not observed even when the current is allowed to flow for prolonged periods. J. F. S.

Cathodic Deposits from Mixed Solutions of Two Simple Metallic Salts. WALTHER HILDEBRANDT CREUTZFELDT (*Z. anorg. Chem.*, 1921, **121**, 25—52).—Mixtures of salts of the following pairs of metals, copper-cadmium, copper-lead, copper-iron, silver-copper, silver-cadmium, and silver-zinc, have been electrolysed by various currents and voltages and binary, fine-grained, crystalline deposits obtained. It is shown that the composition of the deposit changes continuously with the current density and the composition of the mixture. By changing these factors, a series of mixed crystals may be deposited which varies from one pure constituent to the other constituent. Measurements of the *E.M.F.* of the deposit show that they are readily oxidised, and when placed in water they lose the more electropositive constituent in a few hours. In order that a deposit of a given concentration should be obtained, it is necessary that the current density should be increased with increasing metal concentration in the solution. A more vigorous agitation of the solution acts in the same sense as an increased current density, whilst an increased temperature acts in the opposite sense. The dependence of the *E.M.F.* of the deposit on the composition is considered in connexion with Tammann's theory. The partition of both atom types in the electrolytic deposit is not the normal one observed in mixed crystals from molten mixtures, but a completely unordered one. The probability for the unprotected atoms of the electropositive metal is given by $\Sigma w = p^{s-1} \cdot q + p^{2s-4} \cdot q^2 + p^{3s-7} \cdot q + \dots$, in which p is the molecular fraction of the less electropositive metal, q that of the electropositive metal, and $s-1$ the number of atoms of the less electropositive metal necessary to protect one atom of the more electropositive metal from the action of reagents. The fraction α of the unprotected atoms of the more electropositive metal is given by the equation $\alpha = (q - \Sigma w)/q$. The *E.M.F.* is assumed to be proportional to the number of unprotected atoms. It is shown that the potential-composition curve is determined by a whole number s . Four copper atoms are necessary to protect a single cadmium or lead atom, seven silver atoms are required for a single copper atom, and twenty-two copper atoms are necessary to protect a single iron atom. J. F. S.

Determination of the Specific Heat of Solid Substances by the Adiabatic Electrical Method. ERNST COHEN and A. L. TH. MOESVELD (*Z. physikal. Chem.*, 1922, **100**, 151—158).—The specific heat of cadmium sulphate has been determined by an adiabatic electrical method previously described (this vol., ii, 156). The calorimeter liquid used was bromoform (specific heat 0.1241) and three determinations, using 823 and 676.5 grams respectively of $\text{CdSO}_4 \cdot 8/3\text{H}_2\text{O}$, were carried out. The value 0.200 between 17° and 21° was obtained, which agrees well with 0.2008 found by Cohen, Kruisheer, and Moesveld (*A.*, 1921, ii, 156). It is shown

that the values found by Holsboer (0.2225) (A., 1901, ii, 226) and by Seibert, Hulett, and Taylor (A., 1917, ii, 231) are untrustworthy.
J. F. S.

Determination of the Higher Point of Inversion of the Specific Heat of the Saturated Vapour of Benzene. G. BRUHAT and A. DELAYGUE (*Compt. rend.*, 1922, 174, 937—939).—Using a Cailletet apparatus with the tube jacketed with glycerol electrically heated, the authors have determined the two points of inversion of the specific heat of the saturated vapour of benzene. The values obtained are 122° and 258° respectively. From a theoretical study of the specific heat of the saturated vapour of benzene, using the characteristic equation for benzene, they obtain the values 121° and 254°.
W. G.

Specific Heats. II. M. PADOA (*Gazzetta*, 1922, 52, i, 25—29; cf. this vol., ii, 27).—The views expressed in the former paper lead to the conclusion that the low specific heats of elements deviating markedly from Dulong and Petit's law are due to the high number of valencies used by the atoms to ensure the stability of the crystalline edifice and to the exceptional energy of the corresponding linkings. Thus, if it were possible to separate the atoms of the abnormal element to such an extent that, although participating in the formation of the crystalline network, such atoms were no longer able to exert mutually disturbing actions, their specific heats should increase to the values exhibited by the other elements. Such a condition should be attained in solid solutions of an element of abnormal specific heat in excess of another of normal specific heat. Experimental confirmation of these views is furnished by measurements of the specific heats of silicon-iron and sulphur-selenium mixtures. In the former case, the atomic heat of silicon is 4.74—4.83 in alloys containing 95—50% of silicon, whilst the values for 33.6 (FeSi), 14 and 10% of silicon are, respectively, 5.27, 6.04, and 6.42. Heating of the 10% silicon mixture at above 1000°, followed by rapid cooling, fails to alter the specific heat. In sulphur-selenium mixtures containing 4, 9, 28.77, 90.35 (rhombic), and 90.35 (monoclinic)% of sulphur, the values of the atomic heat of sulphur are respectively 7.03, 6.00, 5.87, 5.50, and 5.78.
T. H. P.

Method of Formation of the Atoms in Carbon Compounds; HANS BEUTLER (*Z. anorg. Chem.*, 1921, 121, 67).—In a previous paper (this vol., ii, 259) it was shown that the lattice energy of carbon compounds alternated from member to member. This fact was deduced from the behaviour of the melting point and the heat of combustion of the homologues of aliphatic series. It is now pointed out that the recent work of Becker and Janke (this vol., ii, 128) experimentally confirms the author's hypothesis, since this work shows that the even members of the monocarboxylic aliphatic acids crystallise in the hexagonal and the odd members in the tetragonal system.
J. F. S.

Moment of Inertia and Structure of the Carbon Dioxide Molecule. A: EUCKEN (*Z. physikal. Chem.*, 1922, **100**, 159—170).—A theoretical paper in which the moment of inertia of the carbon dioxide molecule and its structure are considered. It is shown to be probable that in the molecule of carbon dioxide the carbon atom is situated practically on the line which joins the two oxygen atoms and performs small elastic circular vibrations round these atoms. The moment of inertia vertical to the line joining the oxygen atoms has the value 50×10^{-40} cm². gram, and the mutual distance of the oxygen atoms 2.0×10^{-8} cm. Carbon dioxide and presumably sulphur dioxide are to be treated thermally as diatomic gases; on this basis the chemical constant i for carbon dioxide has the value 0.80, and the molecular heat at high temperatures, in consequence of the linear vibration of the oxygen atoms and the circular vibrations of the carbon atom, approaches the limiting value $C_{v\infty} = 5/2R + 4/2R + 4/2R = 13/2R$. J. F. S.

Some Relationships between the Critical Temperature and the Melting and Boiling Points. MAURICE PRUD'HOMME (*J. Chim. physique*, 1921, **19**, 188—189).—The following two relationships are found to hold for the critical temperature (T_c), the freezing point (T_f), and the boiling point (T_1) of members of the zero group: $T_1(T_c - T_1)/T_f(T_c - T_f) = 1 + \epsilon$, where ϵ is a fraction having a mean value 0.05, and $T_c = (T_f - T_1)(1 + \epsilon')$ where ϵ' has very nearly the same value as ϵ . These formulæ hold for other substances and have been confirmed in sixty different cases. J. F. S.

Factors Determining the Hygroscopic Properties of Soluble Substances. I. Vapour Pressures of Saturated Solutions. GRAHAM EDGAR and W. O. SWAN (*J. Amer. Chem. Soc.*, 1922, **44**, 570—577).—The vapour pressures of saturated aqueous solutions of potassium chloride, potassium nitrate, ammonium chloride, ammonium sulphate, ammonium nitrate, ammonium dihydrogen orthophosphate, sodium nitrate, carbamide, and a mixture of ammonium chloride and potassium nitrate have been measured at temperatures between 20° and 30°. The relationship of the vapour pressures of saturated aqueous solutions to the hygroscopic properties of soluble substances is discussed. The theory relating the vapour pressure of a saturated solution to the temperature and solubility is considered, and on the basis of the Clausius-Clapeyron equation and van't Hoff's equation the expression $\log_e P_1 - \log_e P_2 = i(S_2 - S_1) - Q_1/R(1/T_1 - 1/T_2)$ is deduced. This equation gives calculated vapour pressures which are in good agreement with those found. J. F. S.

The 25°-Isotherms of the Systems Magnesium Nitrate-Sodium Nitrate-Water and Magnesium Sulphate-Magnesium Nitrate-Water. DOUGLAS NORMAN JACKMAN and AGNES BROWNE (*T.*, 1922, **121**, 694—697).

Heat of Formation of Compounds of Metallic Magnesium with Metallic Zinc, Cadmium, Aluminium, and Calcium. WILHELM BILTZ and GEORG HOHORST (*Z. anorg. Chem.*, 1921, **121**, 1—21).—The heat of formation of the intermetallic compounds of magnesium with zinc, cadmium, aluminium, and calcium has been calculated from a series of determinations of the heat of solution of the individual metals and the compounds in hydrochloric acid of various concentrations. The metals were used in the form of fine powders or thin foil, and the solution was hastened by the use of small quantities (about 8 mg.) of a platinum catalyst. The following values of the molecular heat of solution in $\text{HCl}, 8\text{H}_2\text{O}$ at 18° are recorded: magnesium, 113.1 Cal.; zinc, 33.55 Cal.; aluminium, 125.1 Cal.; calcium, 130.1 Cal.; cadmium, 19.77 Cal.; MgZn_2 , 167.6 Cal.; MgCd , 123.7 Cal.; Mg_4Al_3 , 779 Cal.; and Mg_4Ca_3 , 800 Cal. The difference between the sum of the heats of solution of the constituent metals and that of the compounds gives the heat of formation of the compounds from the solid metals thus: $\text{Mg} + 2\text{Zn} = \text{MgZn}_2 + 12.6$ Cal.; $\text{Mg} + \text{Cd} = \text{MgCd} + 9.2$ Cal.; $4\text{Mg} + 3\text{Al} = \text{Mg}_4\text{Al}_3 + 49$ Cal.; and $4\text{Mg} + 3\text{Ca} = \text{Mg}_4\text{Ca}_3 + 43$ Cal. The densities of the compounds and that of calcium have been determined and the following values of d_4^{25} obtained, MgZn_2 , 5.126; MgCd , 5.383; Mg_4Al_3 , 2.151; Mg_4Ca_3 , 1.701; Ca, 1.542. The molecular volumes are calculated and compared with the sum of the atomic volumes, and it is shown that in all cases the compound is formed with a contraction in volume. J. F. S.

Heat of Reaction of Oxygen with Hæmoglobin. EDWARD F. ADOLPH and LAWRENCE J. HENDERSON (*J. Biol. Chem.*, 1922, **50**, 463—490).—Estimations of the heats of reaction of oxygen and carbon monoxide with hæmoglobin at 22° gave average values of 6,950 and 14,700 cal., respectively. The individual values, however, showed large variations, the extreme values for oxygen being 1,500 and 10,900 cal. and those for carbon monoxide 8,300 and 25,200 cal., although the same apparatus gave consistent results when used for inorganic reactions. The authors conclude from their own results and from those of others that K and Q for oxyhæmoglobin are not related by the van't Hoff isochore, and discuss various factors which may account for this. E. S.

Adhesion Forces in Solutions. II. Adhesion Series. NIKOLAI SCHILOV, NAD. BULYGINA, NIK. ZEREVTINOV, LIDIE LEPIN, OLGA MICHAJLOVA, MICH. DUBININ, SERG. WOSNESSENSKI, AGNESS IVANITZKAJA, LIDIE ORLOVA, and JOH. SASLAVSKY (*Z. physikal. Chem.*, 1922, **100**, 425—462; cf. A., 1920, ii, 591).—In an earlier paper (*loc. cit.*) it was shown that the adsorption of a series of salts of the same anion by charcoal increases with increasing valency of the kation; such a series is termed "convalent." A series of acids under the same treatment gave decreased adsorption with increasing valency of the anion; such a series is termed "antivalent." A series where the univalent ions come at one end, the bivalent at the other, and the tervalent between or irregu-

larly among the uni- and bi-valent ions is termed a mixed series. A number of adsorption experiments have been carried out on the adsorption of electrolytes by alumina, ferric oxide, manganese dioxide, peat, wool, and finely divided metals. The results show in the case of alumina that the adsorption series for acids and for copper salts are both convalent, with ferric oxide and acids the adsorption series is also convalent; manganese dioxide, acids, and copper salts all give convalent series. Peat gives an antivalent adsorption series with acids. In the case of finely divided metals, the adsorption of copper salts by tungsten and antimony is antivalent but by nickel salts convalent. The work with finely-divided metals was rendered difficult owing to chemical action occurring between the two phases; it is shown that an adsorption always precedes a chemical action. Thus iron powder was kept in contact with silver nitrate and it was found that for one hundred and fifty minutes silver was removed from solution to the extent of 3—8% without iron passing into solution, but once the chemical action commenced it proceeded very rapidly to completion. The adsorption of a series of chlorides by wool is convalent. Coagulation series have been investigated for the action of electrolytes on mastic sols, colloidal ferric hydroxide, arsenic sulphide, antimony sulphide, manganese dioxide, and for suspensions of charcoal in alkalis, and in tannic acid, and iron oxide in *N*/50-hydrochloric acid. The coagulation series of mastic sols is antivalent for acids and for copper salts, but for sulphates it is convalent, although the hydrogen-ion falls among the multivalent ions. The nitrates and chlorides both formed mixed series. With positively charged ferric hydroxide sols, the anion series is convalent, in the case of the acids, copper salts, and potassium salts, whilst the kations all formed mixed series. Arsenic sulphide and antimony sulphide both give an antivalent series for the anions and a convalent series for the kations, whilst manganese dioxide gives an antivalent series for anions and a mixed series for kations. The electrode potential of metals in acids has been divided into similar series, and from the measurements of Ostwald (*ibid.*, 1887, i, 583) it is shown that zinc, cadmium, tin, lead, iron, and antimony give convalent series, mercury and copper antivalent series, and silver and bismuth mixed series. From the work of other investigators it is shown that the influence of anions on the solubility, compressibility of solutions, and the abnormal elevation of the boiling point is convalent, whilst the influence of anions in acid solution on the rate of hydrolysis of esters is antivalent, but in alkaline solution convalent. A calculation of the molecular contraction in the formation of solid chlorides and sulphates gives rise in both cases to convalent series. The experimental results are discussed, and it is shown that the series is due to the processes being controlled by molecular forces rather than by ionic forces. Such molecular forces are termed "cohesion forces" where similar molecules are concerned, and "adhesion forces" where dissimilar molecules participate.

J. F. S.

Validity of the Laws of the Internal Friction of Liquids. W. HERZ (*Z. anorg. Chem.*, 1921, **121**, 95—98).—A theoretical paper in which the author examines the formulæ put forward by Bingham and Harrison (A., 1918, ii, 382) and Batschinski (A., 1913, ii, 928) to represent the fluidity of the benzene haloids. Extrapolating to the absolute zero leads to negative values for the fluidity, and from this the author concludes that the fluidity is not a strict linear function of either the temperature or the specific volume.
J. F. S.

The Viscosities of some Hydrocarbons. G. CHAVANNE and (Mlle) H. VAN RISSEGHEN (*Bull. Soc. chim. Belg.*, 1922, **31**, 87—94; cf. Bartoli and Stracciati, A., 1886, 215; also Thorpe and Rodger, T., 1897, 360).—Viscosity measurements of some hydrocarbons lead to the following conclusions: Viscosity increases directly with the number of side chains, for example, 2:2:3:3-tetramethylbutane is a solid; high viscosity is thus conditioned by the presence of tertiary butyl groups, which also determine high melting and low boiling points. Cyclic compounds have greater viscosity than the corresponding aliphatic compounds, but in this case the introduction of a methyl group diminishes viscosity; this is also the case with polymethylenes, the viscosities of which are considerably greater than those of the corresponding aromatic substances.
H. J. E.

Thermal Evolution of Gases Absorbed by Charcoals and Carbonised Lignites. STUART McLEAN (*Trans. Roy. Soc. Canada*, 1921, **15**, iii, 73—84).—An investigation of the heat developed when air, oxygen, nitrogen, or carbon dioxide is absorbed by wood or cocoanut charcoal, or lignite carbonised at various temperatures between 350° and 550°. Oxygen develops the greatest amount of heat per unit volume of gas adsorbed. During the adsorption, both carbon dioxide and carbon monoxide are formed. The greatest evolution of heat per unit mass of adsorbent occurs with carbon dioxide. The thermal effect for air is much smaller than for oxygen, and less carbon dioxide and carbon monoxide are produced. In the case of oxygen adsorption, the amount of gas adsorbed diminishes until a constant value is attained on repeating the experiment. The same holds for the heat developed per unit mass of adsorbent. The heat developed by the adsorption of carbon dioxide is not accounted for by the latent heat of evaporation. The coarse kinds of charcoal adsorb more oxygen and form carbon dioxide more readily than other kinds. J. S. G. T.

Influence of the Hydrogen-ion Concentration on the Permeability of Dead Membranes, on Adsorption by Protein Sols, and on the Metabolism of Cells and Tissues. ALBRECHT BETHE (*Biochem. Z.*, 1922, **127**, 18—33).—The diffusion of acid dyes through parchment is accelerated in acid solution and depressed in alkaline solution, whilst the reverse is true for basic dyes. If the dyes are allowed to diffuse into a protein solution, for instance, milk, gelatin, or serum, there is preferential distribution of the

dye in the protein solution if the acid dye is dissolved in acid solution and the basic dye in alkaline solution. The process can then be reversed by addition of alkali or acid. The analogy is extended to vital staining, where the hydrogen-ion concentration is assumed to play an essential rôle. H. K.

Substantive Cotton Dyeing. RUDOLF AUERBACH (*Kolloid Z.*, 1922, **30**, 166—168).—The influence of various salts on the dyeing of cotton by substantive dyes was investigated. In each case an optimum concentration of the salt was found, and this was almost inversely proportional to its precipitating power on the colloid systems. The amount of dye taken up by the threads also decreases with increasing precipitating power of the salt. The strong mineral acids do not follow the same rule, no optimum concentration being found. W. T.

Pressure of Oxygen in Equilibrium with Silver Oxide. FREDERICK G. KEYES and H. HARA (*J. Amer. Chem. Soc.*, 1922, **44**, 479—485).—The equilibrium pressure of oxygen over silver and silver oxide has been measured up to about 800°; the present results confirm and extend the previously published results of Lewis (*Z. physikal. Chem.*, 1906, **55**, 449). The following equation, ordinarily derived by the use of the perfect gas law and by assuming the heat constant, is found empirically to represent the data exactly: $\log p = -2859/T + 6.2853$, where the pressure is in atmospheres, and the temperature in degrees absolute. The Nernst heat theorem as given by Pollitzer to fit the data of Lewis entirely fails to represent the present data. Neglecting only the difference in the coefficient of expansion between silver and silver oxide, the following equation is derived from the Clausius equation for the external heat of the reaction, in calories per molecule of oxygen, $Q = 6582(v - 20.7)p/T$, where v calculated from the equation of state of oxygen is given in c.c./mol. The value for the internal heat at 25°, calculated with the aid of Kopp's rule, is 12642 cal., in agreement with the mean of the measurements and computations (12640) considered by Lewis. The internal heats, although they pass through a minimum at about 400—500°, increase again with rising temperature. The analogy between this chemical reaction and a simple evaporation, therefore, breaks down, since no sign is shown of a critical point, with the heat equal to zero, although Δv appears to be diminishing progressively. J. F. S.

A Simple Dialyser. A. GUTBIER and A. MAYER (*Z. anorg. Chem.*, 1922, **121**, 215—216).—A simple and efficient dialyser can be constructed as follows. A polished ring of wood, bone, or horn is grooved on the outer side, a piece of parchment paper is well soaked in distilled water and then folded over a test-tube or beaker (according to the size of dialyser required) to form a kind of bag, the glass vessel is then removed and the parchment bag tied around the ring. If necessary (for sensitive systems), in place of the ring a disk of the same material with a groove along its edge and a hole in the plate to fill and empty the bag can be used. W. T.

Temperature Dependence of the Solubility, the Activity, and Osmotic Coefficients of Salts. J. N. BRÖNSTED (*Z. physikal. Chem.*, 1922, **100**, 139—150).—Formulæ are developed to represent the dependence of the activity and osmotic coefficients on the temperature. These have the form $\delta \log_e f / \delta T = \alpha c / RT^2$ and $\delta \phi / \delta T = \alpha c / 2RT^2$, in which f is the activity coefficient and ϕ the osmotic coefficient, c the concentration, and $\alpha = \delta U_1 / \delta c$. In the case of potassium chloride in 0.1*N*-potassium chloride the value $\delta \log_e f / \delta T$ is calculated to 0.000092 and $\delta \phi / \delta T = 0.000046$. Further formulæ are developed for the dependence on temperature of the solubility of sparingly soluble salts in pure water and in salt solutions. These formulæ have been verified by means of solubility determinations of β -cobalt croceonitrate in water, *N*/10-sodium nitrate, and potassium nitrate at various temperatures. J. F. S.

Physical Chemistry of Lipoids. Diffusion of Methylene-blue through Organic Solvents. S. LOEWE (*Biochem. Z.*, 1922, **127**, 231—240; cf. A., 1912, ii, 741, 742).—The author has examined qualitatively the distribution and diffusion of methylene-blue from a gelatin gel in one limb of an inverted Y-shaped apparatus through a supernatant organic solvent (carbon tetrachloride, benzene, toluene, ether), containing in solution one of a great variety of substances belonging to the groups of plant resins, wool-fat and its products, and various lipoids, into a gelatin gel in the other limb. With a few exceptions, the amount of methylene-blue taken up from the gelatin gel by the organic solvent and its dissolved substance and by the pure gelatin gel is small. H. K.

Electrical Charges of Colloidal Particles and Anomalous Osmosis. JACQUES LOEB (*J. Gen. Physiol.*, 1922, **4**, 463—486).—In a system consisting of water and salt solution separated by a collodion-gelatin membrane, the whole being on the acid side of the isoelectric point of the membrane, the transport curve of water to salt solution shows a rise up to a concentration of the salt of $M/32$, then a fall up to a concentration of $M/4$, and subsequently a continuous rise. The preliminary rise is the greater the greater the valency of the kation. On the alkaline side of the isoelectric point, curves of a similar nature are obtained, but in this case it is the valency of the anion which influences the preliminary rise.

The fluctuations in those curves ("anomalous osmosis") are explained as due to the effect of the salts on the potential difference across the membrane and on the potential difference between the solution in the pores of the membrane and the membrane itself.

Both these effects should disappear when the whole system is at the isoelectric point of the membrane; and it is, in fact, found, under these conditions, that solutions of salts composed of uni- and bi-valent ions behave like sucrose solutions. Salts containing ter- or quadri-valent kations or quadrivalent anions still behave anomalously, probably owing to the fact that the isoelectric gelatin forms loose compounds with the multivalent ions, thus setting up a potential difference between itself and the solution. C. R. H.

An Optical Method for the Determination of the Reciprocal Solubility of Slightly Miscible Liquids. C. CHÉNEVEAU (*Compt. rend.*, 1922, **174**, 815—817).—The process employed consists in using the method of autocollimation, whilst making it differential. The refractive indices of the liquid considered as the solvent and of the solution are measured in a specially constructed prism divided into two cells. A formula is given by means of which, from the readings taken, it is possible to calculate the solubility of the one liquid in the other. The results obtained are in very close agreement with those obtained by gravimetric methods.

W. G.

Application of the Electron Theory of Chemistry to Solids. (SIR) J. J. THOMSON (*Phil. Mag.*, 1922, [vi], **43**, 721—757; cf. A., 1921, ii, 252).—The part played by electrons in determining the structure of solids is considered. Each kind of atom is associated with a definite number of electrons with which it holds other atoms in chemical combination. The simplest case is that of a chemical element. In the crystalline state each unit cell will contain one atom and a definite number of electrons; one for a univalent atom, two for a bivalent atom, and so on. The arrangement of the electrons in the unit cell determines the shape of the cell and the crystalline structure. Possible unit cells are limited to (1) Parallelepiped; (2) Hexagonal prisms; (3) Rhombic Dodecahedra; (4) Cubo-octahedra.

The univalent element gives the simplest type of cell. The atom is situated at the centre of a parallelepipedon (or cube) with an electron at each corner and each electron held in common by the atoms in eight such parallelepiped. For a bivalent element the electrons may be arranged at the corners of an hexagonal prism or in cubes with additional electrons at the centres of one set of parallel faces. The cells of tervalent elements may be hexagonal prisms with an electron at the centre of each end, cubes with electrons at the centres of two sets of parallel faces, or as rhombic dodecahedra. Similarly, the four electrons of quadrivalent elements may be arranged as in the face-centred cube or as in the hexagonal prism with two electrons along the axis at equal distances from the centre, and so on.

The symmetries represented by the triclinic, monoclinic, rhombic, and tetragonal systems in crystallography can be obtained if an assemblage of regular cells be strained homogeneously in any way without fracture. The cells would still maintain an atom in each cell and the original number of electrons.

Making the assumptions with regard to the forces between the atoms and electrons given in the previous paper, the stability of the above electronic arrangements and their effect on some physical properties is discussed. The values for the bulk modulus, the critical frequency, and the dielectric constant calculated for elements of different valencies, agree closely with those found by experiment. Expressions are given for the potential energy per unit volume of solid, the compressibility, the latent heat of fusion, etc., for a

number of types of unit cells. It is shown that the potential energy of an atom on the surface will be greater than that in the interior of the crystal and this excess will be proportional to the surface tension.

The constitution of salts may be inferred from their physical properties. From the magnitude of the compressibility of potassium chloride and sodium chloride it is deduced that the chlorine and sodium or potassium atoms are present as singly positively charged units with one electron per unit cell. The other six electrons are arranged as a regular octahedron about the chlorine atom at a distance considerably smaller than the length of the cube. The number of unit cells occupied by a chemical molecule and the presence of chemical groups (for example, CN or NH_4) in crystals can also be indicated by compressibility measurements. It is shown that Richard's value for the compressibility of the diamond can be explained on the assumption that the carbon atoms are arranged in groups in the crystal. The stability of chains of carbon atoms is discussed. A long chain of carbon atoms is unstable. A stable arrangement for chains of CH_2 is possible if this group be regarded as equivalent to an atom of a bivalent element with two disposable electrons.

W. E. G.

Effect of Electrolytes on the Constitution of Soap Solutions, as Deduced from Electromotive Force. CYRIL SEBASTIAN SALMON (T., 1922, 121, 711—715).

Hysteresis Phenomena and Coagulation of Sols with Ultramicros of Rod-like Structure, in particular Vanadium Pentoxide compared with Fibrin Sols. G. WIEGNER, J. MAGASANIK, and H. GESSNER (*Kolloid Z.*, 1922, 30, 145—165).—Vanadium pentoxide sols contain ultramicros of elongated rod-like structures similar to fibrin sols; in course of time these ultramicros grow, this being accelerated by an increase in concentration of the sol. The tendency to coagulate is much increased after this growth, and can be brought about by filter-paper, boles, carbon, silk threads, and silicic acid and gelatin gels. This gelatinisation is favoured or perhaps conditioned by vanadyl salts formed by the reduction of the vanadium pentoxide. The serum obtained from the gel coagulates more sol; this is accounted for by its high content of vanadyl salts. Salts (contained in filter-paper) favour the reduction to vanadyl salts and therefore accelerate the coagulation. Vanadic acid stabilises the sol. Dilution of sol and consequently decrease of concentration of the active vanadic acid ions brings about gelatinisation. These results show a close analogy to fibrin sols. Quantitative investigations are now being carried out.

W. T.

The Protective and Flocculating Action of Hydrophilic Colloids and Hydrophobic Sols. H. FREUNDLICH and E. LOENING (*Festschrift Kaiser Wilhelm Ges. Förderung Wiss. Zehnjährigen Jubiläum*, 1921, 82—89).—It was found by Brossa and Freundlich (A., 1915, ii, 241) that the flocculating value of electro-

lytes for ferric oxide sol decreased with increase in the percentage of albumin present. In addition Gann (A., 1917, ii, 21) found that egg-white had a coagulating action on acidic gold sol in the absence of electrolytes. An attempt is made to correlate these facts. By experiments with both gold and silver sols it was shown that the sensitisation of a hydrophobic sol by a hydrophilic colloid is merely a coagulation which is too slight to become immediately observable. It can be detected only by the fact that when the sol is thus sensitised, smaller amounts of electrolytes are required for flocculation. Measurements of the flocculation value of electrolytes showed that with increasing gelatin content the value diminished to a low figure. In this way the sensitisation of the ferric oxide sol by albumin is not essentially a different phenomenon from the coagulation of gold sol by egg-white. The transition from coagulating to protective action observed by Gann is a general phenomenon. It probably depends on the fact that the oppositely charged hydrophilic sol in low concentration coagulates the particles of hydrophobic sol, whereas in higher concentration the former actually envelops and thus protects them. The properties of the hydrophobic sol are thus completely masked. Silver sol protected by gelatin has the same charge as pure silver sol and is therefore not reversed in charge by addition of gelatin. The action in this case is considered due to the amphoteric nature of the protective hydrophilic colloid. CHEMICAL ABSTRACTS.

Capillary-electric Phenomena in Lyophile Sols. H. R. KRUYT and H. G. DE JONG (*Z. physikal. Chem.*, 1922, **100**, 250—265).—The influence of the electrolytes potassium chloride, barium chloride, potassium sulphate, potassium thiocyanate, potassium ferriyanide, sodium chloride, lithium chloride, strontium chloride, magnesium sulphate, cadmium sulphate, and lanthanum nitrate on the viscosity of agar sols of various concentrations has been measured at 50°. It is shown that above the temperature at which gelatinisation occurs (40°) agar sols follow the Poiseuille law exactly. Agar sols exhibit the quasi-viscous effect noted by Smoluchowski, and the particles are discharged by kations at concentrations corresponding with the valency of the added kation. The electrical behaviour of the agar sol is very similar to that of a suspensoid, and the electrical charge has a capillary-electric character. An emulsoid sol possesses two stabilising factors: the electric charge and the hydration, both of which must be removed before a coagulation can be effected. If the charge only is removed, a lyophile sol remains, but if the hydration is removed a suspensoid remains. Salting-out is a combined discharge and dehydration. Albuminous substances do not form ion-disperse solutions, but colloid disperse sols. The amino-acidic character exhibits itself only in the molecules which form the boundary layer of the particles and in those which form the double layer. J. F. S.

Convertibility of Chemical Energy and the Conception of Affinity. R. PLANK (*Z. physikal. Chem.*, 1922, **100**, 372—392).—A mathematical paper in which the maximum work of reversible

reactions is considered and from the consideration it is shown that the conception of affinity at present adopted is unsatisfactory. Suggestions are made for changing the present conception.

J. F. S.

The Le Chatelier-Braun Principle. CARL BENEDICKS (*Z. physikal. Chem.*, 1922, **100**, 42—51).—A discussion of the Le Chatelier-Braun theorem as formulated by Chwolson (*Lehrb. d. Physik*, 1905, Braunschweig). A number of cases are brought forward, chiefly metallographic, for which the theorem does not hold, and it is shown that the theorem is not generally applicable. It is always true for a system in equilibrium, and is to be regarded as a general criterion of stable equilibria, for only when the theorem holds can there be a stable equilibrium. At extremely high temperatures and pressures, the theorem holds more often.

J. F. S.

An Explanation of Liesegang's Rings. S. C. BRADFORD (*Science*, 1921, **54**, 463—464; cf. *A.*, 1916, ii, 474; 1917, ii, 366; 1920, ii, 235, 593).—Objection is raised to the views of McGuigan (*ibid.*, 1921, **54**, 78), and particularly to the statement that the chromate of itself is unable to diffuse in the gelatin. Further, bands of lead chromate can be obtained in gelatin under suitably chosen conditions. It is maintained that the attractive force described by McGuigan is that of adsorption.

A. A. E.

Influence of Intensive Drying on Internal Change. A. SMITS (*Z. physikal. Chem.*, 1922, **100**, 477—478).—The author directs attention to the experiments of Baker (*T.*, 1912, **51**, 2339) on the intensive drying of nitrous anhydride and nitrogen tetroxide. He points out that the large change in boiling point brought about in these substances by excessive drying probably indicates that the internal change has been stopped and that fractional distillation of such an extremely dry unary system will probably result in the separation of the pseudo-components [cf. also Baker, *T.*, 1922, **121**, 568].

J. F. S.

Change of Properties of Substances on Drying. HERBERT BRERETON BAKER (*T.*, 1922, **121**, 568—574).

The Dushman Equation for the Velocity of a Unimolecular Reaction. W. E. GARNER (*Nature*, 1921, **108**, 211).—It is suggested that the term ν in Dushman's equation (*A.*, 1921, ii, 315) $\kappa = \nu e^{(-N h \nu)/(RT)}$ is a frequency characteristic of some degree of freedom in the decomposing molecule, and is not related to the frequencies of the activating radiation. The "period of existence" of the molecule (the time corresponding with one molecular vibration) will then be $1/\nu$. It is argued, with the support of Tolman's data (*A.*, 1921, ii, 248), that the exact agreement obtained by Dushman for observed and calculated values of κ in the case of phosphine is accidental.

A. A. E.

Ignition Point of Detonating Gas [Hydrogen and Oxygen]. ALEXANDER MITSCHERLICH (*Z. anorg. Chem.*, 1921, **121**, 53—66).—The ignition temperature of detonating gas has been determined for

a variety of conditions in porcelain and glass tubes. The conditions which were varied, included the rate of flow of the gas, the diameter of the tube, the pressure and the dilution of the gas. It is shown that the ignition temperature of detonating gas at 150 mm. is highly dependent on the rate of flow in the sense that it increases with decreasing velocity, but beyond a given velocity further increase has but a slight influence on the temperature of ignition. The following values illustrate this fact, $v=280$, $t=592^\circ$; $v=187$, $t=592^\circ$; $v=130$, $t=593^\circ$; $v=93$, $t=594^\circ$; $v=37$, $t=601^\circ$, where v is the number of c.c. passing a cross-section of 1 sq. cm. per minute. When the value of v is kept constant, it is shown that the ignition temperature increases with increasing pressure, thus, $p=150$ mm., $t=592^\circ$; $p=200$, $t=607.5^\circ$; $p=250$, $t=622^\circ$; $p=300$, $t=630.5^\circ$; $p=400$, $t=644^\circ$; $p=500$, $t=651.5^\circ$; $p=600$, $t=659.5^\circ$; $p=650$, $t=663.0^\circ$. The diameter of the porcelain or glass tube is without influence on the explosion temperature for the diameters 3.6, 5.5, 9.5, and 11 mm., but this is not true for narrow tubes; thus with tubes less than 0.5 mm. diameter no definite ignition temperature could be observed.

J. F. S.

Chemical Kinetics of Perchloric Acid and its Salts.

G. BREDIG and J. MICHEL (*Z. physikal. Chem.*, 1922, **100**, 124—138).—The velocity of reaction in the reduction of aqueous perchloric acid by tervalent titanium, tervalent molybdenum, and bivalent chromium salts in hydrochloric acid and sulphuric acid solutions has been measured for various concentrations at 40° . In the case of titanium, which is most completely examined, the velocity is proportional to the first power of the concentration of the tervalent titanium, the perchloric acid, or the perchlorate. The concentration of sulphuric acid or hydrochloric acid has only very slight influence on the velocity in dilute solutions of the reactants. The influence of the acids increases from a definite acid concentration (4.45*N*-sulphuric acid, 4.69*N*-hydrochloric acid) linearly with the increasing concentration of the acids. The form of the kinetic equation is of the first order and of much lower order than is demanded by the equation representing the reaction, namely, $4\text{Ti}(\text{SO}_4)_3 + 4\text{H}_2\text{SO}_4 + \text{HClO}_4 = 8\text{Ti}(\text{SO}_4)_2 + 4\text{H}_2\text{O} + \text{HCl}$. As in most similar cases, an intermediate reaction of a lower order must be assumed, the nature of which has not been ascertained. The reaction velocity of the titanium reaction increases three times for an increase in temperature of 10° . In the present experiments, the times required for an equal amount of reduction of perchloric acid in the presence of the same excess of sulphuric and hydrochloric acids at the same temperature are in the ratio: $\text{Ti}^{\text{III}} : \text{Mo}^{\text{III}}$ (olive-green) : $\text{Cr}^{\text{II}} : \text{Mo}^{\text{III}}$ (orange) = 1 : 18 : 1300 : 40000. J. F. S.

Kinetic Study of Alkaline Solutions of Iodine. O. LIÉVIN

(*Compt. rend.*, 1922, **174**, 868—870).—In alkaline medium iodine is converted into iodate by processes which differ according to the degree of alkalinity. The alkali, the concentration, and the iodide formed all influence the reaction. As the amount of alkali hydroxide used for a given weight of iodine increases the free iodine

disappears more rapidly but the hypiodite disappears more slowly. The presence of the iodide accelerates the reaction. Thus the iodide is a product of the reaction which it catalyses and the sodium hydroxide retards a reaction in which it is used up. Dilution causes a diminution in the velocity of the reaction. If sodium carbonate or the tribasic phosphate are used as the alkali then the reaction is accelerated by the addition of alkali, in so far as the formation of iodate is concerned. Further with sodium carbonate as the alkali, dilution of the system causes an increase in the velocity of reaction.

W. G.

Velocity of Decomposition of Silver Permanganate. A. SIEVERTS and H. THEBERATH (*Z. physikal. Chem.*, 1922, **100**, 463—475).—The thermal decomposition of silver permanganate takes place according to the equation $\text{AgMnO}_4 = \text{AgMnO}_3 + \text{O}$, and in the presence of water the residue combines with half a molecule of water. The process of the decomposition at 30° may be approximately expressed by the equation for an autocatalytically accelerated reaction, $dx/dt = Kx(a-x)$, where a is the initial amount of silver permanganate and $(a-x)$ the amount of silver permanganate undecomposed at time t . The decomposition product, the nature of which has not been established, accelerates the reaction proportionally to its mass. The constants of the decomposition velocity of the various preparations are different. The presence of water has a very strong influence on this reaction. Dry silver permanganate decomposes very slowly even at 50° , but small traces of water increase the decomposition velocity very much, whilst larger additions of water have little further influence. The addition of powdered pumice and the decomposition product of the reaction changes only the initial velocity. Temperature has a very marked influence on the reaction. At 0° , even in the presence of water and the decomposition product, the decomposition does not take place. At 50° , the decomposition process is no longer represented by the same equation as at 30° ; the tx curves for 50° are characterised by a long, almost straight line. Comparison with the experiments at 30° shows that an increase of 20° in the temperature of reaction causes the initial velocity to increase from 12 to 20 times, the mean velocity between 19% and 38% decomposition, 6.1—7.6 times, and between 38% and 57% decomposition, 3.4—4.3 times.

J. F. S.

Separation of Halogens from Organic Compounds. H. VON EULER and A. FAHLANDER (*Z. physikal. Chem.*, 1922, **100**, 171—181).—Determinations have been made of the velocity and extent of the separation of halogens from the sodium salts of chloroacetic, bromoacetic, and bromopropionic acids in water to which finely-divided silver, silver oxide, copper oxide, lead oxide, and platinum sponge have been added. The results show that the hydrolysis of a 0.1*N*-solution of sodium chloroacetate is not noticeably accelerated either at 75° or 100° by the presence of finely-divided silver of 1μ diameter in an hour. At 100° , the hydrolysis of the chloroacetate solution amounted to 8.8% in ninety minutes, but in the

presence of 5 grams of copper oxide in 25 c.c. of the 0.1*N*-solution it amounted to 9.6% in the same time. At 75°, in five hours 2.6% of the same solution was hydrolysed, but with 1 gram of finely-divided silver there was no increase in the amount decomposed, with 2 grams of silver oxide the amount was 7.2%, and with 4 grams of copper oxide, 3.8%, all in 25 c.c. of *N*/10-solution. It is shown that the accelerating action cannot be attributed to the amount of the oxides dissolved. In the case of the most concentrated bromoacetate solution employed, the velocity increases proportionally with the amount of silver oxide added, but more slowly with more dilute solutions. The velocity of bromine separation is roughly one hundredth of that occasioned by the presence of the same amount of silver oxide (cf. Donnan, T., 1904, **85**, 555; 1910, **97**, 1882). J. F. S.

Reduction of Nitro-compounds by Stannous Chloride. III.

HEINRICH GOLDSCHMIDT, EINAR STORM, and ODD HASSEL (*Z. physikal. Chem.*, 1922, **100**, 197—207; cf. A., 1904, ii, 607; 1906, i, 734).—A number of experiments are described on the reduction of *m*-nitroaniline, *m*-nitrobenzenesulphonic acid, *o*-nitrobenzenesulphonic acid, and *o*-nitroaniline by stannous chloride and bromide in the presence of hydrochloric, hydrobromic, sulphuric, and benzenesulphonic acids and lithium, ammonium, potassium, calcium, and cadmium chlorides. It is shown that in the reduction by stannous chloride and hydrochloric acid a portion of the acid may be replaced by a metallic chloride without any reduction of the velocity of reaction ensuing. Cadmium chloride behaves differently from the other metallic chlorides, and reduces the velocity constant from 10.35 to 5.14. In the reduction with stannous bromide and hydrobromic acid, a portion of the hydrobromic acid may be replaced by metallic bromides without reduction of the velocity of reaction, but cadmium bromide brings a marked reduction in the velocity; here the constant is reduced from 33.37 to 8.47, an action which is attributed to the formation of complex salts. The addition of strong acids such as sulphuric and benzenesulphonic acids has but little action on the velocity of reaction. Reduction with stannous chloride and sulphuric acid in the absence of hydrochloric acid proceeds very slowly. Thus, 0.1*N*-stannous chloride and *N*-hydrochloric acid has a velocity constant 9.96 with 0.033*N*-*m*-nitroaniline, but if the hydrochloric acid is entirely replaced by *N*-sulphuric acid, the value falls to 0.44. J. F. S.

The Influence of Temperature and Constitution on the Decomposition Velocity of Substituted Malonic Acid. HEINRICH JAKUBOWICZ (*Z. anorg. Chem.*, 1922, **121**, 113—127).—The temperature-velocity curves are given for malonic acid and some of its derivatives up to 110°. For malonic acid, the decomposition becomes measurable at 66°, and the temperature coefficient was found to be 2—3 for 10° increase. The temperature-velocity curves for diethyl- and diallyl-malonic acids run parallel with those of malonic acid. The introduction of a hydroxyl group slightly increases the velocity of decomposition. The monochloro-acid

decomposes much more rapidly and occupies a position between the allyl and phenyl derivatives. The introduction of another chlorine atom reduces the velocity considerably; that is, the more symmetrical compound is the more stable. The dichloro-derivative decomposes more rapidly than its dibromo-analogue. The values of K at 100° are phenylmalonic acid 0.1970, chloromalonic acid 0.1855, allylmalonic acid 0.1321, hydroxymalonic acid 0.0820, malonic acid 0.0755, methylmalonic acid 0.0598, dichloromalonic acid 0.0585, dibromomalonic acid 0.0224. W. T.

Slow Hydrolysis of Salts. A. TIAN (*J. Chim. physique*, 1921, **19**, 190—216; cf. A., 1921, ii, 439).—The author discusses the hypothesis put forward by Wagner (A., 1913, ii, 200, 765) to explain the slow hydrolysis of salts and finds it at variance with facts, and puts forward a new hypothesis, which has the following form. The slow hydrolysis of salts is always preceded by a normal hydrolysis, limited by the reverse reaction which always occurs between ions and is extremely rapid. As soon as the solubility product of one of the substances (acid or base) produced by the hydrolysis has been reached, a new phase appears and at the same time a new cause of retrogradation of the hydrolysis. This supplementary retrogradation is due to a reaction between the two phases (colloid and aqueous solution) present; it is realised with a velocity which increases with the surface of contact. This cause of retrogradation is very great at first, when the colloidal particles are very small, but as a consequence of their union the surface of the particles decreases and with it the speed of the supplementary retrogradation, and from this point the hydrolysis increases. The progression of the hydrolysis is therefore as slow as the evolution of the colloid. This hypothesis has been tested by means of conductivity measurements on solutions of ferric chloride in the presence of silica gels and gelose, and found to be in keeping with the experimental data.

J. F. S.

Catalysis. XIII. Temperature Coefficient of Catalysed and Non-catalysed Reactions. R. M. PURKAYOSTHA and N. R. DHAR (*Z. anorg. Chem.*, 1922, **121**, 156—166).—The reaction $\text{H}_2\text{C}_2\text{O}_4 + \text{KMnO}_4 + \text{MnSO}_4 + \text{H}_2\text{SO}_4$ has a temperature coefficient 2.96 between 10° and 20° , almost the same value as that found by Dhar for a similar reaction with chromic acid as the oxidising agent (T., 1917, **111**, 727). The reaction with permanganate is unimolecular with respect to the oxidising agent; in the case of chromic acid reaction the rate was found to be independent of the concentration of the oxidising agent. The reaction between mercuric chloride and phosphorous acid was found to be bimolecular for phosphorous acid and semimolecular for mercuric chloride. The temperature coefficient is 3.4 at 30 – 40° and 3.26 at 40 – 50° . The photochemical reactions $\text{Na}_2\text{SO}_3 + \text{O} = \text{Na}_2\text{SO}_4$ and $\text{NaClO} = \text{NaCl} + \text{O}$ are discussed and are regarded as semimolecular reactions. All the reactions with a high temperature coefficient were found to be sensitive to light rays. W. T.

Peculiar Catalytic Action in Chemical Synthesis by Glow Discharge. FRITZ PANETH (*Z. physikal. Chem.*, 1922, **100**, 367—371).—When a glow discharge is allowed to pass through a tube containing tin electrodes and a low pressure of hydrogen, there is no combination between the hydrogen and the tin, but if the hydrogen contains a small amount of methane, tin tetrahydride is the product. The action is explained by the assumption that the excited hydrogen atom contains a higher quantic electron, and when this comes in contact with an atom of tin, vapour combination occurs. The present action is discussed in connexion with the formation of active nitrogen and triatomic hydrogen.

J. F. S.

Reactions on Metallic Surfaces. OTTO RUFF (*Z. physikal. Chem.*, 1922, **100**, 419—424).—It is shown that metallic calcium when alloyed with more electro-positive metals such as strontium, barium, sodium, or potassium, or with calcium nitride, combines more readily with nitrogen than pure calcium. From this observation it is concluded that the heteropolar nature of a metallic surface favours the combination with a homopolar gas, and from this it is assumed that it acquires influence charges from the surface valencies of the metal which determine its position and behaviour towards the surface.

J. F. S.

The Structure of the Atom and the Physical and Chemical Properties of the Elements. NIELS BOHR (*Z. Physik*, 1922, **9**, 1—67).—An address delivered before the Physical and Chemical Societies of Copenhagen. A résumé is given of the recent work on the series spectra of the elements (cf. A., 1921, ii, 137) and their dependence on the orbit of the electrons within the atom. On the basis of his previous theories, the author develops an interpretation of the periodic table of the elements. In order to arrive at the relative stability of the electronic configurations in the atoms of the elements, the process of formation of an atom from the positive nucleus is followed step by step. Thus an element with an atomic number N is built up by the attachment of N successive electrons, each electron giving rise to a spectrum. The actual increase in charge of the nucleus, which occurs throughout the process, is taken into account. For the first two elements, hydrogen and helium, the knowledge of the spectra produced during the combining process is fairly exhaustive. For the remaining elements, the arc and spark spectra may be represented with good approximation by formulæ of the Rydberg type, $\nu = K/(n'' + \alpha_{k'})^2 - K/(n' + \alpha_k)^2$.

The orbit of the first electron is circular and the final stationary condition is attained when n and $k=1$. The combination of the second electron, as the spectrum of helium shows, takes place in two different ways. In the normal condition, the second electron follows the same type of path as the first, but in a different plane and in the metastable condition it moves in a 2_1 orbit ($n=2$ and $k=1$). The third electron, as in the lithium atom, is more loosely bound than the first two electrons and describes an eccentric orbit

2₁. For a small part of its path it approaches the nucleus to within a distance comparable with that of the innermost electrons. The fourth, fifth, and sixth electrons follow similar orbits. In the carbon atom, the configuration of the paths of the four loosely bound electrons possesses a tetrahedral symmetry. The seventh electron, as in the nitrogen atom, and the eighth, ninth, and tenth electrons follow circular paths of the type 2₂, lying within the region of the type 2₁ and being tightly bound. For neon, there will be two electrons with a path 1₁, four electrons with elliptical paths 2₁, and four electrons with a circular path 2₂. The paths of the electrons of this atom will possess a high degree of symmetry. In a similar manner, the stability of the electronic configurations of the elements with higher atomic numbers is considered. Particular attention is directed to sodium, where it is shown that the first terms of the *P* and *S* series spectra correspond with electronic orbits 3₁ and 3₂, so that the last bound electron is less tightly held than the last electron in the lithium atom. With the beginning of the fourth period orbits of the type 4₁ appear, but these are comparatively unstable, the outer electron of potassium being very loosely held—being only twice as fast as the corresponding 3₃ orbit. In the case of scandium and the elements with higher atomic numbers, the 3₃ orbits become more stable, and unsymmetrical electronic arrangements are produced which are accompanied by the appearance of colour, of paramagnetism, variable valency, and an increase in the complexity of the spectra. Throughout the first long period these irregularities occur, but when there are six each of electrons in the 3₁, 3₂, and 3₃ orbits the electronic configuration again becomes symmetrical. Thus the spectra of copper becomes less complex than that of iron, and at the end of the period is found the element krypton with a very symmetrical electronic arrangement. Colour is explained as due to the transference of an electron from one orbit to another, and occurs only with an unsymmetrical arrangement of the inner electrons. In the last period of the table electrons with orbits of the type 7₁ will be present. The Röntgen spectra also point to the same stability relationships as were found with the series spectra.

W. E. G.

Ionisation Potential and the Size of the Atom. A. S. EVE (*Trans. Roy. Soc. Canada*, 1921, 15, iii, 37—40).—The author tabulates the values of the respective ionisation potentials, the atomic diameters as determined by Bragg (A., 1920, ii, 537), and the cube roots of the atomic volumes, so far as these constants are all known for the elements of groups 1—7 and for the inert gases. In the first group, the products of the ionisation potential by either the atomic diameter or the cube root of the atomic volume are approximately constant and fairly concordant, the respective mean values being 18.3 and 15.5. It is concluded that the work done in removing an exterior electron is inversely proportional to the atomic radius. The same holds for the elements Mg, Ca, Sr, and Ba of group II, whilst the values for Zn, Cd, and Hg differ

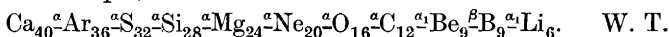
considerably from the mean values for these four. This difference is possibly related to the fact that whilst the former have only a single ring of external electrons, the latter, according to Urbach, have a double ring of electrons in the outer zone. In the case of neon and argon, the diameters as deduced by Bragg afford values of the products in far better agreement with theory than those found by using the cube roots of the respective atomic volumes.

J. S. G. T.

The Atomic Weight of isoHelium. MAXIMILIAN CAMILLO NEUBURGER (*Physikal. Z.*, 1922, **23**, 145—146).—A theoretical paper in which the author applies his theory of the nucleus (this vol., ii, 208) to calculate the atomic weight of Rutherford's *iso*-helium. The assumption is made that oxygen is composed of one α -particle, four *iso*helium nuclei, and two electrons, nitrogen of one α -particle, three *iso*helium nuclei, one positively charged hydrogen atom, and two β -particles, and carbon of four *iso*helium nuclei and two β -particles. The maximum change in mass which can occur during the collision of an α -particle with atoms of oxygen, nitrogen, or carbon is taken as 0.009 unit, and from the known atomic weights of oxygen, nitrogen, carbon, helium, and hydrogen it is found that the atomic weight of *iso*helium is 3.00113 ± 0.006 .

W. E. G.

The Genesis of the Elements. MAXIMILIAN CAMILLO NEUBURGER (*Physikal. Z.*, 1922, **23**, 133—136).—A theoretical paper which deals with the structure of the atomic nucleus. The author proposes a modification of the Meitner nuclear model which embraces all the elements and not merely the radio-elements. Taking into account the recent work of Rutherford and Aston, he is able to give definite nuclear formulæ to the lighter elements, for example, nitrogen = $\alpha + 3\alpha_1 + H^+ + 2\beta$, oxygen = $\alpha + 4\alpha_1 + 2\beta$ (α = Helium nucleus, α_1 = *iso*helium nucleus, H^+ = hydrogen nucleus and β = nuclear electrons). By making certain assumptions as to the existence of isotopes, the genetic relationship of the lighter elements is given, for example,



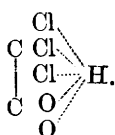
Suggestions for the Construction of a Periodic Table on a Wider Basis. D. BALAREFF (*Z. anorg. Chem.*, 1921, **121**, 22—24).—A method of arrangement of the elements, which takes account of the various valency states of the elements, is described. The method consists in taking nine equal rectangular sheets of glass; these are placed parallel to one another; on the first sheet all elements of zero valency are marked in the positions they would occupy in the Mendeléev system, and on the second sheet all elements which exhibit univalency are marked, and so on. Hence each sheet of glass has those elements marked on it which exhibit a given valency. On bringing the sheets close together, the Mendeléev system is obtained, but at the same time relationships depending on the valency are brought out and emphasised.

J. F. S.

Twenty-eighth Annual Report of the Committee on Atomic Weights. Determinations Published during 1921. GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1922, **44**, 427—437).—The report of the Atomic Weight Committee is discussed, and much of the numerical data concerned with recent determinations of the atomic weight of oxygen, fluorine, chlorine, nickel, zinc, germanium, cadmium, antimony, lanthanum, and bismuth is reproduced. J. F. S.

An Electrical Doublet Theory of the Nature of the Molecular Forces of Chemical and Physical Interaction. R. D. KLEEMAN (*Physical Rev.*, 1921, **18**, 303—312; cf. A., 1910, ii, 492).—It has already been shown that the attraction between two atoms is proportional to the product of the square roots of their atomic weights; the suggestion is now made that a neutral atom with a positive nucleus surrounded by electrons is an electrical doublet. Since the force between two such doublets would on the average be an attraction proportional to the product of the moments of the two doublets, it follows that the electrical moment of an atom is proportional to the square root of its atomic weight. A. A. E.

Nature of the Ionogen Linking. HUGO KAUFFMANN (*Z. physikal. Chem.*, 1922, **100**, 238—249).—It is shown that the introduction of methoxyl groups into the ortho- and para-position of triphenyl carbinol, fuchsines, and similar substances increases the basic character of these substances, whilst in the meta-position the basic character is unchanged. It is shown that the basicity is not centralised in one carbon atom, but distributed over all the ortho- and para-positions and that every methoxyl group introduced in those positions has an active share of the total basicity of the compound. In salts with a radicle as kation, the basic character is not centralised, but is spread over the whole kation, and consequently the positive charge of the kation is not situated on a single atom but is spread over the whole ion. The valency of an anion in union with such an ion is therefore a divided valency which acts in parts between the anion and the positions on the kation where the positive charge is located. Hence the ionogen linking is a divided linking. In the case of acetic acid it is represented as $\text{CH}_3 \cdot \text{C} \begin{smallmatrix} \text{O} \\ \nearrow \\ \text{O} \end{smallmatrix} \text{H}$ and in trichloroacetic acid as in



the annexed formula. The author then discusses homo- and hetero-polar linkings, and shows that these are only limiting cases and that most linkings are intermediate between these. From the discussion, the following results are drawn. The valency has its seat in the atomic nucleus. Valency is measured by the number of lines

of electric force which lead from the nucleus of an atom to the connecting electrons. To bring this statement into line with the usual chemical valency numbers, it is necessary to divide the above-mentioned number by $4\pi e$, where e is the absolute value of the charge of an electron. A result of this statement is that all valencies

are positive; negative valencies are impossible and that which has hitherto been termed negative valency is the other end of the line of force from the electron. The characteristics of the homo- and hetero-polar linkings are illustrated by means of the electric moment. If M_A represents the electric moment of the valency of an atom A , M_B that of an atom B , and M_{AB} that of the linking $A-B$, then $M_{AB} = M_A - M_B$. If the atom nucleus of A is similar to that of B , then M_{AB} is zero. It follows that the electric moment of a pure homopolar valency is always zero. When M_{AB} is equal to M_A , the linking is heteropolar and the electric moment is the greater the more pronouncedly heteropolar is the linking. J. F. S.

Double and Triple Bonds, and Electron Structures in Unsaturated Molecules. E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 438—451).—A theoretical paper dealing with electron structure of unsaturated molecules of compounds of carbon, nitrogen, and boron. It is suggested that multiple linking involves the transfer of two electrons from the inner to the outer shell in one or both of two atomic nuclei, the group of eight being preserved about each, with two jointly held electrons constituting the bond. This hypothesis is sufficient to explain the restricted region of the periodic system in which elements characterised by multiple bond formation occur. To meet requirements imposed by the facts relating to stability, reactivity, and free rotation, the electrons of unsaturated octets are assumed to be held in equilibrium positions at greater distances from the nucleus than in the ordinary case, the transfer from the extended position to the usual one liberating energy. No attractive force between electrons is assumed, and the electron arrangement is taken as cubic, although subject to distortion. On this basis, a mechanism is provided for addition and condensation reactions. Many interesting points of view are afforded in the study of conjugation, the structure and substitution reactions of benzene, and tautomeric displacement of double bonds. Formulæ are illustrated and discussed which represent, more satisfactorily in several cases than other current hypotheses, many of the properties of chain hydrocarbons, the oxides of carbon, the carbonyl and carboxyl groups, nitrogen, oxygen, and the hydrides and oxygen-containing ions of boron.

J. F. S.

Mesohydry. II. GIUSEPPE ODDO (*Gazzetta*, 1922, **52**, i, 42—56).—A claim for priority (cf. A., 1907, ii, 15) principally over Kauffmann (*Ahrens Sammlung*, 1907, **11**, 1—102; 1918, **12**, 1—112), Gebhard (A., 1912, ii, 242), and Hantzsch (A., 1908, ii, 462; A., 1910, i, 200).

T. H. P.

Mesohydry. III. Relation between the Affinity of Acids and the Atomic Ratio O : H in their Functional Groups, and the Constitutional Formulæ of the Acids. GIUSEPPE ODDO (*Gazzetta*, 1922, **52**, i, 56—79; cf. A., 1907, ii, 15, and preceding abstract).—Starting with the conception that tetragonal meso-

hydric nuclei, $M \begin{array}{c} \diagup O \\ \diagdown O \end{array} H$, are not capable of dissociation and that

they become so in solution only in so far as they undergo hydrolytic transformation into the group, $O:M\cdot OH$, the author shows that an intimate relation exists, for all acids, between the number of oxygen and hydrogen atoms existing in the functional acid group and the force of affinity.

With the monobasic acids, there are the following five different types, that in which $nO:nH$ has the value 2:1 required by the non-ionisable mesohydric nucleus, being taken as a basis: (1) $nO:nH=4:1$, acids even more energetic than HCl , such as $HClO_4$; (2) $nO:nH=3:1$, acids as energetic as HCl , such as $HClO_3$; (3) $nO:nH=2:1$, very weak acids, such as $R\cdot CO_2H$; (4) $nO:nH=2:2$ (or more), acids somewhat more energetic than the 2:1-acids, such as H_2CO_2 ; (5) $nO:nH=1:1$ (or more), very feeble acids, such as $HClO$.

With the dibasic acids, if the oxygen and hydrogen atoms constituting the dibasicity are distributed between two oxidisable atoms, the relations for each of the acid functional groups thus resulting are the same as for the monobasic acids, except for the mutual influence of the two groups, this being marked in the 1:2-position, slight in the 1:3-position, and almost zero in the 1:4-position. Thus, succinic acid is almost equivalent to acetic acid in this respect, and dithionic acid to nitric acid or to $R\cdot SO_3H$. If, however, the oxygen and hydrogen atoms causing the dibasicity are united to the same oxidisable atom, only two types result: (1) $nO:nH=4:2$, acids of the average energy of monobasic acids of types (1) and (2), for instance, sulphuric acid; (2) $nO:nH=3:2$, very weak acids, such as H_2SO_3 and (3) $nO:nH=2:2$, still weaker acids, such as H_2SO_2 . With tri- and poly-basic acids, the relations are the same as with dibasic acids. T. H. P.

Space Formulæ. FRIEDRICH RINNE (*Z. physikal. Chem.*, 1922, **100**, 408—418).—A theoretical paper in which the spacial configuration of crystalline substances and the atomic diameter are considered on the bases of the Barlow and Pope hypothesis of close packing, the molecular volume, and the X-ray measurements of crystal structure. J. F. S.

Still-head for the Prevention of Spray. FRIEDRICH L. HAHN (*Z. anal. Chem.*, 1922, **61**, 52—53).—The lower end of the delivery tube, below the cork closing the distillation flask, is blown into the form of an elongated bulb of slightly smaller diameter than that of the neck of the flask. An internal tube extends from an opening at the shoulder of the bulb to nearly the bottom of the latter, and the bulb itself is filled with pieces of broken glass. The vapours from the flask pass through the tube into the bulb, and then escape through the delivery tube to the condenser. Since

the bulb is contained in the neck of the flask, reflux action is but slight and distillation is rapid. W. P. S.

A Sodium Press for the Laboratory. ERNST BECKMANN (*Ber.*, 1922, **55**, [B], 766—768).—The instrument is figured and fully described in the original. The essential features are the construction of the press cap in two separable portions whereby cleaning is greatly facilitated, the arrangement of the piston in such a manner that it has only a vertical and not a rotatory motion, the provision of a powerful wheel in place of the handle usual in copying presses, and a calibration device whereby the weight of the sodium wire can be ascertained from the readings of the rotations of the wheel. H. W.

Apparatus for Hydrogenation at Ordinary Pressures. J. KLIMONT (*Chem. Zeit.*, 1922, **46**, 275).—An ordinary distillation flask of about 150 c.c. capacity has a glass tube sealed horizontally into the neck and bent at right angles inside the flask so that it passes vertically downwards, and ends in a small depression blown in the bottom of the flask, which is also provided with a rubber stopper carrying a short glass tube bent at right angles, which may be connected with a manometer, and a thermometer dipping into the liquid in the flask. The flask is filled by means of a long-stemmed funnel with a mixture of the substance to be hydrogenated and the catalyst, which is heated by means of a Bunsen burner and kept in constant agitation by a stream of hydrogen, which enters through the tube dipping into the liquid and leaves through the other side tube. H. C. R.

A Reversible Turbidity Phenomenon. RAPHAEL ED. LIESEGANG (*Kolloid Z.*, 1922, **30**, 165—166).—The double salts mercuric silver iodide and copper silver iodide undergo a colour change at 70° and 45°, respectively, and have found application as colour thermoscopes. A similar change at a lower temperature is produced by a mixture of 18 c.c. of 10% gelatin solution, 1 c.c. of 20% potassium ferricyanide, and 1 c.c. of nitric acid (*d* 1.148). This is completely clear, but becomes opaque on solidification and again clear on liquefaction. After hydrolysis of the gelatin, the turbidity is fainter. Nitric acid can be replaced by hydrochloric, citric, and other acids. W. T.

Inorganic Chemistry.

Triatomic Hydrogen. II. GERALD L. WENDT and ROBERT S. LANDAUER (*J. Amer. Chem. Soc.*, 1922, **44**, 510—521; cf. A., 1920, ii, 425).—Triatomic hydrogen has now been prepared by three new methods, the Siemens glass tube ozoniser, the high frequency Tesla discharge, and the thermionic emission methods. Attempts to show its presence in hydrogen produced as nascent hydrogen from

solutions of hydrogen-ions were unsuccessful. This hydrogen is catalytically decomposed by finely divided platinum, nickel, copper, lead, antimony, and cadmium. It is unaffected by contact with silver, mercury, tin, bismuth, molybdenum, zinc, or aluminium. Contraction in volume occurs when this hydrogen is produced by the electrical discharge at 3 mm. pressure. This is particularly marked at the temperature of liquid ammonia and solid carbon dioxide. Triatomic hydrogen is condensed to the liquid form by exposure to the temperature of liquid oxygen. The spectrum of hydrogen at the temperature of liquid oxygen shows a progressive intensification of the secondary line spectrum at the expense of the primary series spectrum, which is probably due to the gradual formation of the triatomic form. The present work is held to confirm the mechanism of the formation previously advanced, and also it shows that the new gas is probably H_3 and not *iso*- H_2 , an atomic species proposed by Harkins as a constituent of heavier atoms (cf. Harkins, A., 1920, ii, 479, 745). J. F. S.

Constitution of Haloids. WILHELM BILTZ (*Z. physikal. Chem.*, 1922, **100**, 52—67).—A theoretical paper in which the author discusses the constitution of the haloids from considerations of the melting point, temperature of decomposition, and electrolytic conductivity of the molten compounds. In the case of the platinum, iridium, and vanadium compounds, it is shown that the heat of formation of the highest chloride is much less than that of the remaining lower chlorides; he therefore considers that the higher chlorides are to be considered as co-ordination complexes of the same type as the ammines. In the case of the melting points of the chlorides, it is shown that the lower chlorides have much lower values than the higher chlorides, and in the same way the lower chlorides have a much smaller conductivity in the molten condition than the higher chlorides. All haloids melting between 960° and 450° are good conductors, those melting between 450° and 200° are partly good conductors, partly poor conductors, and some do not conduct at all, and those melting below 200° , with the exception of the gallium compounds, do not conduct at all. The lower chlorides are therefore regarded as true salts, whilst the higher compounds are regarded as complexes. A comparison of the electro-valency towards chloride with the atomic number indicates periodicity as shown by a curve made by plotting the two values. J. F. S.

Significance of the Density of Hydrogen Bromide with Reference to the Atomic Weight of Bromine. GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1922, **44**, 595—601; cf. Guye, A., 1919, ii, 333).—A discussion on the determination of atomic weight from gas densities, particularly in the case of the atomic weight of bromine from the gas density of hydrogen bromide. The pitfalls of such determinations are carefully described. It is pointed out that no method of extrapolation can be satisfactory or convincing where, as in the case of hydrogen bromide, the accuracy of the numerical data diminishes as the region to be

extrapolated approaches. The conclusion cannot be avoided that whilst in the case of hydrogen bromide the gas density method of determining molecular weights may be regarded as an interesting and satisfactory corroboration of gravimetric evidence, its value ceases at that point. To use such as a criterion on which to judge the best gravimetric evidence cannot be justified on scientific grounds. On the other hand, from the point of view of the general application of Avogadro's hypothesis to gases at low pressures, the results of the very careful density determinations, published from Guye's laboratory, are particularly significant and convincing.

J. F. S.

Adsorption of Iodine by Silver Iodide. FRANK E. E. GERMANN and RALPH N. TRAXLER (*J. Amer. Chem. Soc.*, 1922, **44**, 460—464).—Carey Lea's experiments indicate that iodine is strongly adsorbed from solution by silver iodide (A., 1888, 1). This point has been investigated; dry thoroughly washed silver iodide precipitated from *N*-solutions of silver nitrate by potassium iodide was added to aqueous and alcoholic solutions of iodine, but there was no appreciable adsorption. In the same way, moist silver iodide precipitated from *N*- and 0.1*N*-solutions of silver nitrate gave negative results. Decolorisation of the iodine solution was obtained with unwashed silver iodide both from *N*- and 0.1*N*-solutions, using an excess of silver nitrate. The decolorisation was due to a chemical reaction between the iodine in solution and the silver nitrate occluded in the silver iodide and adsorbed on its surface. Unwashed silver iodide precipitated from dilute solutions of silver nitrate and potassium iodide decolorised the iodine solutions most easily, due to the greater adsorption of silver nitrate by the silver iodide and the larger quantity of solution held because of the increased porosity. A sherry-red solution of iodine in alcohol contains about 0.008 millimol. per c.c. From the above, it is concluded that there is no adsorption of iodine from solution by silver iodide above a maximum limit of 0.02 millimol. per gram of silver iodide. Hence if Carey Lea worked with 25 c.c. of sherry-red solution of iodine, he must have added more than 10 grams of silver iodide to obtain complete decolorisation.

J. F. S.

Vapour Pressure of Selenium Oxychloride. VICTOR LENHER, G. B. L. SMITH, and G. G. TOWN (*J. Physical Chem.*, 1922, **26**, 156—160).—The vapour pressure of selenium oxychloride has been determined at temperatures from 84.3° to 117.2° by means of a modified Ramsay and Young apparatus and from 123.5° to 177.2° by the distillation method. The results are recorded for every degree over the whole range of temperature. The vapour pressure is expressed by the formula $\log P = 5.8503 + 0.000219T - 830.9/(T - 178)$, where *P* is the pressure in millimetres of mercury and *T* the temperature in absolute degrees. Selenium has no influence on the vapour pressure between 90° and 120°, selenium monochloride has no influence on the vapour pressure between 91° and 135°, neither does selenium tetrachloride up to its saturation point show any effect between 89° and 130°. Selenium oxychloride,

when distilled under reduced pressures, has a light straw colour, m. p. $10\cdot8^{\circ}$, b. p. $177\cdot2^{\circ}/744$ mm.; when distilled under atmospheric pressure, it decomposes slightly and becomes reddish-brown; this decomposition reverses to some extent on cooling. There is a small amount of dissociation between 265° and 290° , since the mean value of the molecular weight over this range of temperature is $151\cdot4$. The following minor decompositions occur at or near the boiling point under atmospheric pressure. $2\text{SeOCl}_2 \rightleftharpoons \text{SeO}_2 + \text{SeCl}_4$; $2\text{SeCl}_4 \rightleftharpoons \text{Se}_2\text{Cl}_2 + 3\text{Cl}_2$; $2\text{Se}_2\text{Cl}_2 \rightleftharpoons \text{SeCl}_4 + 3\text{Se}$; and $4\text{SeOCl}_2 \rightleftharpoons \text{Se}_2\text{Cl}_2 + 2\text{SeO}_2 + 3\text{Cl}_2$. J. F. S.

Nitrosylselenic Acid. JULIUS MEYER and WALTER WAGNER (*Ber.*, 1922, **55**, [B], 690—692).—*Nitrosylselenic acid*, $\text{NO}\cdot\text{O}\cdot\text{SeO}_2\cdot\text{OH}$, a colourless, crystalline, snow-like mass, is obtained by the action of liquid nitrogen trioxide on ice-cold, anhydrous selenic acid, a large excess of the former being used initially and the greater part being subsequently allowed to evaporate. It has m. p. 80° (decomp.). It is somewhat unstable even at the atmospheric temperature, and is immediately decomposed by water. H. W.

Cathodic Reduction of Elementary Nitrogen. FR. FICHTER and RICHARD SUTER (*Helv. Chim. Acta*, 1922, **5**, 246—255).—Tschirch's view that absorption of atmospheric nitrogen by leguminous plants is due to electronic action receives support from the work of Hiedemann (A., 1921, ii, 694). Since, further, biochemical oxidation can be reproduced electrochemically by use of high potential differences (Fichter, this vol., ii, 23), the attempt has been made to reduce nitrogen to ammonia by similar means. Rayleigh's contradiction (T., 1897, **71**, 181) of Davy's original positive result can be disregarded, since he employed platinum electrodes and a high current density instead of gold electrodes and a low density. Experiments are now described in which, after making full allowance for the effects of impurities by blank experiments, on an average $0\cdot3$ mg. of ammonia per 160 amp. min. was consistently obtained from nitrogen under 200 atm. pressure by the use of platinum electrodes of large surface, freshly and thickly platinised, the electrolyte being 1% sulphuric acid (cf. Fischer and Priess, A., 1913, ii, 285; Tiede and Schleede, A., 1921, ii, 328). The cathode surface quickly loses its efficiency, and has to be renewed. Its activity cannot be restored by oxidation (Willstätter and Waldschmidt-Leitz, A., 1921, ii, 185). No definite evidence of ammonia formation could be obtained when a mercury cathode was employed. J. K.

Formation and Decomposition of the Higher Nitrogen Oxides. MAX BODENSTEIN, FRIEDRICH BOËS, (FRL.) LINDNER, and RAMSTETER (*Z. physikal. Chem.*, 1922, **100**, 68—123).—The equilibria $\text{N}_2\text{O}_4 \rightleftharpoons 2\text{NO}_2$ and $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ have been investigated over the temperature range $281\cdot7$ to $403\cdot8^{\circ}$ Abs., and $498\cdot9^{\circ}$ to $825\cdot3^{\circ}$ Abs., respectively. The velocity of the reaction $2\text{NO} + \text{O}_2 = 2\text{NO}_2$ has been determined at a series of temperatures. It is shown that the equilibrium $2\text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_4$ is represented by the formula

$\log p_{\text{NO}_2}^2/p_{\text{N}_2\text{O}_4} = \log k_p = -2692/T + 1.75 \log T + 0.00483T - 7.144 \times 10^{-6}T^2 + 3.062$. This equation embodies the measurements of Wourtzet (A., 1920, ii, 108) between 0° and 84° , and the corrections made by the authors on measurements of the rate of oxidation of nitric oxide. The dissociation $2\text{NO}_2 \rightleftharpoons 2\text{NO} + \text{O}_2$ is to be represented by the equation $\log p_{\text{NO}}^2 \cdot p_{\text{O}_2}/p_{\text{NO}_2}^2 = \log k_p = -5749/5 + 1.75 \log T - 0.00050T + 2.839$. Both constants are true for values of p measured in atmospheres. The experimental measurements in both the above cases were effected by introducing suitable quantities of pure nitrogen tetroxide into a quartz flask and measuring the pressure with a quartz glass manometer at different temperatures. The older measurements on the velocity of combination of oxygen with nitric oxide at lower temperatures ($0-90^\circ$) and low pressures were extended to higher temperatures ($140-390^\circ$), at which the reverse reaction is considerable. The measurements were made, as before, by observing pressure changes as indicated by a bromonaphthalene manometer. The reaction takes place, as expected, according to the equation $dx/dt = kC_{\text{O}_2} \cdot C_{\text{NO}}^2 - k'C_{\text{NO}_2}^2$. The velocity increases with increasing temperature, but more slowly the higher the temperature, until eventually it is practically independent of the temperature. According to the present observations, the decomposition of nitrogen dioxide must also be measurable, and measurements were made at temperatures of $319-383^\circ$ and the velocity shown to be given by $dx/dt = k'C_{\text{NO}_2} - kC_{\text{NO}}^2 \cdot C_{\text{O}_2}$. The value of k' increases with temperature 1.5 times for an increase of 10° ; k/k' gave a good agreement with the value of K deduced from the measurements. The theory of gas reactions of the third order is considered, and it is shown that simultaneous collisions between three molecules are not too few to give true trimolecular reactions, as is stated by Trautz (A., 1916, ii, 422). In the present work at 0° , where the greatest velocity is observed, it is shown that one hundred thousand times as many such collisions occur as lead to reaction, and that, from the variation of the interval between collisions of two molecules with the temperature and the probability of triple collisions, the unusual dependence of this reaction on the temperature may be deduced. J. F. S.

Purification of Phosphoric Oxide. GEORGE INGLE FINCH and RAYMOND HAROLD KELSALL PETO (T., 1922, 121, 692-693).

The Behaviour of Amorphous Carbon and Sulphur when Heated: Sulphides of Carbon. J. P. WIBAUT (*Rec. trav. chim.*, 1922, 41, 153-171; cf. A., 1919, ii, 190; also Mixter, A., 1893, ii, 571).—The sulphur which is retained by carbon after a mixture of the two elements has been heated has now been further investigated and the author considers that it is chemically combined, although no definite compound has been isolated. The product is probably a mixture of carbon with a sulphide of carbon which is practically non-volatile at 1000° , although the quantity of sulphur retained depends on the nature of the carbon and on the extent of its surface (cf. Langmuir, A., 1915, ii, 467). It is pointed out that these results are analogous to those obtained by Lowry

and Hulett (A., 1920, ii, 536) and by Rhead and Wheeler (T., 1912, **101**, 831, and 1913, **103**, 461) in the case of carbon and oxygen. It is suggested that the sulphur present in coal as iron pyrites is fixed by the carbon in the process of coking. H. J. E.

Processes in Gas Generators and Blast Furnaces. H. VON JÜPTNER (*Z. physikal. Chem.*, 1922, **100**, 231—237).—A theoretical paper in which relationships between carbon monoxide and carbon dioxide in gas generators and blast furnaces is discussed. It is shown that the direct reduction of iron oxide by carbon in the blast furnace is advantageous, for it involves a reduction in the amount of fuel used, but the process is slow. In the electric blast furnace, better results are obtained with porous wood charcoal than with the denser coke, and also the liquid condition of the ore accelerates the process. J. F. S.

The State of Carbonic Acid in Aqueous Solution. A. THIEL (*Z. anorg. Chem.*, 1922, **121**, 211—214).—A theoretical paper. Wilke (this vol., ii, 52) assumed that the increase in the strength of carbonic acid caused by the addition of neutral salts is due to the formation of orthocarbonic acid. This is shown to be incorrect. No other explanation is offered. W. T.

Solubility of Potassium Permanganate in Solutions of Potassium Sulphate and Sodium Sulphate. H. M. TRIMBLE (*J. Amer. Chem. Soc.*, 1922, **44**, 451—460).—The solubility of potassium permanganate in solutions of sodium sulphate and potassium sulphate of concentrations varying between 0 and 10.75% and 0 and 21.80%, respectively, have been determined at 25°. The densities of the mixed solutions and of solutions of the single salts have also been determined for a series of concentrations. It is shown that the solubility of potassium permanganate in solutions of potassium sulphate decreases with increasing concentration of the sulphate. In solutions of sodium sulphate the solubility increases to a maximum with increasing concentration of sodium sulphate. The maximum solubility lies at about 6% of sodium sulphate, after which there is a slow decrease in solubility to a minimum in solutions which contain the maximum amount of sodium sulphate soluble in the presence of permanganate crystals. For the lower concentrations of each sulphate, potassium sulphate acts powerfully to decrease the solubility of potassium permanganate in solutions of sodium sulphate, whilst sodium sulphate increases its solubility in solutions of potassium sulphate to a much smaller degree. J. F. S.

Thermal Decomposition of Potassium Permanganate. E. MOLES and M. CRESPI (*Z. physikal. Chem.*, 1922, **100**, 337—345).—The thermal decomposition of potassium permanganate has been investigated at temperatures up to 542°. It is shown that pure dry potassium permanganate shows the first signs of decomposition at 200°. The pressures observed when permanganate is heated at lower temperatures than this are due to the presence of carbonates and substances containing water. The

decomposition is complete at 240° , and the oxygen pressure of the residue up to 485° corresponds with that of pure manganese dioxide. From 485° upwards the two dissociation curves diverge from one another, and this divergence indicates the formation of the complex assumed by Askenasy and Solberg (A., 1912, ii, 1167). The absorption equilibrium does not coincide with the liberation equilibrium, a behaviour which is also observed with manganese dioxide. From the dissociation values of potassium permanganate, the heat of dissociation has been calculated and the value 60,000 cal. obtained. The absence of potassium hydroxide in the residue after heating has been established from conductivity measurements, and it is therefore proved that potassium oxide is not one of the decomposition products of potassium permanganate as indicated by Rudolf (A., 1901, ii, 388) in the equation $10\text{KMnO}_4 = 3\text{K}_2\text{MnO}_4 + 7\text{MnO}_2 + 2\text{K}_2\text{O} + 6\text{O}_2$; consequently it is assumed that manganite must be formed according to the equation $10\text{KMnO}_4 = 2\text{K}_2\text{MnO}_4 + 3\text{K}_2\text{MnO}_3 + 5\text{MnO}_2 + 6\text{O}_2$. J. F. S.

Electrolytic Production of Sodium Perborate. PEDER CHR. ALSGAARD (*J. Physical Chem.*, 1922, 26, 137—155).—A long account of experimental work on the electrolytic preparation of sodium perborate is given (*Tidskr. kem. Farm. Terap. Kristiania*, 1916, Nos. 17, 18), which is followed by an account of the author's own experiments. It is shown that by electrolysing a solution containing 45 grams of borax, 130 grams of sodium carbonate, 45 grams of sodium hydrogen carbonate, 2 grams of potassium dichromate, and 2 grams of sodium silicate per litre at 10° between a suitably shaped copper pipe as cathode and a platinum anode by means of a current of 6 amperes at 7—8 volts a yield of 11.55 grams of sodium perborate per litre may be obtained. This corresponds with a 40% current efficiency. [Cf. *J. Soc. Chem. Ind.*, 1922, 326A.] J. F. S.

The Preparation of Sodium Hydrogen Carbonate. E. TOPORESCU (*Compt. rend.*, 1922, 174, 870—873).—A study of the equilibrium of the four salts, sodium chloride, sodium hydrogen carbonate, ammonium chloride, and ammonium hydrogen carbonate, with their saturated solutions at 15° , together with measurements on certain mixtures of two or three of them together. From the results, a solubility diagram has been constructed by Le Chatelier's method (cf. A., 1921, ii, 248). From this diagram it is possible to calculate the amount of the different salts which will crystallise when a solution of known initial composition is progressively evaporated. W. G.

The Manufacture of Sodium Carbonate by the Ammonia Process. H. LE CHATELIER (*Compt. rend.*, 1922, 174, 836—841).—Using the results of Toporescu (cf. preceding abstract), diagrams are constructed by means of which it is possible to calculate the theoretical yields in the ammonia-soda process, under different conditions, and starting with mixtures of any initial composition. The theoretical maximum yield may be considerably reduced by

very slight changes in the initial composition. These results, obtained by studying the concentration of solutions initially very dilute, are applied to manufacturing conditions in which salts are added to a fixed amount of water, which is kept constant throughout the separation of the sodium hydrogen carbonate. It is possible to calculate the amount of water, on the one hand, or salt, on the other, which it may be necessary, under the manufacturing conditions, to add in order to get the maximum yield of pure sodium hydrogen carbonate.

W. G.

Density of Aqueous Solutions of Ammonium Perchlorate.

A. MAZZUCHELLI and S. ANSELMi (*Gazzetta*, 1922, **52**, i, 147—152).—The densities of aqueous ammonium perchlorate solutions of $p\%$ concentration or n -normality are given by the equations, $d_{15}=0.99913+4.6826 \cdot 10^{-3} \cdot p+1.425 \cdot 10^{-5} \cdot p^2+2 \cdot 10^{-7} \cdot p^3$; $d_{25}=0.99907+4.7898 \cdot 10^{-3} \cdot p+1.920 \cdot 10^{-5} \cdot p^2+1.33 \cdot 10^{-8} \cdot p^3$, and $d_{15}=0.99913+5.632 \cdot 10^{-2} \cdot n-5.24 \cdot 10^{-4} \cdot n^2-5.2 \cdot 10^{-5} \cdot n^3$. The results show that ammonium perchlorate dissolves in water with increase of volume at 25° and with decrease of volume at 15° , and thus support de Boisbaudran's view (cf. Roozeboom, "Heterogene Gleichgewichte," II, i, 402) that no fundamental distinction can be drawn between salts dissolving with contraction and those dissolving with expansion of volume.

T. H. P.

The Decomposition of Ammonium Nitrate by Heat.

HORACE LEONARD SAUNDERS (T., 1922, **121**, 698—711).

The Ammonium Carbonate-Carbamate Equilibrium.

RUDOLF WEGSCHIEDER (*Z. anorg. Chem.*, 1921, **121**, 110—112).—A theoretical paper in which the author makes an attempt to explain the divergences of the views of Faurholt (this vol., ii, 272) and the author (A., 1916, ii, 617) in connexion with the equilibrium in a solution of ammonium carbamate. It is shown that the equilibrium in such solutions cannot be regarded as definitely settled until some hypothesis is put forward which will explain the older results and those of Faurholt, or until it is shown that the results of Fenton and of Burrows and Lewis, despite their agreement, are erroneous.

J. F. S.

Purity of Atomic Weight Silver. I. Gases in Pure Silver and Iodine.

GREGORY PAUL BAXTER and LEON WOODMAN PARSONS (*J. Amer. Chem. Soc.*, 1922, **44**, 577—591).—The amount of gases contained in silver and iodine which has been purified for atomic weight work has been determined. It is shown that iodine sublimed in air yields small quantities of gases when resublimed in a vacuum. The proportions varied from 0.0005% in the case of crude iodine to 0.00015% in the case of the purest material. These proportions are far smaller than those found by Guye and Germann (A., 1914, ii, 727). Crude silver, when converted into iodide in a vacuum, was found to yield 0.006% of gas, whilst the purest material when treated in the same way yielded only 0.00063%. In this case also, the proportion of gas found in the pure metal

is only one-seventh that found by Guye and Germann. The foregoing figures are based on the assumption that the iodine and the silver are responsible for all the gas evolved, and that the gas is as heavy as air. It has been shown to be likely that a portion of the gas obtained was either liberated from the walls of the apparatus or diffused through the reaction tube. Furthermore, in the case of silver, at least, a large portion of the gas was found to be hydrogen. There is therefore good reason to believe that the real percentages are smaller than those given above. When the maximum corrections are applied, the atomic weights of silver and of elements referred to silver are affected in the most unfavourable cases by only 0.002 unit.

J. F. S.

Purity of Atomic Weight Silver. II. Solid Impurities.

GREGORY PAUL BAXTER (*J. Amer. Chem. Soc.*, 1922, **44**, 591—594; cf. preceding abstract).—Atomic weight silver when examined spectroscopically shows the presence of only calcium as impurity, and this in an amount not greater than 0.00004%. It is therefore concluded that in the present state of the most accurate chemical analysis the purity of atomic weight silver is fully adequate.

J. F. S.

The Absorption of Nitrogen by Calcium and its Alloys.

OTTO RUFF and HELMUTH HARTMANN (*Z. anorg. Chem.*, 1922, **121**, 167—177).—Methods of preparing calcium alloys are given. The rate at which alloys rich in calcium absorb nitrogen depends on volume relationship, temperature, potential of the added metal, and the calcium nitride content of the alloy. The contraction of calcium in the formation of calcium nitride keeps the exposed surface porous, but pure calcium is almost passive towards nitrogen. Metals more strongly positive than calcium accelerate the adsorption (K, Ba), of the others, some have no effect (Mg, Pb, Sn), others retard it (As, Sb), and some inhibit it (Bi, Cu, Zn). The addition of more positive metals has a loosening effect on the valency electrons of calcium. Calcium nitride acts as a catalytic agent in all cases. With calcium alloys containing 5% of the nitride, pure argon can be obtained from atmospheric nitrogen in a few minutes even at a temperature below 320°.

W. T.

Zinc Borate. T. C. N. BROEKSMIT (*Pharm. Weekblad*, 1922, **59**, 265—268).—The admixture of solutions containing equivalent weights of zinc sulphate and borax causes the precipitation of a gelatinous mass, which is very difficult to filter and wash. When dry, it contains boric acid, even after prolonged washing, but zinc oxide is also present. The precipitate is soluble in boric acid solution if it is kept moist, but becomes insoluble when dried.

S. I. L.

Thallous Nitrite in certain Complex and Double Nitrites.

V. CUTTICA and A. PACIELLO (*Gazzetta*, 1922, **52**, i, 141—147).—Although thallium closely resembles in physical properties the heavy metals, thallous nitrite exhibits a chemical and physico-chemical behaviour quite different from that shown by the nitrites

of these metals. In aqueous solution, thallous nitrite, like the alkali nitrites, is highly dissociated, and the salt shows no tendency to form either complex or double nitrites. In the compounds described below, this nitrite enters with the character of the alkali nitrites.

Cupric thallous nitrite [*thallous cuprinitrite*], $\text{Ti}_3[\text{Cu}(\text{NO}_2)_5]$, forms opaque, black, rounded crystals, yields pale green, aqueous solutions, and is decomposed by dilute acid, with formation of a blue solution and liberation of nitrous acid. At the ordinary temperature, both the solid salt and its aqueous solutions are stable.

In order to trace the displacement of the equilibria produced in solution of cupri-nitrous complexes by variation of the relative concentrations of the components, conductivity measurements have been made on solutions containing cupric chloride and barium nitrite in different proportions. The conductivity-composition curve shows two inflexions, due to the appearance of two complexes corresponding with the ions $[\text{Cu}(\text{NO}_2)]$ and $[\text{Cu}(\text{NO}_2)_2]$.

Thallous nickelonitrite, $\text{Ti}_4[\text{Ni}(\text{NO}_2)_6]$, forms stable, flesh-red crystals and yields stable, green, aqueous solutions.

Barium thallous nitrite, $\text{TiNO}_2 \cdot 2\text{Ba}(\text{NO}_2)_2$, forms golden-yellow, prismatic crystals and is stable in the air and very readily soluble in water.

Lead thallous nitrite, $\text{Pb}(\text{NO}_2)_2 \cdot 2\text{TiNO}_2 \cdot \text{H}_2\text{O}$, forms orange-yellow crystals and in aqueous solution, especially when heated, undergoes partial hydrolysis with separation of lead hydroxide. T. H. P.

Thallium Bismutho-, Stibio-, and Arseno-thiosulphates.

G. CANNERI (*Gazzetta*, 1922, 52, i, 37—41; cf. Carnot, A., 1877, i, 50; Hauser, A., 1903, ii, 487; Szilágyi, A., 1921, ii, 199, 207).—*Thallous bismutho-thiosulphate*, $\text{Ti}_3\text{Bi}(\text{S}_2\text{O}_3)_3$, prepared either from the double compound, $\text{Ti}_2\text{S}_2\text{O}_3 \cdot 2\text{Na}_2\text{S}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ (cf. Vortmann and Padberg, A., 1890, 12), and bismuth chloride or from potassium bismutho-thiosulphate and a thallous salt, forms a sparingly soluble, microcrystalline, yellow powder. It is moderately stable in neutral solution at a low temperature, but decomposes with formation of sulphur dioxide and bismuth sulphide when gently heated, the decomposition being retarded by alcohol and accelerated by a trace of acid. The salt is soluble in excess of potassium bismutho-thiosulphate solution, yielding a clear liquid, with which alcohol forms a microcrystalline, orange-yellow precipitate containing both thallium and potassium.

Thallous stibio-thiosulphate, $\text{Ti}_3\text{Sb}(\text{S}_2\text{O}_3)_3$, similarly prepared, forms a white, microcrystalline powder, and is stable in a dry atmosphere, but in presence of moisture rapidly reddens, owing to formation of antimony oxysulphide: $2\text{Ti}_3\text{Sb}(\text{S}_2\text{O}_3)_3 \rightleftharpoons \text{SbOS}_2 + 4\text{SO}_2 + 3\text{Ti}_2\text{S}_2\text{O}_3$.

Thallous arseno-thiosulphate, $\text{Ti}_3\text{As}(\text{S}_2\text{O}_3)_3$, similarly obtained, forms a white powder and decomposes more readily than the preceding compounds, in accordance with the equations: $2\text{Ti}_3\text{As}(\text{S}_2\text{O}_3)_3 = \text{As}_2\text{S}_3 + 3\text{Ti}_2\text{S}_3\text{O}_6$, $\text{Ti}_2\text{S}_3\text{O}_6 + 2\text{H}_2\text{O} = \text{Ti}_2\text{S} + 2\text{H}_2\text{SO}_4$, and $\text{Ti}_2\text{S} + \text{H}_2\text{SO}_4 = \text{Ti}_2\text{SO}_4 + \text{H}_2\text{S}$. T. H. P.

Density and Molecular Volume of the Oxides of Lanthanum, Praseodymium, Neodymium, Samarium, and Europium.

WILHELM PRANDTL (*Ber.*, 1922, 55, [B], 692—694).—The densities of the earth oxides depend greatly on their method of preparation and on the temperature to which they have been subjected. The nitrates when ignited give very voluminous, porous oxides which cannot be freed from adsorbed gases and consequently have low densities. The oxides obtained from sulphates are only deprived of the last traces of sulphur trioxide with great difficulty. Compact oxides are most conveniently prepared from the oxalates; the present series is therefore obtained by ignition of the latter in an electrically heated furnace at about 900° until constant in weight. Praseodymium sesquioxide is prepared by the reduction of the black oxide, Pr_4O_7 , by hydrogen at 900°. The following data are recorded :

Oxide.	Colour.	d_4^{15} .	Molecular volume.
La_2O_3	Pure white	6.51	50.08
Pr_2O_3	Greenish-yellow	6.87	48.01
Nd_2O_3	Reddish-bluish-grey	7.24	46.49
Sm_2O_3	White with yellow tinge	7.43	46.95
Eu_2O_3	Almost white with reddish-yellow tinge	7.42	47.44
Gd_2O_3	Colourless	7.407	48.95
Pr_4O_7	Black	6.71	
Eu_2O_3 (from the nitrate)		6.55	

H. W.

Corrosion of certain Aluminium Alloys. L. ROLLA (*Gazzetta*, 1922, 52, i, 79—87).—The author applies Desch's method of investigating corrosion, in which the metal is made the positive pole in the electrolysis of sodium chloride solution (A., 1911, ii, 381) to various aluminium-zinc and aluminium-magnesium alloys, which were prepared in a current of hydrogen in the electric furnace.

[With MARIO FRASSINETI].—The results obtained with the aluminium-zinc alloys show that solid solutions of zinc in aluminium undergo corrosion in such a way that neither of the two components exerts a true protecting action on the other. This result indicates that, although the solution pressure of the aluminium is greater than that of the zinc, the phenomenon is not electrochemical, but purely chemical in character. Corrosion effected by means of electrolytic chlorine does not modify substantially the ratio between the weights of the disintegrated metals remaining adherent and those dissolved or precipitated when the alloys are treated with either sea-water or sodium chloride solution. The results obtained are fully confirmed by micrographic investigation of the corroded alloys.

[With MARIO BULLI].—Two magnesium-aluminium alloys containing (1) 5.68% Mg and 93.3% Al and (2) 6.9% Mg and 92.18% Al, with small proportions of iron, silica, and carbon, were examined, the latter undergoing the more rapid corrosion. In either case, a voluminous precipitate, mostly aluminium hydroxide, was formed, and the proportion of magnesium removed was greater than that

of the aluminium. The protective action of the adherent stratum of aluminium hydroxide exerts an important influence on the course of the corrosion, rendering it discontinuous. T. H. P.

Solubility of Aluminium Nitrate Crystals in Solutions of Nitric Acid of Various Strengths at Various Temperatures.

LOWELL H. MILLIGAN (*J. Amer. Chem. Soc.*, 1922, **44**, 567—570).—The solubility of the enneahydrate of aluminium nitrate has been determined in nitric acid of concentrations varying from 4.98% to 72.4% at 0.4°, 20°, 40°, and 60°. The solubility increases with increasing temperature for constant nitric acid concentration, and for the same temperature decreases rapidly with increasing nitric acid concentration. J. F. S.

The Electrochemical Behaviour of Alloys of Manganese with Copper, Nickel, Cobalt, and Iron.

G. TAMMANN and E. VADERS (*Z. anorg. Chem.*, 1922, **121**, 193—208).—The mixed crystals of manganese with other metals show the following limiting concentrations for the action of chemical reagents and in their electrochemical behaviour: Au-Mn 0.50 mol. Au. Ag-Mn 0.75 mol. Ag. Cu-Mn 0.50 mol. Cu. Ni-Mn 0.50 mol. Ni. Co-Mn 0.50 mol. Co. Fe-Mn none. The manganese employed was not pure, and therefore these limits are only approximate. More silver (0.75 mol.) is necessary to protect the manganese than the more positive metal copper (0.5 mol.). This limit in the case of silver holds for precipitation of metals as well as for the potential of the alloys.

In the case of copper, however, a sharp limit for the action of chemical reagents could not be obtained, but the potential showed a sudden change at the concentration 0.5 mol. Cu, and the decomposition potential of the element $\text{Cu}[\text{MnCl}_2]_{\text{Mn}_x}\text{Cu}_{1-x}$ is independent of the composition of the alloy when $x < 5$; with $x > 5$ it decreases with decreasing amount of copper to zero. The same applies to the nickel and cobalt alloys. In the case of nickel-manganese alloys a sharp limit (0.5 mol. Ni) is found for the evolution of hydrogen from hydrochloric acid, and for the precipitation of cadmium from cadmium chloride solutions; this limit does not exist in the case of the cobalt-manganese alloys. Iron is the least able to protect the manganese in these alloys. W. T.

Preparation of Green Manganous Sulphide.

FRIEDRICH L. HAHN (*Z. anorg. Chem.*, 1922, **121**, 209—210).—For the preparation of the green sulphide the following procedure is necessary. One hundred grams of manganese sulphate are dissolved in 300 c.c. of water. One hundred c.c. of 20% ammonia solution are saturated with hydrogen sulphide, and another 100 c.c. of the ammonia added (colourless ammonium sulphide). Thirty c.c. of this are saturated with sulphur at the boiling temperature and then made up to 100 c.c. with the colourless solution (yellow ammonium sulphide). To a boiling mixture of 5 c.c. of the manganese solution, 20 c.c. of 20% ammonia, and 100 c.c. of water, are added 30 c.c. of the yellow ammonium sulphide. The precipitated manganese sulphide

is dark green. To this is immediately added the colourless and yellow ammonium sulphide and the warm manganese salt is added in portions, the mixture being kept almost boiling and well stirred. If the manganese salt is added too rapidly, the flesh-coloured sulphide separates.

W. T.

Structure and Simple Displacement of Iron. O. MÜGGE (*Z. anorg. Chem.*, 1921, **121**, 68—72).—In previous papers (*Jahrb. Min.*, 1899, **2**, 63; 1901, **14**, 314), it was shown that ordinary (α) iron could not possess a plane-centred cubic structure. It is now shown, in keeping with the measurements of Westgren and Lindh (this vol., ii, 152), that the simple displacement of iron is in keeping with a space-centred cubic structure. The simple displacement which accompanies the working of α -iron is impossible in γ -iron above the transition point. Consequently, the behaviour of α -iron on working is quite different from that of γ -iron. A characteristic feature of the simple displacement in the working of α -iron is a relatively large increase in volume, which may amount to two-thirds. This is due to the formation of relatively wider concave channels.

J. F. S.

The Colour of Ferric Oxide. J. ARVID HEDVALL (*Z. anorg. Chem.*, 1922, **121**, 217—224).—The colour of ferric oxide may vary from bright yellow to bluish-black. The light-coloured variety is obtained by the cautious heating of any of the sulphates of iron; the darker varieties are obtained by heating any of the other compounds of iron. The sulphate also gives the darker variety on heating with a flux or alone at 650°. When heated at 650—1000°, all the varieties become brown or dark violet; above 1000°, they become black or bluish-black (the colour of specular iron ore). Heating at above 650° causes a permanent change in colour. These varieties are explained either by the assumption of the existence of several stable modifications of ferric oxide or by that of different crystalline forms of the same modification. The author examined specimens of ferric oxide prepared by twenty-seven different methods; they were all crystalline. The bright yellow variety consisted of thin plates, the others were small grains or short prisms. They all gave the same X-ray spectrum, and therefore belong to the same system. The change from the light yellow to the darker variety was studied; it took place at 700°, the leaflets losing their form and becoming granular.

W. T.

Cobalt-Tungsten Alloys. KARL KREITZ (*Metall u. Erz*, 1922, **19**, 137—140).—In the cobalt-tungsten series there is evidence of the formation of two compounds, Co_6W , melting at 1500° and CoW , melting at 1650°. Between 0 and 40% of tungsten, the alloys consist of a series of mixed crystals; from 40—70% of tungsten, of a mixture of eutectic and mixed crystals or of eutectic and the alloy CoW , according as the tungsten is less or more than 45%. The eutectic contains 44.5% of tungsten and melts at 1480°. Addition of tungsten to cobalt rapidly increases the hardness and brittleness and reduces the specific electrical

conductivity. Up to 3% of tungsten the alloys are more readily attacked by sulphuric acid than is cobalt; with more than 3% the resistance of the alloys to attack by acids rapidly increases. [Cf. *J. Soc. Chem. Ind.*, 1922, May.] A. R. P.

The Hydrolysis of the Roseocobaltic Salts. P. JOB (*Compt. rend.*, 1922, 174, 943—946).—By a quantitative application of the method previously described (this vol., ii, 301), using an oxygen electrode, the author has shown that, under the influence of hydroxyl ions, the roseocobaltic salts are converted into hydroxo-salts and that the equilibrium constant of this reaction at 16° is 6×10^{-10} . The constant of hydrolysis of the roseo-ion is calculated as being 1.2×10^5 . W. G.

Electrolytic Reduction of Chromic Chloride to the Bivalent State. M. C. TAYLOR, W. A. GERSDORFF, and E. J. TOVREA (*J. Amer. Chem. Soc.*, 1922, 44, 612—614).—When chromic chloride solution is electrolysed in a two-compartment cell between a spiral spongy lead cathode and five graphite anodes, it is reduced to chromous chloride. With a total cathode surface of 1.24 (dm.)² and a current of 1.6 amperes, a current efficiency of 96% may be obtained over the period required to reduce 87% of the chromium, if the solution is kept stirred and if the current is reduced when hydrogen commences to be evolved. With a steady and unchanged current strength the efficiency is only 53% for the same amount of reduction. J. F. S.

Normal Chromium Azide and the Formation of Complex Salts. E. OLIVERI-MANDALÀ and G. COMELLA (*Gazzetta*, 1922, 52, i, 112—115).—The compound $\text{CrN}_9, 3\text{C}_6\text{H}_5\text{N}$, the behaviour of which indicates it to be a complex salt of the formula $\left[\text{Cr} \left(\text{N}_3 \right)_3 \left(\text{C}_6\text{H}_5\text{N} \right)_3 \right]$ (cf. A., 1919, ii, 468), may be obtained in better yield and purer condition by concentrating in a vacuum an alcoholic solution of chromium azide containing pyridine in solution.

Chromium azide, $\text{Cr}(\text{N}_3)_3$, prepared by prolonged treatment of an absolute alcoholic solution of crystallised chromium nitrate with anhydrous sodium sulphate and evaporation of the filtered liquid with the calculated proportion of sodium azide in a vacuum, forms a highly hygroscopic, dark green, amorphous mass. If the alcoholic solution of the chromium azide is not thoroughly dry, partial hydrolysis occurs, with formation of the basic azides, $\text{OH} \cdot \text{Cr}(\text{N}_3)_2$ and $\text{CrN}_3(\text{OH})_2$.

The compound $\text{CrN}_9, 3\text{NaN}_3$ forms green crystals, with ammonia yields a blue coloration and with silver nitrate, not silver azide, but a highly explosive complex salt, so that it evidently contains a complex anion, $[\text{Cr}(\text{N}_3)_6]'''$, analogous to $[\text{Cr}(\text{CN})_6]'''$ and $[\text{Cr}(\text{SCN})_6]'''$. The corresponding free acid, $\text{H}_3\text{CrN}_{18}$, could not be isolated owing to its ready decomposability. T. H. P.

New Views on the Constitution of the Chromic Acid. N. R. DHAR (*Z. anorg. Chem.*, 1921, 121, 99—102).—A theoretical paper in which the author considers the behaviour of chromic

acid in solution. It is suggested that chromic acid is an acid of medium strength, and that it dissociates in the two stages $\text{H}_2\text{CrO}_4 \rightleftharpoons \text{H}^+ + \text{HCrO}_4'$, $\text{HCrO}_4' \rightleftharpoons \text{H}^+ + \text{CrO}_4''$, but the dissociation constant of the first stage is extremely large in comparison with that of the second stage. Similar behaviour is found in the case of maleic and dipropyl malonic acid. J. F. S.

The Preparation of Gaseous Metallic Hydrides from Alloys and Solutions. FRITZ PANETH, ADOLF JOHANNSEN, and MAX MATTHIES (*Ber.*, 1922, **55**, [B], 769—775).—The gaseous hydrides of bismuth (A., 1919, ii, 67—68) and tin (A., 1920, ii, 41) have been obtained by melting the respective metals with magnesium and decomposing the products so formed with dilute acids. The yields, however, are very small and uncertain. Numerous attempts have therefore been made to find more favourable conditions for the formation of the alloys, but these have not resulted in any improvement in the preparation of the hydrides, and have led the authors to the conclusion that the process cannot be regarded as a simple decomposition of the magnesium bismuthide or stannide. Evidence in favour of this view is found in the observation that the relatively best yields of hydride are obtained from those portions of the mixtures in which the magnesium and tin or bismuth have not been melted together completely, that bismuth hydride is obtainable from magnesium which is merely coated with fused metallic bismuth, that the well-defined compounds, Na_3Bi and Na_4Sn , do not give a trace of metallic hydride, and, in particular, that thorium-*C* deposited on magnesium foil continues to evolve the metallic hydride for a long time after removal of the thin film is complete. It therefore appears possible to obtain metallic hydrides from suitable solutions of the metals instead of from their alloys and, in this connexion, the production of tin hydride by the action of magnesium on a solution of tin sulphate is described in detail; the operation proceeds with such uniformity and gives such good yields that it is suitable for lecture demonstration purposes. A solution of stannous chloride in hydrochloric acid may replace that of tin sulphate, but, in this case, the deposit formed when the gas is led through the heated Marsh tube consists of colourless stannous chloride (due to the hydrogen chloride carried forward in the gas) instead of metallic tin. This possibly accounts for the previous non-observance of the formation of tin hydride when tin is used for evolving hydrogen in Marsh's test for arsenic. H. W.

The Preparation of Gaseous Metallic Hydrides by the Spark Discharge. FRITZ PANETH, MAX MATTHIES, and EDGAR SCHMIDT-HEBBEL (*Ber.*, 1922, **55**, [B], 775—789).—Attempts are described to produce bismuth hydride by passing active hydrogen over bismuth powder, but the gas is not formed in identifiable amount. Small quantities of it are produced when rods of bismuth are used as electrodes in the formation of active hydrogen. Better results are obtained by the analogous use of lead, and the further experiments are mainly performed with this metal. The

yields with the disposition of apparatus outlined above are small and very irregular, in spite of the apparent uniformity in the conditions, but some improvement can be effected by using finely divided lead or, preferably, granulated lead packed round the platinum electrode and arranging the tube (it is figured and described fully in the original) in such a manner that the hydride produced is removed rapidly from the neighbourhood of the discharge. Even under these conditions, the experiments are very uncertain, and the yields of hydride are found to diminish with increasing purity of the reagents, thus indicating that some impurity is functioning as catalytic accelerator. Systematic search has shown that methane and the vapours of ethyl alcohol, ethyl ether, glycerol, light petroleum, paraffin, and the pyrogenic vapours from caoutchouc and paper have a very marked positive action. On the other hand, mercury, oxygen, iron, iodine, sulphur, sulphur dioxide, hydrogen sulphide, silicon hydride, ammonia, arsine, and stibine have no appreciable effect. Subsequent experiments are therefore performed in general with the addition of coal gas which is purified by successive treatment with concentrated sulphuric acid, alkaline sodium hyposulphite solution, potassium hydroxide (50%), calcium chloride, and phosphorus pentoxide. The arrangement of the apparatus is sketched and described in detail in the original. The product, which is condensed by liquid air, contains the metallic hydride mixed with a relatively large excess of hydrocarbons or the products derived from them under the action of the electric discharge, and the mixtures cannot be approximately separated by any available process of fractionation. It is therefore necessary to elaborate a method for the analysis of minute amounts of metallic hydride in the presence of an indefinite mixture of hydrocarbons. This is effected by decomposing the hydride by heat and measurement of the pressure of the resultant gases; the latter are cooled by liquid air, whereby only the hydrogen remains in the gaseous condition, and this is then absorbed by a heated palladium capillary. The pressure of residual gas is then estimated under the same conditions as previously, the difference in the readings giving the amount of hydrogen. The deposit of metal is weighed. The method gives satisfactory results with stibine and with tin hydride, to which the formula, SnH_4 , is assigned. With lead hydride it is unsatisfactory, since this substance cannot be separated by fractionation from unsaturated hydrocarbons, which subsequently become hydrogenated by the hydrogen derived from the hydride.

Under the experimental conditions adopted, volatile hydrides are formed from lead, bismuth, tin, antimony, tellurium, germanium, arsenic, and selenium, but not from aluminium, zinc, or mercury.

H. W.

Mineralogical Chemistry.

New Hypothesis of the Origin of Natural Fuels. G. CAGNI (*Gazzetta*, 1922, 52, i, 87—93).—The author advances and discusses the view that coal, natural graphite, petroleum, etc., may have had their origin in organic compounds, even of great complexity, existing on the earth long prior to the appearance of life.

T. H. P.

The Constitution of Anthracite. ARTHUR GROUNDS (*J. Soc. Chem. Ind.*, 1922, 41, 88—93t).—Three constituents can be recognised in anthracitic coals, namely fusain, occurring to the extent of about 1% or less, a glossy constituent similar in appearance to the vitrain of bituminous coals and designated ψ -vitrain, which forms the major portion of the seams, and a constituent similar to the clarain of bituminous seams present to the extent of 5—10% at most in the anthracites examined. The fusain was generally soft, porous, and pulverulent, and could be separated from the other constituents by fractional sieving. In certain cases, a harder variety was found associated with the soft fusain, and this contained a higher percentage both of ash and of volatile organic matter than the latter. Whilst the fusain in bituminous seams usually contains less volatile organic matter than the associated coal, the anthracitic fusain sometimes contains more and sometimes less. In one case, the dense fusain contained 23.22% compared with 11.60% for the adjacent ψ -vitrain, calculated on a moisture- and ash-free basis. The ash of fusain varies widely from about 3.0—15.0% and is much higher than the ash of ψ -vitrain, which usually varies from 0.1 to 1.5%. The water-soluble constituent of the ash of ψ -vitrain amounts to 1.7 to 6.9% of the total, and thereby differs widely both from that of vitrain, which usually contains about 70% of water-soluble substance, and of fusain, which varies from 10 to 50%. This variation with fusain is doubtless due to its porous nature, which allows the percolation of saline solutions which deposit their solid matter in the fusain on being subjected to concentration by heat. In all the seams examined, the ψ -vitrain gives an almost constant $\text{Al}_2\text{O}_3 : \text{SiO}_2$ ratio of 1.10, very similar to that of the fusain examined by the author (1.17), but very different from that of the ordinary vitrain of bituminous seams (2.55).

G. F. M.

Some Constituents of Lignites. II. R. CIUSA and M. CROCE (*Gazzetta*, 1922, 52, i, 125—128; cf. A., 1921, ii, 343).—The various natural organic compounds found in lignites may be grouped, according to their melting points, in the following classes: (1) fictelite, m. p. 46°; dinite, m. p. 35°; and scheerite, m. p. 44°; (2) simonellite, m. p. 62°; (3) konleinite, m. p. 108—114°; (4) branchite, m. p. 75—81°; bombicite, m. p. 75°; hartite, m. p. 75°; the hydrocarbon of Terni lignite (*loc. cit.*), m. p. 75°, and hofmannite, m. p. 71°.

The authors find that, when purified, all the substances of group (4), as well as mixtures of them, have m. p. 74—75°, and all have compositions and molecular weights corresponding with the formula $C_{20}H_{34}$.

The dihydrocamphene, $C_{20}H_{34}$, m. p. 74—75°, obtained by Étard and Méker (A., 1898, i, 443), and by Houben (A., 1906, i, 21), has been prepared by various methods and is found to have m. p. 85—86° (cf. Hesse, A., 1906, i, 375), its mixture with hartite having m. p. 52°.

T. H. P.

Fossil Wax of Monte Falò. R. CIUSA and R. VOIS (*Gazzetta*, 1922, 52, i, 135—136).—This wax, m. p. 47—49° (crude), 50—52° (purified), contains the paraffin hydrocarbons $C_{23}H_{48}$, $C_{24}H_{50}$, and $C_{26}H_{54}$, together with higher members of the series, and is free from compounds containing sulphur or oxygen.

T. H. P.

Stasite, a New Mineral Dimorphous with Dewindtite. ALFRED SCHOEP (*Compt. rend.*, 1922, 174, 875—877).—As a dirty yellow material, this occurs mixed with torbernite at Kasolo, Katanga, Belgian Congo. Under the microscope, it is seen to consist of minute, flattened prisms of a golden-yellow colour and with straight extinction, d 5.03. In the oxidising flame it fuses to a black globule, and it is soluble in nitric acid to a yellow solution. The extremes of several analyses made on two lots of material dried at 100° are given under I (also CaO 0.30, MgO trace).

	PbO.	UO ₃ .	P ₂ O ₅ .	Ign.	H ₂ O.	Insol.
I.	25.53—26.20	55.77—56.28	10.32—10.60	6.24—6.71	5.60	0.40—1.17
II.	26.40	57.19	10.68	—	5.70	—

The mean values calculated to 100% given under II correspond with the formula $4PbO, 8UO_3, 3P_2O_5, 12H_2O$, identical with that for dewindtite (this vol., ii, 305). The new mineral is thus dimorphous with dewindtite, differing from it in colour, density, and form of the crystals.

L. J. S.

Aphthitalite from Kilauea. H. S. WASHINGTON and H. E. MERWIN (*Amer. Min.*, 1921, 6, 121—125).—On the walls of hot (about 800°) crevices in new lava are bright blue encrustations of small, hexagonal plates of aphthitalite, which on cooling become nearly white. In cooler parts of the crevices the encrustation consists of thenardite. The aphthitalite is optically uniaxial with ω 1.487, ϵ 1.492; analysis gave

SO ₃ .	Cl.	K ₂ O.	Na ₂ O.	CaO.	CuO.	H ₂ O.	Insol.	Total.
51.50	0.03	23.72	22.76	0.39	0.46	0.25	0.76	99.87

corresponding with K_2SO_4 43.88, Na_2SO_4 52.12, or $K_2SO_4 : Na_2SO_4$ about 1:1.5. The variable composition of aphthitalite and its relation to arcanite (orthorhombic K_2SO_4) are discussed. Anhydrous copper sulphate crystallised from hot sulphuric acid is orthorhombic (pseudo-hexagonal) with β 1.72 and $\gamma - \alpha$ 0.02, and is thus related crystallographically to the alkali sulphates. The alkalis and copper were probably volatilised as sulphides, which in contact with the air are deposited as sulphates.

L. J. S.

A Tantalate and Columbite from South Dakota. WILLIAM P. HEADDEN (*Amer. J. Sci.*, 1922, [v], **3**, 293—299).—Analyses of fragments of brown or greyish-black columbite: I—III, from the Old Mike mica mine in Custer Co.; IV, from Harney City, Pennington Co.; V and VI, from Tin Mountain, Custer Co. Fragments of a black tantalate (presumably tapiolite) gave VII—XIII. Crystals determined to be tapiolite from Prospect (near the Old Mike mica mine) gave XIV.

	Cb ₂ O ₅ .	Ta ₂ O ₅ .	TiO ₂ .	SnO ₂ .*	FeO.	MnO.	Total.	d.
I.	68.00	9.88	0.53	0.88	5.45	14.79	99.53	5.201
II.	67.20	10.10	0.92	0.96	5.96	15.08	100.22	5.421
III.	63.90	13.74	0.80	0.54	5.92	14.95	99.85	5.496
IV.	34.60	46.02	1.52	0.38	13.32	4.31	100.15	6.444
V.	27.22	53.47	1.30	0.44	11.91	5.66	100.00	6.725
VI.	28.81	53.67	1.63	0.38	12.00	5.20	100.69	6.845
VII.	8.63	69.55	1.50	5.29	10.84	4.19	100.00	6.954
VIII.	5.49	76.08	2.84	0.22	14.16	1.21	100.00	7.019
IX.	6.97	77.24	0.81	1.18	13.60	1.02	100.82	7.180
X.	5.56	78.28	1.33	0.28	13.35	1.22	100.62	7.468
XI.	4.32	79.50	0.92	0.32	13.42	1.56	100.04	7.794
XII.	3.69	81.40	0.58	0.12	12.55	1.73	100.07	7.878
XIII.	1.97	83.57	trace	0.10	13.28	1.19	100.10	7.975
XIV.	5.18	77.23	1.38	0.32	14.84	0.42	100.00	7.190

* Including some WO₃; small amounts of cassiterite have been deducted.

From these analyses it is seen that with increasing tantalic acid, not only is there an increase in density, but also iron replaces manganese.

L. J. S.

Analytical Chemistry.

Xylenol-blue and its Proposed Use as a New and Improved Indicator in Chemical and Biochemical Work. ABRAHAM COHEN (*Biochem. J.*, 1922, **16**, 31—34).—The author recommends as an indicator *5-hydroxy-1:4-dimethylbenzenesulphonephthalein* (xylenol-blue), which has an acid range from P_H 1.2 (red) to P_H 2.8 (yellow), and an alkaline range from P_H 8.0 (yellow) to P_H 9.6 (blue). This new indicator possesses several advantages over thymol-blue, in place of which it can be successfully employed.

W. O. K.

Influence of Ethyl Alcohol on the Colour Change of Phenolphthalein. RUDOLF WEGSCHEIDER (*Z. physikal. Chem.*, 1922, **100**, 532—536).—It is shown that the presence of alcohol in acidimetric titrations increases the amount of alkali necessary to produce a colour change with phenolphthalein as indicator. The cause of the slight increase is discussed and it is shown to be probable that a combination of the alcohol with the phenolphthalein explains the experimental results. (Cf. Hildebrand, A., 1909, ii, 25).

J. F. S.

The Application of the Iodine Electrode in Potentiometric Titrations. I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, **41**, 172—191).—When an iodine electrode is used for the titration of an iodide by means of silver nitrate, it is found that in a neutral solution an error of 0.8% occurs, probably due to adsorption. In a solution containing free sulphuric acid the error is negligible, although the potential requires a considerable time to reach constant value. By means of the iodine electrode, an iodide may be titrated with silver nitrate in presence of an equivalent quantity of bromide or twenty times the equivalent of chloride. Mercuric perchlorate is a suitable reagent for accurate titration of iodides; mercuric nitrate in nitric acid solution is useless, as the acid oxidises a portion of the iodide. By using the perchlorate, a quantity of iodide as small as 0.6 mg. may be estimated with accuracy; good results are obtained in presence of an equivalent quantity of bromide or a large excess of hydrochloric acid.

Mercuric chloride may be estimated accurately by the potentiometric method by using the iodine electrode. Other metals have been investigated from this point of view, and it is found that the method is applicable to thallous salts, probably to palladium and some other rare metals, but not to lead or bismuth. H. J. E.

Hydrated Oxalic Acid as an Oxidimetric Standard. ARTHUR E. HILL and THOMAS M. SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 546—557).—The trustworthiness of crystallised oxalic acid as a standard in oxidation processes has been investigated. It is shown that crystals of hydrated oxalic acid as usually prepared from aqueous solution contain several tenths per cent. of included water, which is not entirely lost by four months' exposure to atmospheres of the same aqueous tension as the crystals or higher. Crystals superficially dry will lose this included water in about twenty-four hours if ground to pass a 100-mesh sieve and set in an atmosphere of an aqueous tension in equilibrium with the hydrate. A mixture of the hydrated and anhydrous oxalic acid is the only desiccating agent giving an aqueous tension in equilibrium with the hydrate at all temperatures. The powdered hydrate can be dried in about an hour in a current of air passed over this desiccating agent, so that its oxidimetric value agrees with that of sodium oxalate within 0.025%. J. F. S.

Pipettes. VERNEY STOTT (*J. Soc. Glass Tech.*, 1921, **5**, 307—325).—Pipettes should be adjusted for a particular time of delivery, and when testing pipettes it is important to record both the time of delivery and the capacity. The time required for the delivery of the contents of the pipette should be within certain limits, since pipettes are untrustworthy if the time of delivery is too short and also if it is too long. A definite time should be allowed for drainage when graduating, testing, or using pipettes. W. P. S.

Device for the Removal of Fumes. M. FISCHLER (*Chem. Zeit.*, 1922, **46**, 224).—A device for the removal of fumes during the oxidation of organic substances with sulphuric and nitric acids

consists of a wide earthenware or sheet-iron tube which is bent so as to enter the flue of a fume chamber; the lower end of the tube is provided with a small siphon trap whilst a wide side-tube receives the neck of the flask in which the material is being treated. A tubulure on the side tube admits the bent stem of a tapped funnel so that further quantities of acid may be added to the flask when necessary. The upper end of the tube may be slotted to receive a burner which aids the draught. W. P. S.

Detection of Oxygen in Organic Compounds. JEAN PICCARD (*Helv. Chim. Acta*, 1922, **5**, 243—244).—It is suggested that the fact that solutions of iodine in solvents free from oxygen are blue, but brown in alcohol, ether, or acetone, can form the basis of a method for the qualitative detection of oxygen in organic compounds. Since the brown colour depends on the formation of an additive compound with the oxygen atom, iodine in excess of this requirement must be avoided. Thus, although benzene containing 2% of ether dissolves iodine with a colour scarcely distinguishable from that obtained with pure benzene, a distinct brown colour is observable on the addition of the same proportion of ether to a solution (almost colourless) of iodine in one million parts of benzene if a layer 90 cm. deep be examined. J. K.

Clinical Method for the Estimation of Chlorides in Blood. HERMAN FRIEND (*J. Biol. Chem.*, 1922, **51**, 115—119).—For clinical purposes, plasma and not whole blood should be used for chloride estimations. In the method described, the plasma is separated immediately to prevent alterations in the distribution, precipitated by shaking with alumina cream, and chlorides estimated in the filtrate by titration with silver nitrate. E. S.

Catalytic Analyses. I. Estimation of Chloric Acid. SHIN-ICHIRO HAKOMORI (*J. Chem. Soc. Japan*, 1922, **43**, 62—70).—This method is based on the fact that the ferrous-ion acts as a catalyst in the reaction between chloric acid and hydriodic acid (Green, *J. Physical Chem.*, 1908, **12**, 389). To a solution containing approximately potassium iodide 10%, ferrous ammonium sulphate 3%, and 0.2% of the sample, about 3*N*-hydrochloric acid is added, and after ten to fifteen minutes the mixture is titrated with sodium thiosulphate solution. K. K.

The Estimation of Total Sulphur in Urine. ROBERT ROBISON (*Biochem. J.*, 1922, **16**, 134—136).—Sulphur can be best estimated in the urine by a modification of Benedict's method. 2.5 C.c. of a solution of copper nitrate (40 grams) and copper chloride (15 grams) in water (100 grams) are added to the urine (10 c.c.) and the mixture is evaporated to dryness, and then heated over a plate or small flame to oxidise the sulphur. After being heated for a further twenty minutes, the residue is dissolved in 2*N*-hydrochloric acid (10 c.c.) and diluted with distilled water (300 c.c.). The oxidised sulphur is then estimated as barium sulphate.

W. O. K.

Analysis of Chlorosulphonic Acid. G. WEISSENBERGER and A. ZODER (*Z. anal. Chem.*, 1922, **61**, 41—48).—Volumetric methods, which depend on the estimation of the total acidity of the sample (after suitable dilution) and subsequent titration of the hydrochloric acid, yield untrustworthy results owing to the fact that the large quantity of sulphate ions present interferes with the titration of the chloride by Mohr's or Volhard's methods. The quantity of chlorosulphonic acid and of free sulphuric acid found is too high and the sulphur trioxide is too low. Gravimetric methods yield correct results for the hydrochloric acid and the sulphuric acid. Fairly correct results are also obtained by distilling the sample and collecting the portion which has b. p. 154—156°.

W. P. S.

Estimation of very small Quantities of Injurious Acids in Air. G. LAMBRIS (*Z. anal. Chem.*, 1922, **61**, 20—40).—Flue gases may contain sulphuric, sulphurous, and hydrochloric acids, which, when allowed to escape into the atmosphere, may have an injurious effect on vegetation. A method for the estimation of these acids consists in passing the air at the rate of about 100 litres per hour for two or three hours through an absorption vessel packed with cotton wool moistened with water and then through a second vessel containing cotton wool moistened with hydrogen peroxide. The sulphuric and hydrochloric acids are absorbed in the first vessel, whilst the sulphurous acid is absorbed and oxidised to sulphuric acid in the second vessel. The contents of the vessels are subsequently titrated and the quantities of the different acids estimated in the usual way. About 10% of the sulphurous acid is retained in the first vessel; this may be removed and conveyed over into the second vessel by means of a current of air free from acidity, or its quantity may be estimated by neutralising the contents of the vessel, using methyl-orange as indicator, then adding hydrogen peroxide, and titrating the sulphuric acid formed by the oxidation of the sulphurous acid. The method is suitable for the estimation of 1 part of acid per 500,000 parts of air.

W. P. S.

Estimation of Sulphate-ion as Barium Sulphate I. K. P. CHATTERJEE (*Z. anorg. Chem.*, 1922, **121**, 128—134).—The author carried out the precipitation under various conditions. The amount of hydrochloric acid added to make the precipitate granular and easily filtered should not exceed 0.1% of the volume of the liquid. Excess of barium chloride is not as detrimental as an excess of hydrochloric acid provided the precipitate is well washed. Rapid precipitation results in a stronger adsorption of the mother-liquor than slow precipitation. Dry barium sulphate gives up the adsorbed chloride more readily than the wet salt.

W. T.

Cathodic Deposition of Tellurium and Selenium from their Oxy-acids and their Electroanalytical Estimation. ERICH MÜLLER [with MENZEL and SCHUBERT] (*Z. physikal. Chem.*,

1922, **100**, 346—366).—The detection of selenium and tellurium may be effected as follows: (a) selenium:—2 c.c. of the solution containing selenium is treated with 3 drops of concentrated sulphuric acid and a few small crystals of hydrazine sulphate and heated. A red coloration or precipitate indicates the presence of selenium. This reaction is sensitive to 5 mg. of selenium per litre; (b) tellurium:—1 c.c. of solution with 1 c.c. of concentrated ammonia and a few crystals of hydrazine sulphate when boiled give a brown coloration or precipitate if tellurium is present. This reaction is sensitive to 10 mg. of tellurium per litre; (c) selenium and tellurium in the same solution:—3 c.c. of solution are treated with 3 drops of concentrated sulphuric acid and a little hydrazine sulphate and boiled, a red coloration of selenium results; this is filtered, the filtrate made alkaline with ammonia, more hydrazine sulphate added, and the solution again boiled; a brown coloration indicates tellurium; (d) selenious acid in the presence of selenic acid:—3 c.c. of the solution are treated with 5 c.c. of concentrated sulphuric acid and a little sodium sulphite and boiled; a red precipitate or coloration indicates selenious acid. The reaction is sensitive to 5 mg. of selenium per litre. After filtration, 3 c.c. of concentrated hydrochloric acid and more solid sodium sulphite are added and the solution is boiled; a red precipitate or coloration indicates selenic acid; the sensitiveness is the same as above; (e) tellurous acid in the presence of telluric acid: these two acids cannot be detected in the presence of one another by simple reduction, since both acids are reduced, although at different rates. On electrolysis in sulphuric acid solution, the tellurous acid alone is reduced, and when this is complete the solution is concentrated and boiled with hydrochloric acid and sodium sulphite, when a brown precipitate or coloration indicates telluric acid. The cathodic decomposition potential of tellurous acid in 2*N*-sulphuric acid is -0.08 volt. No deposition potential could be obtained for tellurium from a 2*N*-sulphuric acid solution of telluric acid, from which it follows that tellurium cannot be deposited from telluric acid. A simple decomposition potential could not be observed for selenium from selenious acid, although selenium was seen to be deposited at about 0.05 volt, but the first selenium deposited appears to act as an insulating diaphragm and prevents further deposition; when the voltage is raised so that hydrogen is liberated, the selenium leaves the electrode in flakes. On adding copper sulphate to the sulphuric acid solution of selenious acid, the selenium and copper are deposited together in a conducting form at $+0.15$ volt, so that all the selenium may be deposited at this potential. Selenium cannot be electrolytically deposited from selenic acid on platinum either at 20° or 80° . Tellurium in tellurous acid may be quantitatively estimated as follows. A maximum weight of 0.25 gram of tellurous acid is dissolved in 175 c.c. of 2*N*-sulphuric acid and electrolysed for two and a half hours between two platinum Winkler electrodes which are connected directly with a single lead accumulator. The solution must be rapidly stirred during the electrolysis. The deposit, which is uniformly dense and grey, is washed with water and alcohol

and dried over sulphuric acid in a desiccator. The average error of the method is $\pm 0.1\%$. Tellurous acid may be estimated in the presence of telluric acid by this method, and after the tellurium from the tellurous acid has been removed the solution is boiled with hydrochloric acid to reduce the telluric acid to tellurous acid, and the estimation of this then carried out as before. Selenium may be estimated in selenious acid as follows. A quantity of selenious acid containing not more than 0.07 gram of selenium is dissolved in 2*N*-sulphuric acid and mixed with a quantity of copper sulphate in 2*N*-sulphuric acid such that the concentration of copper is four times that of the selenium, and electrolysed for two hours at the ordinary temperature with rapid stirring between two Winkler platinum electrodes which are connected directly with a single lead accumulator. The deposit of copper and selenium is washed with water and alcohol and carefully dried. The weight of the copper is known from the amount of copper sulphate solution used. The method is good, but suffers in accuracy on account of the small amount of selenium which may be used in a determination. Several attempts are described which were designed for the estimation of selenious acid in the presence of tellurous acid, but all failed to give the desired result. J. F. S.

The Estimation of Nitrogen in Nitric Esters. H. KESSELER, R. RÖHM, and G. LUTZ (*Z. angew. Chem.*, 1922, **35**, 145).—The esters are saponified at 40—50° with aqueous potassium hydroxide (1 : 1), the nitrates and nitrites so obtained reduced to ammonia with Devarda's alloy (50% copper, 45% aluminium, and 5% zinc), and the ammonia distilled into *N*/10-sulphuric acid and titrated back with *N*/10-sodium hydroxide with methyl-red as indicator. The method is specially recommended for nitro-starches, to which other rapid methods cannot be applied. H. C. R.

Colorimetric Estimation of Phosphorus. LUIGI LOSANA (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 60—62).—The method developed by the author (cf. Namias, *Stahl und Eisen*, 1890) is based on the observation that treatment of ammonium phosphomolybdate with hot sodium thiosulphate solution yields a liquid coloured intensely blue owing to the formation of molybdenum compounds which have not been identified. The optimum conditions have been fixed and two colorimeters designed, one for low and the other for moderately high percentages of phosphorus. [Cf. *J. Soc. Chem. Ind.*, 1922, May.] T. H. P.

A Rapid Colorimetric Method for the Estimation of the Inorganic Phosphorus in Small Amounts of Serum. FREDERICK F. TISDALL (*J. Biol. Chem.*, 1922, **50**, 329—337).—The estimation is performed on 1 c.c. of serum. Proteins are removed by means of trichloroacetic acid, and the inorganic phosphates then precipitated as strychnine phosphomolybdate by the addition of a strychnine molybdate reagent (cf. Embden, A., 1921, ii, 462). After centrifuging and washing with the minimum amount of water, the precipitate is dissolved in 1% sodium hydroxide,

diluted, and the colour produced on reduction with 20% potassium ferrocyanide and concentrated hydrochloric acid compared with a standard. The error does not exceed 5%. E. S.

Gravimetric Estimation of Hydrogen Phosphide and a New Apparatus for Gas Analysis. L. MOSER and A. BRUKL (*Z. anorg. Chem.*, 1921, **121**, 73—94).—The reactions of phosphine with solutions of iodic acid, silver nitrate, mercuric chloride, gold chloride, and copper sulphate have been investigated with the object of finding a gravimetric method for the estimation of high concentrations of phosphine. The various methods for estimating small quantities of phosphine are discussed. Phosphine containing only a few per cent. of hydrogen is best prepared by the action of 1 : 10-sulphuric acid on aluminium phosphide, and gas obtained by this method was used in all analyses described. When phosphine is led into a 2*N*-solution of iodic acid, the gas is completely absorbed, but occasionally a small amount of fog, due to the inflammable hydride, is formed; this, however, is completely absorbed in half an hour. The solution is then heated and a current of carbon dioxide passed through until all the iodine has been distilled into a solution of potassium iodide. The amount of iodine is determined by titration with thiosulphate, and the phosphoric acid left in the flask estimated as magnesium pyrophosphate. The results obtained in both cases are identical. The reaction is represented by the equation $8\text{HIO}_3 + 5\text{PH}_3 = 5\text{H}_3\text{PO}_4 + 4\text{I}_2 + 4\text{H}_2\text{O}$. The error is a little more than 0.1%. Phosphine is shown to react with excess of silver nitrate in stages according to the equations : (1) $3\text{AgNO}_3 + \text{PH}_3 = \text{PAg}_3 + 3\text{HNO}_3$; (2) $\text{PAg}_3 + \text{AgNO}_3 + 2\text{H}_2\text{O} = \text{H}_3\text{PO}_2 + 4\text{Ag} + \text{HNO}_3$; (3) $\text{H}_3\text{PO}_2 + 2\text{AgNO}_3 + \text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 2\text{Ag} + 2\text{HNO}_3$; (4) $\text{H}_3\text{PO}_3 + 2\text{AgNO}_3 + \text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 2\text{Ag} + 2\text{HNO}_3$. The total action is therefore represented by the equation $8\text{AgNO}_3 + \text{PH}_3 + 4\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 8\text{Ag} + 8\text{HNO}_3$. By the action of a cold saturated solution of silver acetate added drop by drop to a vessel through which a steady stream of phosphine is added, the authors have been able to prepare *silver phosphide*, PAg_3 . This substance is an easily oxidisable, velvety, black powder which cannot be dried without decomposition; it is not decomposed by air-free cold water, but in water containing air it decomposes into metallic silver. It is rapidly decomposed by boiling water, concentrated nitric acid, warm hydrochloric acid with the liberation of phosphine, and concentrated sulphuric acid with the liberation of sulphur dioxide. The estimation of phosphine by means of silver nitrate takes place in a closed absorptiometer which consists of a bulb (120 c.c. capacity) to the bottom of which a glass tube 10 cm. long and 3 mm. bore is attached, and to the top a capillary tube which is bent twice at right angles for connecting with a gas burette. The capillary carries a tap which, in addition to the ordinary bore, is also bored along its axis. The apparatus is placed with its lower tube in a beaker containing *N*/10-silver nitrate solution and filled with the liquid and the gas drawn in and the apparatus shaken. After fifteen minutes the liquid is all run into the beaker and the apparatus

washed with a little dilute nitric acid and water, and the washings added to the beaker. The solution is then treated with hydrochloric acid, filtered, and the phosphoric acid in the filtrate estimated as magnesium pyrophosphate. The results obtained by this method are in excellent agreement with those obtained by the iodic acid method. The substitution of an ammoniacal solution of silver nitrate for aqueous silver nitrate has no advantage, and attempts to estimate the phosphine by weighing the precipitated silver failed. A $N/5$ -solution of mercuric chloride can be used as absorbent for phosphine. The method of work is the same as described for silver nitrate. The reactions taking place are given by the equations (1) $6\text{HgCl}_2 + 2\text{PH}_3 = 3\text{HgCl}_2 \cdot \text{P}_2\text{Hg}_3 + 6\text{HCl}$; (2) $6\text{HgCl}_2 + \text{PH}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 6\text{HCl} + 6\text{HgCl}$; (3) $8\text{HgCl}_2 + \text{PH}_3 + 4\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 8\text{HCl} + 8\text{HgCl}$. When the absorption is complete, the liquid and precipitate are boiled with bromine water, the mercury is removed by hydrogen sulphide, and the phosphoric acid determined as magnesium pyrophosphate. The results are uniformly good. A $N/5$ -solution of gold chloride is a good absorbent for phosphine; the method employed is the same as described above. The following reactions occur during the absorption: (1) $3\text{AuCl}_3 + \text{PH}_3 + 3\text{H}_2\text{O} = 3\text{AuCl} + \text{H}_3\text{PO}_3 + 6\text{HCl}$; (2) $4\text{AuCl}_3 + \text{PH}_3 + 4\text{H}_2\text{O} = \text{H}_3\text{PO}_4 + 4\text{AuCl} + 8\text{HCl}$; (3) $3\text{AuCl} + \text{PH}_3 = \text{Au}_3\text{P} + 3\text{HCl}$; (4) $3\text{Au}_3\text{P} + \text{AuCl}_3 + 6\text{H}_2\text{O} = 10\text{Au} + 3\text{H}_3\text{PO}_2 + 3\text{HCl}$; (5) $3\text{H}_3\text{PO}_2 + 2\text{AuCl}_3 + 3\text{H}_2\text{O} = 2\text{Au} + 3\text{H}_3\text{PO}_3 + 6\text{HCl}$; (6) $3\text{H}_3\text{PO}_3 + 2\text{AuCl}_3 + 3\text{H}_2\text{O} = 2\text{Au} + 3\text{H}_3\text{PO}_4 + 6\text{HCl}$. The total and completed action is represented by the equation $8\text{AuCl}_3 + 3\text{PH}_3 + 12\text{H}_2\text{O} = 8\text{Au} + 24\text{HCl} + 3\text{H}_3\text{PO}_4$. After the action is completed, the gold in solution is precipitated by hydrogen sulphide, filtered, and the phosphoric acid in the filtrate estimated as above after oxidation by bromine water. A $N/5$ -solution of copper sulphate is a good but much slower absorbent for phosphine than the other salts mentioned. The analysis, using this salt, is carried out as in the case of gold. The absorption occurs according to the equations: (1) $3\text{CuSO}_4 + \text{PH}_3 + 3\text{H}_2\text{O} = \text{H}_3\text{PO}_3 + 3\text{Cu} + 3\text{H}_2\text{SO}_4$; (2) $4\text{CuSO}_4 + \text{PH}_3 + 4\text{H}_2\text{O} = 4\text{Cu} + \text{H}_3\text{PO}_4 + 4\text{H}_2\text{SO}_4$; (3) $3\text{CuSO}_4 + 2\text{PH}_3 = \text{Cu}_3\text{P}_2 + 3\text{H}_2\text{SO}_4$; (4) $\text{Cu}_3\text{P}_2 + 3\text{Cu} = 2\text{Cu}_3\text{P}$.
J. F. S.

Estimation of Krypton and Xenon in Absolute Values by Spectrophotometry. CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1922, **174**, 908—913).—A modification of previous work (A., 1911, ii, 439, 1134). The authors have prepared mixtures of pure argon with differing amounts of pure krypton on the one hand and pure xenon on the other. For the mixtures containing krypton, the pressures at which the intensity of the line $\lambda = 5870.91$ of the krypton is just equal to that of the argon lines $\lambda = 5860.54$ and 5912.31 respectively have been determined for each mixture. For the xenon mixtures, the xenon line $\lambda = 4671.22$ and the argon line $\lambda = 4702.5$ have been used. These figures thus give a means of calculating the amounts of krypton or xenon in argon-krypton and argon-xenon mixtures respectively. The limits of dilution at which measurements can be made are for krypton $0.5-4.5 \times 10^{-3}$

and for xenon $2-8 \times 10^{-4}$. If the mixture to be examined contains too much krypton or xenon, it must first be diluted with pure argon, but if it is too dilute it must be concentrated by fractionation, using coconut charcoal.

W. G.

Estimation of Carbon in Cast Iron and Steel by Corleis's Apparatus. G. BATTA and H. THYSSEN (*Bull. Soc. chim. Belg.*, 1922, **31**, 112—117).—By means of a number of blank experiments, errors in the estimation have been traced to incomplete drying of the gas before absorption of the carbon dioxide by alkali. Detailed experimental methods based on a considerable number of analyses have been worked out and are recommended.

H. J. E.

Rapid Analysis of Potassium Perchlorate. VICTOR LENHER and MARTIN TOSTERUD (*J. Amer. Chem. Soc.*, 1922, **44**, 611—612).—The following method is described as the most satisfactory for the estimation of perchlorate. A 0.5 gram sample is mixed in an agate mortar with 1.0 gram of manganese dioxide, transferred to a porcelain crucible, and heated for fifteen minutes at $600-700^{\circ}$. After cooling, the mass is extracted with hot water, filtered, and the chlorine determined by either Mohr's or Volhard's method. The results are about 0.2—0.3% low, due to loss by volatilisation. A blank experiment with the manganese dioxide should always be carried out. Greater accuracy is obtained by Lamb and Marden's method (*A.*, 1912, ii, 681) of heating the perchlorate alone in a glass tube and retaining the fumes evolved with a plug of asbestos.

J. F. S.

Estimation of Sodium in Serum without the Use of Platinum Dishes. S. J. WILSON (*J. Biol. Chem.*, 1922, **50**, 301—302).—In the estimation of sodium as pyroantimonate by Kramer and Tisdall's method (*A.*, 1921, ii, 463), the precipitation may be carried out in tinned dishes, in place of platinum ones, without loss of accuracy.

E. S.

Effect of Hydrogen-ion Concentration on the Estimation of Calcium. ALFRED T. SHOHL (*J. Biol. Chem.*, 1922, **50**, 527—536).—In the estimation of calcium in the presence of magnesium and phosphates by McCrudden's method (*A.*, 1910, ii, 243; 1911, ii, 1136) the hydrogen-ion concentration must be kept within the limits P_H 4.0 and P_H 5.6. With a more acid solution, calcium oxalate dissolves, whilst with a less acid one magnesium ammonium phosphate is precipitated.

E. S.

A Rapid and Accurate Method for estimating Calcium in Urine. ALFRED T. SHOHL and FRANK G. PEDLEY (*J. Biol. Chem.*, 1922, **50**, 537—544).—Uric acid and other substances present in the urine which would interfere with the titration by permanganate are oxidised by boiling with ammonium persulphate after acidification with nitric or sulphuric acid. The calcium is then precipitated by addition first of oxalic acid and then of ammonia until neutral to methyl-red, which brings the solution to P_H 4.8—5.3 (cf. preceding abstract). After remaining over-night, the precipitate is filtered

on to a hardened filter-paper, washed, transferred to the original flask, and the calcium oxalate estimated by titration with permanganate. E. S.

The Analytical Chemistry of Colloidal Disperse Systems. I. Estimation of Silver Ion in the Presence of Colloidal Silver. A. GUTBIER, J. HUBER, and O. KUPPINGER (*Ber.*, 1922, 55, [B], 748—752).—The method depends on the precipitation of the protected metallic colloid in reversible form by the addition of methyl alcohol and titration of the silver remaining in solution by Volhard's method. To avoid adsorption of silver ions by the precipitate, it is necessary, before precipitation, to convert the dissolved silver into the complex form, which can be most conveniently effected by means of solid ammonium carbonate.

A measured volume of the protected colloidal system, prepared at the atmospheric temperature and in the dark, is agitated with a corresponding excess of pure solid ammonium carbonate until the salt is completely dissolved and the precipitated silver carbonate has again passed entirely into solution. The mixture is slowly poured into methyl alcohol which has been freshly distilled over lime, after which it is allowed to remain at rest for about twenty-four hours until the precipitate has completely subsided. The supernatant liquid should now be colourless. The precipitate is carefully washed with alcohol by decantation and finally on the filter. The filtrate and washings are united, freed from alcohol by evaporation on the water-bath, cooled, acidified with nitric acid, and titrated according to Volhard's method. H. W.

The Preparation of Lead Test-papers and Notes on the Titration of Zinc with Sodium Sulphide. E. OLIVIER (*Bull. Soc. chim. Belg.*, 1922, 31, 102—109).—Experimental details of the method used in the author's laboratory for titrating zinc solutions are described and instructions for making and testing the lead papers used as indicators given. The presence of free ammonia, owing to its solvent action on zinc sulphide, introduces an error; the substance should be removed by boiling or by neutralisation. Further, ammonium salts should not be present in excess, otherwise the clearness of the end-point is impaired. H. J. E.

Estimation of Zinc as Sulphate. A. GUTBIER and K. STAIB (*Z. anal. Chem.*, 1922, 61, 97—103).—Zinc salts may be converted into sulphate by evaporation with sulphuric acid in a platinum basin, heating the residue at about 500° for fifteen minutes, cooling it, adding a small quantity of water, and repeating the evaporation and heating; the residue then consists of anhydrous zinc sulphate, and may be weighed as such; zinc sulphate does not dissociate below 675°. If desired, the sulphate may be heated over a blast-flame until no further loss in weight occurs, and the resulting zinc oxide weighed. W. P. S.

Rapid Analysis of White Metal and Similar Alloys. L. BERTIAUX (*Ann. Chim. Analyt.*, 1922, 4, 77—79).—Antimony is

estimated in one portion by solution of the sample in sulphuric acid followed by titration with permanganate. A second portion of 10 grams is mixed with fine tin filings equal to ten times the antimony content of the alloy and the mixture is treated with sufficient nitric acid to dissolve everything. The resulting mass is boiled with a large quantity of water to precipitate completely the tin and antimony, the liquid is cooled, made up to bulk, and an aliquot part filtered through a dry paper and used for the estimation of the other metals by any convenient process. The tin is determined by difference. [Cf. *J. Soc. Chem. Ind.*, 1922.]

A. R. P.

Estimation of Aluminium in Tungsten. VICTOR FROBOESE and KÄTHE FROBOESE (*Z. anal. Chem.*, 1922, **61**, 107—110).—About 3 grams of the finely divided metal are ignited in a platinum crucible for one hour, then fused with the addition of a mixture of potassium carbonate and sodium carbonate, and cooled; the mass is dissolved in water, and the solution filtered. The filtrate, which may contain a trace of aluminium, is evaporated nearly to dryness, acidified with hydrochloric acid, evaporated, the dry residue treated with dilute hydrochloric acid and water, and the solution filtered; this filtrate is boiled, rendered alkaline with sodium hydroxide, again acidified, the aluminium is precipitated as hydroxide by the addition of ammonia, and the precipitate is collected, ignited, and weighed. The main quantity of the aluminium remains in the insoluble portion from the carbonate fusion; this insoluble portion is ignited in a platinum crucible, heated with hydrofluoric acid and a drop of sulphuric acid, fused with potassium pyrosulphate, the mass dissolved in water and sulphuric acid, and the solution filtered. The filtrate is treated with "cupferron" reagent to precipitate the iron, and the aluminium is then precipitated in the usual way in the filtrate from the iron precipitate. W. P. S.

Estimation of Free Acid in Acid Aluminium Sulphate Solutions. H. ZSCHOKKE and L. HÄUSELMANN (*Chem. Ztg.*, 1922, **46**, 302).—The following modification of Ivanov's method (*A.*, 1913, ii, 343, 1078) is recommended. Ten c.c. of the aluminium sulphate solution, 10 c.c. of barium chloride solution (1 : 10), 5 c.c. of potassium ferrocyanide solution (1 : 10) which must not be more than six days old, and 60 c.c. of boiling water are poured in the above order into a 100 c.c. flask. A gelatin solution (1 : 50) is added drop by drop with agitation until the precipitate that is formed becomes flocculent and settles easily. The mixture is cooled and diluted to 100 c.c., allowed to settle, and filtered. Fifty c.c. of the clear, colourless filtrate are diluted with 50 c.c. of water and titrated with *N*/10-sodium hydroxide until neutral to methyl-orange. The temperature of the solution must never exceed 85°, and the excess of potassium ferrocyanide must not be too great, or low results will be obtained. If the quantity of acid present be more than 6 grams per litre, the filtrate remains cloudy, when a few drops of *N*/10-sodium hydroxide should be added before precipitation. H. C. R.

Estimation of Manganese as Sulphate. J. HUBER (*Z. anal. Chem.*, 1922, **61**, 103—107).—Manganese sulphate is rendered anhydrous by heating it at 360—400°; dissociation commences only at 650°.

W. P. S.

Estimation of Manganese by Permanganate and Investigation of some Manganites. P. B. SARKAR and N. R. DHAR (*Z. anorg. Chem.*, 1922, **121**, 135—155).—The authors find that manganese can be accurately estimated by permanganate if one of the following salts is present: magnesium sulphate, potassium nitrate, potassium sulphate, cadmium sulphate, sodium nitrate, potassium fluoride, sodium acetate and lithium, sodium, calcium, barium, and strontium chlorides. Some of the metals of these salts form manganites, others simply coagulate the hydrated manganese dioxide formed and thus make possible a sharp end-point. Coloured salts cannot be used, neither did the titrations succeed in the presence of such sparingly soluble salts as calcium phosphate or sulphate, etc., because the concentration of electrolyte is too small. The preparation, composition, and properties of several manganites are described, and the formation of manganites and the position of the metal in the periodic system discussed. Absolutely pure hydrated manganese dioxide can be prepared by heating a solution of manganous sulphate and sodium nitrate and gradually adding potassium permanganate to the well-stirred mixture. The precipitate is filtered and well washed with hot water.

W. T.

The Estimation of Manganese by Knorre's Persulphate Method. P. NICOLARDOT, M. GELOSO, and E. RÉGLADE (*Ann. Chim. Analyt.*, 1922, **4**, 69—77, 102—110).—Manganese dioxide, precipitated from sulphate solutions by boiling with ammonium persulphate, contains less than the theoretical amount of oxygen unless at least nine times as much iron is present, and if the precipitate is dissolved in ferrous sulphate solution and the excess of the latter titrated with permanganate, the manganese factor of the permanganate varies from $0.498 \times \text{iron factor}$ with pure solutions of manganese sulphate to $0.49176 \times \text{iron factor}$ when the original solution contains a large excess of iron. Variations in the acidity of the solution have very little effect, especially in the presence of iron, as long as the free acid does not exceed 5%; in any case, traces of manganese remain in the mother-liquor and should be estimated by boiling the solution with a further quantity of persulphate and a little silver nitrate and titrating the permanganate so formed with standard sodium arsenite. Of the common metals likely to be present in the solution, cobalt gives very, and nickel slightly, high results. Instructions are given for estimating manganese in ferromanganese and spiegeleisen. [Cf. *J. Soc. Chem. Ind.*, 1922, May.]

A. R. P.

Titration of Tin with Ferric Chloride. L. SMITH (*Z. anal. Chem.*, 1922, **61**, 113—120).—The hydrochloric acid solution of the tin salt is boiled, pieces of zinc foil are added, and, after about

ten minutes, the mixture is again boiled, and a further quantity of zinc is added, followed by hydrochloric acid. When all the metal is in solution, hot water is added slowly so that the boiling is not interrupted, and the solution is then titrated with ferric chloride solution. The end-point of the titration is denoted by the appearance of a greenish-yellow coloration. About 5 grams of zinc are required for each gram of tin to be reduced, and zinc is preferable to aluminium for the purpose.

W. P. S.

Micro-analysis of Organic Substances. G. WELTER (*Ann. Chim. Analyt.*, 1922, **4**, 33—37).—Micro-chemical methods may be used for the estimation of carbon, hydrogen, nitrogen, halogens, sulphur, methoxyl groups, phosphorus, etc., in organic substances; these methods are described briefly. Only a few mg. of the substance are required for an estimation, but all weighings must be made on a balance sensitive to 0.001 mg. The error in the results obtained is about 0.5%.

W. P. S.

The Estimation of Aromatic Hydrocarbons in Mineral Oil Fractions. H. I. WATERMAN and J. N. J. PERQUIN (*Rec. trav. chim.*, 1922, **41**, 192—198).—An attempt to apply the "aniline point" method of Tizard and Marshall (*A.*, 1921, ii, 280) to the estimation of aromatic hydrocarbons in various mineral oils and their products shows that the nature of the fraction influences the result considerably. Experiments carried out with oils containing added benzene, naphthalene, and phenanthrene show that addition of equal weights of these substances does not produce equal effects on the "aniline point."

H. J. E.

Estimation of Glycerol by the Dichromate Method. J. KELLNER (*Z. deut. Oel-Fett-Ind.*, 1921, **14**, 751—752; cf. Steinfels, *Seifensieder Ztg.*, 1915, **42**, 721; Tortelli and Ceccherelli, *A.*, 1914, ii, 750).—Analysis of glycerol by Steinfels's (*loc. cit.*) dichromate method gives low results unless sulphuric acid, *d* 1.230, is used instead of that of *d* 1.175.

CHEMICAL ABSTRACTS.

Physiology of the Phenols. I. The Estimation of Phenols in the Blood. K. F. PELKAN (*J. Biol. Chem.*, 1922, **50**, 491—497).—The method of Folin and Denis (*A.*, 1912, ii, 1011) is modified and made applicable to blood. No heat is used in the precipitation of proteins and the concentration of filtrates, since this would cause a loss of volatile phenols. The estimation is performed on 10 c.c. of blood. Proteins are removed by shaking with tungstic acid and alumina cream, and the uric acid is precipitated by the addition of a solution of silver lactate in lactic acid. Free phenols are then estimated colorimetrically in one portion of the filtrate, using a phosphotungstic-phosphomolybdic reagent, whilst in a second portion the estimation is performed after heating for ten minutes on a water-bath with a few drops of concentrated hydrochloric acid. If the last operation is carried out in a narrow tube no loss of volatile phenols occurs and the difference between the two results then represents conjugated phenols. Since lactic acid gives a coloration with the phosphotungstic-phosphomolybdic

reagent, the standard must be treated with a corresponding amount of the silver lactate reagent (cf. Benedict and Theis, A., 1918, ii, 461). E. S.

Detection of β -Naphthol in Foods, Spices, and Beverages.

YUTAKA KINUGASA and HISAJIRÔ TATSUNO (*J. Pharm. Soc. Japan*, 1922, 18—24).—The method is based on Riegler's method for the detection of nitrous acid (A., 1897, ii, 464). When a solution (1 c.c.) suspected to contain β -naphthol is treated with 2 drops of 0.1% sodium 1:4-naphthylaminesulphonate solution, 1 drop of 0.1% nitrous acid, and 1 drop of hydrochloric acid, shaken, and ammonia added, a red coloration is produced. The colour occurs with 1/1000 mg. of β -naphthol per litre. Colorations are also given by this reagent with the following substances in concentration of 1/100,000: α -naphthol, violet-red; resorcinol, quinol, phloroglucinol, pyrogallol and thymol, all yellow; phenol, orange-red; benzoic and cinnamic acids, almost colourless, and salicylic acid, slight yellow. [Cf. *J. Soc. Chem. Ind.*, 1922, May.] K. K.

Distillation Method for the Estimation of Santalol in Santal Oil. C. W. HARRISON (*J. Assoc. off. Agric. Chem.*, 1921, 5, 166—171).—In the U.S. Pharmacopœia method for estimating santalol in santal oil, the latter is acetylated and a known quantity of the dry product saponified. From the amount of alkali required to saponify the oil, the percentage of santalol present in the original substance is calculated by means of a formula given. When the santal oil is adulterated with a saponifiable oil, the method is not applicable. A modified method, which, however, is not yet completely standardised, is suggested. It consists in acidifying the product obtained after the saponification of the acetylated oil, distilling in a current of steam under specified conditions, and estimating by titration the acidity of the distillate. From this figure the percentage of santalol in the original oil can be calculated. [Cf. *J. Soc. Chem. Ind.*, 1922, 346A.] J. R.

The Estimation of Small Quantities of Dextrose by Bertrand's Process. IRENE GREINER (*Biochem. Z.*, 1922, 128, 274—278).—Accurate results for the estimation of quantities of dextrose less than 10 mg. are obtained by Bertrand's process, if 10 c.c. of the sugar solution are taken, mixed with 10 c.c. of the copper sulphate solution and 10 c.c. of a solution containing 150 grams of sodium carbonate and 30 grams of sodium hydrogen carbonate per litre are added, followed by 10 c.c. of the sodium potassium tartrate solution, and the process carried out in the standard manner, except that, after boiling the solution for three minutes, it is allowed to cool for fifteen minutes. For the titration the use of a 5 c.c. burette graduated in 1/50 or 1/100 c.c. is recommended. A table showing mg. of copper equivalent to 1 to 10 mg. of dextrose is given. H. K.

A Colorimetric Method for the Estimation of Sugars in Normal Human Urine. OTTO FOLIN and HILDING BERGLUND (*J. Biol. Chem.*, 1922, 51, 209—211).—Reducing substances are

removed from the urine by treatment with "Lloyd's alkaloidal reagent," which is described as a concentrated fullers' earth. The sugars are then estimated in the filtrate by the method of Folin and Wu (A., 1920, ii, 337). For total sugar, a separate portion of the filtrate is first hydrolysed by boiling with hydrochloric acid.

E. S.

Inhibition Phenomena in Amylases. URBAN OLSSON (*Z. physiol. Chem.*, 1922, **119**, 1—3; cf. this vol., i, 390).—A method for measuring the liquefaction of starch is based on the principle of recording the time taken by a glass ball to drop in the starch solution contained in an evacuated tube.

S. S. Z.

The Estimation of Pectin as Calcium Pectate and the Application of this Method to the Estimation of the Soluble Pectin in Apples. MARJORY HARRIOTTE CARRÉ and DOROTHY HAYNES (*Biochem. J.*, 1922, **16**, 60—69).—Pectin can be estimated as calcium pectate, empirical formula $C_{17}H_{22}O_{16}Ca$, by precipitation with calcium chloride and hydrochloric acid under determined conditions. A method is described for the extraction of the soluble pectin from apples, and some analytical results are given.

W. O. K.

A Reaction of Wood and some Observations on Anethole. OSKAR ADLER (*Biochem. Z.*, 1922, **128**, 32—34).—All varieties of wood when warmed with a glacial acetic acid solution of phenylhydrazine hydrochloride become coloured green, adhering fragments of bark becoming reddish-brown. The colours fade on prolonged warming. Furfuraldehyde (but not pentoses), oil of anise, and oil of fennel give this green coloration. Anethole is a constituent of these oils and gives the coloration when of commercial purity, but when pure does not. The constituent responsible for the reaction has not been traced, but it distils over with anethole and is produced from anethole by oxidising agents, by the action of ultra-violet light, and by prolonged heating. Known oxidation products of anethole and allied substances do not give the reaction.

H. K.

The Analysis of Partly Hydrolysed Fats. II. W. FAHRION (*Chem. Umschau*, 1922, **29**, 54—55, 60—61, 66—67, 75—76, 88—89).—In using the factor $(100 \times \text{acid number})/(\text{saponification number})$ for calculating the percentage of free fatty acids in a sample of partly hydrolysed fat, it is assumed (1) that the saponification value of the neutral fat is the same as the acid value of the fatty acids obtained from it, and (2) that the free fatty acids have no ester value, their acid value being the same as their saponification value. Neither of these assumptions is justified. The former assumption overlooks the fact that the weight of fatty acids obtained is only about 95% of the weight of fat treated, and involves an error in the percentage of free fatty acids amounting to a maximum of +1.1% when there are 50% present. That the latter assumption is not justified is shown by a list of acid values and saponification values of the fatty acids of various oils and fats. In almost every

case the saponification value is higher than the acid value, the difference being more than 10 units in the case of the fatty acids from cotton seed, apricot kernel, cherry kernel, walnut and linseed oils, and palmitic and oleic acids, especially when the oils or fatty acids have been stored for long periods in the light. This difference is shown to an even greater degree by the fatty acids of kapok and baobab oils and by those of certain marine oils. It has been explained by supposing a linking up of carbonyl groups with ethylenic linkings, but the case of palmitic acid cannot be explained in this way. A third assumption made in using the above formula is that the various glycerides in a fat are all split at the same rate. This is approximately true in the case of alkaline saponification, but it is doubtful if this is so in that of hydrolysis with steam, castor seed lipase, or hydrochloric acid. For example, castor seed lipase scarcely attacks triacetin and hydrolyses tributyrin incompletely, and the neutral fat from a sample of palm kernel oil partly hydrolysed by steam under pressure showed a markedly lower saponification number than the free fatty acids. Therefore the quantity of free fatty acids in partly hydrolysed fats cannot be calculated from the acid number, because the acid number of the fatty acids can appreciably fall both during the process and afterwards.

H. C. R.

The Analysis of Sour Milk. ANDRÉ KLING and ARNOLD LASSIEUR (*Ann. Falsif.*, 1922, **15**, 95—101).—If the state of the milk is such that the sample cannot be made homogeneous, the estimation must be carried out on the whole sample. The "extract at 100°" of a milk no longer fresh must always be suspect, and may be very different from that of the fresh milk. It bears no relation to the appearance of the sample when analysed. The estimation of butter fat is more trustworthy, and varies little with time. The acidity of the fat obtained should, however, be determined to ensure that the glycerides are not partly hydrolysed. The estimation of casein precipitated by acetic acid is quite untrustworthy in the case of sour samples. The estimation of lactose is of doubtful value, but is best done by Hildt's method. The ash is affected by the partial volatilisation of chlorides to the extent of about 2%. The total nitrogen is quite unaffected. It is therefore recommended that decisions on samples of milk which have become sour should be based on estimations of butter fat and total nitrogen.

H. C. R.

A Rapid Method for the Estimation of Acetaldehyde. N. K. SMITT (*Bull. Bur. Bio-Tech.*, 1922, No. 5, 117—118).—Benzidine hydrochloride gives a yellow coloration with acetaldehyde, which increases in intensity with time and finally becomes brown or orange. Formaldehyde gives a similar colour with the reagent, but in this case it develops only slowly. For the estimation of acetaldehyde in solution, the solution is diluted until it contains from 0.1 to 5% and then to 5 c.c. of the diluted solution 5 c.c. of the benzidine hydrochloride solution are added and after thirty

minutes the colour is matched against a set of standard tubes of acetaldehyde to which the reagent was added at the same time. The method is not, however, sufficiently sensitive to be used for the estimation of very small amounts of acetaldehyde. W. G.

Detection of Acetaldehyde in Urine. WILHELM STEPP (*Biochem. Z.*, 1922, **127**, 13—17).—Five % of a diluted urine is distilled through a fractionating column and the vapour absorbed in ice-cold water. The presence of acetaldehyde is best recognised by combination with dimethylhydroresorcinol. H. K.

[Estimation of] Vanillin. E. TSCHIRSCH (*Seifensieder Ztg.*, 1921, **48**, 856).—Two grams of vanillin (m. p. 80—81°) are mixed with 100 c.c. of water and 30 c.c. of *N*/2-potassium hydroxide solution, the mixture being kept cold, and frequently shaken, for two hours; it is then titrated with *N*/2-sulphuric acid. The difference multiplied by 3.8 gives the percentage of vanillin.

CHEMICAL ABSTRACTS.

Estimation of Digitoxin in Digitan. L. E. WARREN (*J. Amer. Pharm. Assoc.*, 1922, **11**, 8—12).—No satisfactory method of estimating digitoxin has been described, but the Keller method as modified by Fromme is considered the best. Digitan is a mixture of the tannates of the glucosides of digitalis diluted with lactose. The Keller method modified by omitting clarification with lead acetate yielded a digitoxin fraction which, when tested pharmacologically, had only about 17% of the activity of pure digitoxin.

CHEMICAL ABSTRACTS.

The Hypobromite Reaction on Urea. PAUL MENAUL (*J. Biol. Chem.*, 1922, **51**, 87—88).—The author was unable to obtain accurate results in the estimation of urea by Stehle's modification (*A.*, 1921, ii, 605) of the hypobromite method.

E. S.

The Gasometric Estimation of Urea. RAYMOND L. STEHLE (*J. Biol. Chem.*, 1922, **51**, 89—92).—A reply to Menaul (cf. preceding abstract).

E. S.

The Electrometric Estimation of Cyanides in the Presence of Haloids. ERICH MÜLLER and HANS LAUTERBACH (*Z. anorg. Chem.*, 1922, **121**, 178—192).—The electrometric estimation of cyanides was carried out by Treadwell (*A.*, 1911, ii, 827). When silver nitrate solution is run into a solution of a cyanide containing a silver electrode a sudden increase of potential is observed when $\text{CN} : \text{Ag} = 2 : 1$ corresponding with the completion of the reaction $2\text{CN}' + \text{Ag}^* = \text{Ag}(\text{CN})_2'$ (1). This sudden change is due to the commencement of the reaction $\text{Ag}(\text{CN})_2' + \text{Ag}^* = 2\text{AgCN}$ (2). The authors found another sharp change in the potential when reaction (2) is completed and the concentration of silver-ion in the solution increases. This second maximum rate of change of potential is more accurate than the first, which gives a slightly low result. This second point is also of importance in the estimation of a

mixture of cyanide and haloids. The solubility products of the silver salts are $\text{AgI}=10^{-16}$; $\text{AgBr}=6.4 \times 10^{-13}$; $\text{AgCN}=4.8 \times 10^{-12}$; $\text{AgCl}=10^{-10}$. Saturated solutions of these salts contain a higher concentration of silver ion than a solution of potassium silver cyanide, because they are all soluble in a solution of potassium cyanide. Hence a solution containing cyanide and haloids should give several sharp changes of potential in an electrometric titration which would correspond with the end of the several precipitations. The solubilities of the bromide, cyanide, and chloride of silver are near to one another and sudden changes of potential corresponding with these three were not observed.

The results obtained were as follows :

(I+CN) three sudden changes giving	(1) $\frac{1}{2}$ CN	(2) $\frac{1}{2}$ CN + I	(3) CN + (I)
(Br+CN) two	"	(1) $\frac{1}{2}$ CN	(2) CN + Br
(Cl+CN) "	"	(1) $\frac{1}{2}$ CN	(2) CN + Cl
(I+Br(or Cl)+CN) three	"	(1) $\frac{1}{2}$ CN	(2) $\frac{1}{2}$ CN + I (3) CN + I + Br(or Cl)
(Br+Cl+CN) two	"	(1) $\frac{1}{2}$ CN	(2) CN + Br + Cl

The apparatus is described.

W. T.

Sensitiveness of certain Tests for Hydrocyanic Acid.

THURE SUNDBERG (*Z. anal. Chem.*, 1922, **61**, 110—112).—The author agrees with the statement of Kolthoff (A., 1918, ii, 128) that the ferrocyanide reaction is the most trustworthy for the identification of hydrocyanic acid; the test will detect as little as 0.023 mg. of hydrogen cyanide in 10 c.c. of solution. Other sensitive tests are the guaiacum-copper sulphate test (0.001 mg. HCN) and the copper-benzidine acetate test (0.005 mg. HCN; A., 1921, ii, 224).

W. P. S.

Modification in the Process of Extraction of Alkaloids.

DOMENICO LIOTTA (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 27—30; cf. A., 1920, i, 587).—The estimation of nicotine in tobacco may be simplified as follows. The dried, powdered material (1.5—3 grams) is completely decolorised by treatment with chlorine and then steeped in water at the ordinary temperature for twenty-four to forty-eight hours. From the resulting solution the nicotine is precipitated by means of silicotungstic acid, the precipitate being calcined; multiplication of the weight of the calcined residue by 0.1139 gives the weight of nicotine present in the sample taken. The method gives results in good agreement with those furnished by the ordinary method, and is doubtless applicable to the estimation of other alkaloids.

T. H. P.

Estimation of the Alkaloids in Extract of Aconite.

A. ASTRUC, E. CANALS, and R. BORDIER (*J. Pharm. Chim.*, 1922, **25**, 161—164).—The official method of the French Codex for the estimation of the alkaloids in extract of aconite gives low results owing to their incomplete extraction by the specified quantity of ether. The following method of operation is recommended in preference: 5 grams of extract are diluted to 25 c.c. with water, 10 c.c. of 10% nitric acid are added, followed by 5 c.c. of ammonia, and the solution is extracted three times with quantities of 100 c.c. of ether with vigorous and repeated agitation during ten minutes

for each extraction. It is then extracted four times with 50 c.c. of ether, and the fourth extract should be free from alkaloid when tested with Valser and Mayer's reagent. The alkaloids in the united ethereal extracts are then transferred to aqueous solution by shaking with dilute nitric acid followed by four washings with water, and they are then precipitated in the usual way from the filtered aqueous solution by adding 15 c.c. of 5% silicotungstic acid and 20 c.c. of 10% nitric acid. The precipitate is collected on a filter and ignited, and the weight of the residue multiplied by the factor 0.793 gives the weight of alkaloid in the 5 c.c. of extract taken.

G. F. M.

Method for the Estimation of Procaine [Novocaine]. A. W. HANSON (*J. Assoc. Off. Agric. Chem.*, 1921, **5**, 163—166).—When novocaine is heated with 0.1*N*-sodium hydroxide solution, it is hydrolysed with a quantitative formation of sodium *p*-aminobenzoate. This compound without extraction can be titrated with a mixed potassium bromide and potassium bromate reagent under specified conditions. The estimation depends on the fact that each molecule of novocaine reacts with 3 molecules (6 atoms) of bromine. [Cf. *J. Soc. Chem. Ind.*, 1922, 345*A*.]

J. R.

The Estimation of the Purine Bases in Urine. E. SALKOWSKI (*Z. physiol. Chem.*, 1922, **119**, 121—124).—Estimations of the purine bases carried out by Fridericia showed that the silver method of the author gives lower results than the Krüger-Schmid method. This is interesting in view of Steudel and Chon's recent results (this vol., ii, 239).

S. S. Z.

Estimation of Uric Acid in Blood. A. GRIGAUT (*Bull. Soc. Chim. Biol.*, 1922, **4**, 11—22).—Proteins are precipitated by metaphosphoric acid and the colorimetric method of Folin and Denis (*A.*, 1913, ii, 162) is then applied directly to the protein-free filtrate.

E. S.

Estimation of Uric Acid in Blood. STANLEY R. BENEDICT (*J. Biol. Chem.*, 1922, **51**, 187—207).—In the colorimetric method described, a new arsenic phosphotungstic acid reagent is used which, with uric acid, produces a much greater depth of colour than the phosphotungstic acid reagent. The new reagent is prepared by adding 50 grams of arsenic pentoxide, 25 c.c. of 85% phosphoric acid, and 20 c.c. of concentrated hydrochloric acid to a solution of 100 grams of sodium tungstate in 600 c.c. of water, boiling for twenty minutes, and finally diluting to 1 litre. For the estimation, proteins are removed from the blood by the tungstic acid method and 5 c.c. of the filtrate are taken. After dilution to 10 c.c., 4 c.c. of a 5% sodium cyanide solution containing 2 c.c. of concentrated ammonia per litre and 1 c.c. of the arsenic phosphotungstic acid reagent are added and the mixture is immersed in boiling water for three minutes. After cooling, the colour developed is compared with a standard. Results obtained by this method are usually somewhat higher than those obtained by the precipitation method of Folin and Wu (*A.*, 1919,

ii, 308). The possible causes of this and the relative merits of the two methods are discussed at some length in the original.

E. S.

A New Colorimetric Method for the Estimation of Plasma Proteins. HSIEN WU (*J. Biol. Chem.*, 1922, **51**, 33—39).—The method depends on the colour reaction which the three proteins give with phospho-18-molybdotungstic acid (phenol reagent) in the presence of sodium carbonate. A tyrosine standard is used, estimations by the Kjeldahl method having shown that, for human plasma, 1 mg. of tyrosine is equivalent to 16.4 mg. of fibrin, 25.2 mg. of globulin, or 27.5 mg. of albumin. Separation of the proteins is effected, in the main, by the method of Cullen and Van Slyke (A., 1920, ii, 398). Fibrin and albumin, after purification, are estimated directly, whilst the albumin and globulin contained in the filtrate from the fibrin are precipitated and estimated together. The value for the globulin is then obtained by difference. E. S.

The Tyrosine Content of Proteins. OTTO FÜRTH and WALTER FLEISCHMANN (*Biochem. Z.*, 1922, **127**, 137—149).—A comparison of the various processes for the estimation of tyrosine in proteins shows that the quantity of tyrosine which can be isolated gravimetrically is far below that estimated. The method of Folin and Denis (A., 1912, ii, 1012), and the colorimetric estimation by the diazo-reaction and by Millon's reagent give maximum values, the most suitable method being the absorption of bromine in acid solution by the protein hydrolysate after removal of substances precipitable by phosphotungstic acid. H. K.

Micro-estimation of Albumin. C. VALLÉE and M. POŁONOWSKI (*Compt. rend. Soc. Biol.*, 1921, **84**, 901—903; from *Chem. Zentr.*, 1921, iv, 1080).—The total nitrogen is estimated in 1 c.c. of the liquid under examination by the method previously described (this vol., ii, 312). In a further 2—3 c.c. of the liquid the albumin is precipitated by addition of two drops of glacial acetic acid and a small quantity of sodium chloride, and heating on a water-bath at 90°. The liquid is made up to the original volume, centrifuged, and the nitrogen estimated in an aliquot portion of the clear liquid. The albumin nitrogen is thus obtained by difference. G. W. R.

Estimation of Pepsin. H. W. VALTEICH and C. C. GLOVER (*J. Amer. Pharm. Assoc.*, 1921, **10**, 595—606).—Comparative examination of methods for the estimation of pepsin showed that whilst Northrup's electrolytic method is trustworthy, the best method is that of U.S.P. IX, although the use of storage eggs instead of fresh eggs is recommended. CHEMICAL ABSTRACTS.

A New Method for the Estimation of Pepsin. KARL GLÄSSNER (*Biochem. Z.*, 1922, **127**, 312—315).—This method is a precipitation method and depends on the observation that globin (readily prepared from hæmoglobin by a slight modification of Strauss and Grützner's method; A., 1921, i, 200) is precipitated from hydrochloric acid solution by ammonia and is insoluble in

excess of ammonia, especially if a few drops of ammonium chloride are added. A series of dilutions of pepsin or gastric juice and acid in geometrical progression are made and 1% globin solution is added to each. After digestion at 40° for fifteen minutes, addition of 3—5 drops of ammonium chloride solution (10%) and 1—2 c.c. of 1% ammonia solution gives a flocculent precipitate in the tubes containing undigested globin. H. K.

Tannase. DONALD RHIND and FRANCIS EDWARD SMITH (*Biochem. J.*, 1922, **16**, 1—2).—A method has been elaborated for estimating the hydrolysing power of tannase by measuring the tannin present in a solution before and after action by the enzyme for varying periods. The tannin is estimated by titrating the whole solution with potassium permanganate in presence of indigo-carmin, the tannin is then removed by Nierenstein's caseinogen method (A., 1911, ii, 236), and the solution is again titrated with potassium permanganate. The difference between the two titrations represents the amount of gallotannin present.

W. O. K.

Estimation of Peroxydase in Milk. FRANCIS E. RICE and TORATORO HANZAWA (*J. Ind. Eng. Chem.*, 1922, **14**, 201—202).—The method of Bach and Chodat for the estimation of peroxydase in plant juices (A., 1904, i, 542) is adapted for milk. It depends on the oxidation of pyrogallol by hydrogen peroxide, the reaction being catalysed by peroxydase. The number of mg. of purpurogallin precipitated by the action of 10 c.c. of milk is called the "peroxydase number." The reaction takes seven days, and air must be excluded. The residue after filtration is washed with light petroleum to remove fat. Whole and skim milk are about equal in peroxydase activity. Heating milk below 68.3° for thirty minutes reduces, but does not destroy peroxydase activity, which is also reduced slightly by keeping on ice for two days. Samples of milk for the estimation of peroxydase cannot be preserved with mercuric chloride or formaldehyde. H. C. R.

Estimation of the Antiscorbutic Vitamin (Vitamin-C). H. C. SHERMAN, V. K. LAMER, and H. L. CAMPBELL (*J. Amer. Chem. Soc.*, 1922, **44**, 165—172).—A modified diet free from vitamin-C and containing an adequate amount of vitamin-A, namely, ground oats 59%, skim milk powder, heated on open trays at 110°, 30%, freshly prepared butter fat 10%, and sodium chloride 1% is recommended. The method of measurement consists in a series of observations on animals receiving no vitamin-C and different measured amounts up to the amount which affords complete protection, and permits optimum growth. The symptoms and autopsy findings are interpreted in terms of the percentage of the required amount of antiscorbutic vitamin which was actually received by the animal in any individual case. W. G.

Blood Analysis. IV. Ashing Methods. M. RICHTER-QUITTNER (*Biochem. Z.*, 1921, **126**, 97—104).—For the estimation of total alkali metals, phosphorus and iron, for example, in blood,

ashing methods can be employed successfully. Corpuscles contain fewer mineral constituents than serum and still less if the flow of blood be stemmed in a vein.

H. K.

Analysis of Blood and Urine. I. LUDWIG PINCUSSEN and ARISTOMENIS FLOROS (*Biochem. Z.*, 1921, **125**, 42—45).—To avoid the expensive torsion balance in Bang's micro-methods, the authors recommend a fine graduated pipette holding 0.1 gram of blood. By working quickly the same pipette can be used for measuring the two drops of blood, for duplicate analysis, without use of an anti-clotting agent. Examples are given of the estimation of the reducing sugar of blood. Bang's method for the analysis of sugar in blood is applicable to sugar in urine if the coagulable protein is removed by addition of 12 c.c. of 0.05% copper sulphate solution to 1 c.c. of diluted urine (1 : 100). The results agree with the macro-method. Other substances which produce a high reduction figure are creatine and uric acid, the urine of persons with an increased uric acid and creatine content showing increased reduction.

H. K.

Analysis of Blood and Urine. II. LUDWIG PINCUSSEN and KATE MOMFERRATOS-FLOROS (*Biochem. Z.*, 1921, **125**, 46—48).—For the micro-estimation of acetone in urine, a brisk current of air is drawn for twenty-five minutes through 1—2 c.c. of urine, mixed with 20—30 mg. of oxalic acid, 0.5 gram of sodium chloride and 5 c.c. of water, and the free acetone absorbed by 10—15 c.c. *N*/100-iodine solution mixed with 1 c.c. of 33% sodium hydroxide solution. The excess of iodine is estimated volumetrically after acidifying. The combined acetone as acetoacetic acid is obtained by changing the receiver and passing the current of air through the boiling solution. For the estimation of ammonia in blood, 5 c.c. mixed with 0.2% potassium oxalate were treated with 0.1 c.c. of sodium hydroxide solution and the volume made up to 25 c.c. exactly with alcohol, whereby protein is precipitated. The solution is filtered rapidly into a vessel containing a drop of dilute acid to fix the ammonia. Twenty c.c. of filtrate were made alkaline with sodium carbonate solution and a current of air was passed through for fifteen minutes at 40° and the ammonia absorbed by 2 c.c. of *N*/50-sulphuric acid.

H. K.

Method for the Estimation of Total Base in Urine. CYRUS H. FISKE (*J. Biol. Chem.*, 1922, **51**, 55—61).—Organic matter is removed from the urine by evaporation with a mixture of sulphuric and nitric acids. Phosphates are removed from the residue by the ferric chloride-ammonium acetate method, after which the filtrate is evaporated to dryness and ignited first with sulphuric acid and then with ammonium carbonate. The residue contains the sulphates of sodium, potassium, calcium, and magnesium. Estimation of sulphate by the benzidine method (*A.*, 1921, ii, 556) gives the equivalent of the bases present.

E. S.

General and Physical Chemistry.

The Rôle of the Physicist in the Development of Chemical Theory. Presidential Address. Delivered at the Annual General Meeting, March 30th, 1922. SIR JAMES WALKER (T., 1922, **121**, 735—745).

Relationships between Molecular Refraction and Other Properties. W. HERZ (*Z. physikal. Chem.*, 1922, **101**, 54—62).—From Berthelot's equation, $M=11.4 d \{T_k/p_k(2-T/T_k)\}$ (A., 1899, ii, 404), and Guye's expression, $MR=1.8T_k/p_k$, in which MR is the molecular refraction and the other symbols have their usual significance, the author has derived the expression $M/d_s=5MR$, where d_s is the density at the boiling point. This expression says that the molecular volume for non-associated liquids at the boiling point has a value equal to five times the molecular refraction. This statement has been tested for thirty-three substances and shown to be fairly in keeping with facts in the case of the simpler aliphatic liquids, but in the case of halogen-substituted compounds, aromatic, heterocyclic, and inorganic substances, large divergences are observed. The expression $MR=M/5d_s=0.9c/d_sT_s$ is deduced, from which $M=11.97c/T_s$ is obtained, where c is the molecular boiling-point elevation constant. This equation is shown to be in keeping with fact to the extent of 10—20%. Further expressions are derived by which from the molecular volume at the boiling point and the molecular refraction the molecular diameter and the internal pressure may be calculated. In many cases it is shown that $ML/MR=8p_k$, where L is the latent heat of vaporisation at the boiling point. A constant relationship is shown to exist between the coefficient of expansion, the molecular refraction, and the critical pressure, which has the form $MRp_k/(1/k_{20}+293)=\text{constant}$ (0.9). Evaluation of this constant for seventeen substances gives figures which lie between the extremes 1.38 and 0.84.

J. F. S.

Regularities in Systems of Bands. A. KRATZER (*Ann. Physik*, 1922, [iv], **67**, 127—153).—The work of Heurlinger (*Diss. Lund.*, 1918), and Lenz (*Verh. Deut. physikal. Ges.*, 1919, **21**, 632) on series lines in band spectra is extended by the application of the quantum theory to the consideration of the anharmonic vibrations of a molecular oscillator. A formula, similar to that deduced empirically by Deslandres (A., 1920, ii, 69) is obtained for the zero lines in a series of bands, and is found to represent very exactly the lines in the band spectrum of oxygen and the lines in the violet band spectrum of cyanogen. The significance of the constants in Deslandres's formula is interpreted on the basis of the quantum theory, and a formula involving nine constants is obtained, to represent the whole of the lines in the violet band spectrum of

cyanogen, exclusive of the fine structure. The application of the theory to the lines in the red band spectrum of cyanogen and the band spectrum of nitrogen is briefly indicated. J. S. G. T.

The Structure of the Balmer Series. OTTO OLDENBERG (*Ann. Physik.*, 1922, **67**, 69—72).—The new measurements of McLennan and Lowe (*A.*, 1921, ii, 666) for the H_{α} , H_{β} , H_{γ} , and H_{δ} lines are not considered to be in opposition to the Sommerfeld theory of the structure of the Balmer series, the differences being explained by the neglect of the small shift which is caused by the steep rise in intensity of a neighbouring line. Experiments with the discharge tube used by Wood (*A.*, 1920, ii, 569) indicate that the third members of the triplets found by McLennan and Lowe are not produced in the absence of nitrogen. The new lines which are observed on the admission of nitrogen are found to be somewhat sharper than the Balmer doublet. W. E. G.

Extension of the X-Ray Spectrum to the Ultra-violet. E. H. KURTH (*Physical Rev.*, 1921, **18**, 461—477).—Certain improvements in technique made it possible to obtain the following values for the convergence wave-lengths in Å.U.: *K* series, carbon 42·6, oxygen 23·8; *L* series: carbon 375, oxygen 248, aluminium 100, silicon 82·5, titanium 24·5, iron 16·3, copper 12·3; *M* series: aluminium 326, titanium 85·3, iron 54·3, copper 41·6; *N* series: iron 247, copper 116. It is suggested that the radiation from solid targets may differ from the radiation from gaseous atoms, especially for the lighter elements. A. A. E.

The Significance of the Half Terms in Spectral Series Formulæ. PAUL D. FOOTE and F. H. MOHLER (*J. Opt. Soc. Amer.*, 1922, **6**, [i], 54—56).—The ratio of the constant a^* for the enhanced spectrum of an alkali earth to the constant a for the arc spectrum of the alkali with the next lower atomic number has been computed on the basis of the quantum theory and compared with the observed values. W. E. G.

The Occurrence of Spark Lines (Enhanced Lines) in the Arc. II. Magnesium, Zinc, and Cadmium. G. A. HEMSALECH and A. DE GRAMONT (*Phil. Mag.*, 1922, [vi], **43**, 834—871; cf. this vol., ii, 176).—Further experimental observations have been made on the spectra observed in liquid and vacuous film arcs and in arcs surrounded by gaseous media. The results point to the existence of four distinct stages in the spectral development of the arc flash (1) the film stage during which the spark lines are enhanced and symmetrically broadened, (2) a short region marked by the strong emission of spark lines, (3) a stage during which the spark lines are but feebly emitted and at the end of which their emission ceases abruptly, and (4) the last period of the flash during which arc lines are alone emitted. The flashing up of the spark lines and their symmetrical broadening at the instant of striking the arc is shown to be due to the momentary establishment of a powerful electric field between the electrodes. The symmetrical broadening of the lines is believed to be due to the Stark effect.

The disappearance of the magnesium spark line λ 4481 at a definite point during the second phase occurs when the electric field is reduced below 500 volts/cm. The spark lines are brought out prominently in liquid air and disappear when the temperature is raised. It is thus impossible to regard these as high temperature lines. The only types of magnesium lines which are emitted in the absence of electrical or special chemical actions are the flame line λ 4571 and the series triplets. A summary of the relative sensitiveness of the various magnesium lines to electrical and chemical actions is given.

W. E. G.

The Spectrum of Glucinum Fluoride. SNEHAMOY DATTA (*Proc. Roy. Soc.*, 1921, [A], **101**, 187—194).—The previous investigation on the band spectra of the fluorides of magnesium, calcium, strontium, and barium (cf. A., 1921, ii, 529) has been extended to a study of the spectrum of potassium glucinum fluoride. The presence of potassium does not interfere with the band spectrum of glucinum fluoride, neither does glucinum oxide present spectra in the vicinity of the fluoride bands. There are six groups of bands all in the ultra-violet between λ 2800 and λ 3400 and all fading towards the red. The strongest band at 3009 was selected for a detailed investigation, and it was shown to consist of three series of lines which depart from the ordinary formulæ. Each group of glucinum fluoride bands is composed of alternating double and single heads, and this is the only similarity they present to the spectra of the other alkaline-earth fluorides. The formula, given in the previous paper for the E_1 group of magnesium fluoride gives satisfactory agreement for the glucinum fluoride bands.

W. E. G.

Emission Bands of Erbium Oxide. E. L. NICHOLS and H. L. HOWES (*Science*, 1922, **55**, 53).—A confirmation of the work of Mallory (*Physical Rev.*, 1919, **14**, 54). At temperatures at, or slightly below, 1000° , there are three regions, in which the principal emission bands of the spectrum of erbium oxide are situated, which are brighter than for an ideal black body at the same temperature.

A. A. E.

N-Series in X-Ray Spectra. V. DOLEJŠEK (*Nature*, 1922, **109**, 582).—By using Siegbahn's apparatus, lines which most probably must be referred to the *N*-series of uranium and thorium have been detected. Calculations show that for these elements, some of the lines must have wave-lengths of about the measured values (8.6—12.0 Å.U. and 9.4—13.5 Å.U., respectively), whilst for bismuth and the elements in its neighbourhood all the *N*-lines must have a wave-length of more than 13 Å.U.

A. A. E.

Spectrophotometric Study of Solutions of Cupric Chloride. FREDERICK H. GETMAN (*J. Physical Chem.*, 1922, **26**, 217—246).—The extinction coefficients of a series of solutions of cupric chloride (2.622—0.8443*M*) have been determined at 28.3° for various wave-lengths lying between $460\ \mu\mu$ and $560\ \mu\mu$. A further series of extinction coefficients of a number of binary mixtures of cupric

chloride with hydrochloric acid, potassium chloride, lithium chloride, calcium chloride, aluminium chloride, and zinc chloride, respectively, have also been determined over the same region of the spectrum; in each case the concentration of the copper salt was kept constant ($0.8443M$), whilst the concentration of the added chloride was progressively increased. It is shown that in solutions of cupric chloride, Beer's law holds only in the region of longer wave-lengths, and that in this region both ions and undissociated molecules may be assumed to possess nearly equal absorbing powers. No apparent relation has been found to exist between absorption and dissociation; in fact, no satisfactory interpretation of the mechanism of the absorption of light by electrolytes seems to be possible, unless the view of Hantzsch be adopted, that absorption is independent of dissociation. The absorption of light by solutions of cupric chloride has been attributed to the presence of complex ions, the composition of which is conditioned, primarily, by the concentration of the solution. In extremely dilute solutions, absorption is assumed to be due to the presence of copper atoms holding in combination as many molecules of solvent as correspond with the co-ordination number of the metal, which, in this case, is four. In extremely concentrated solutions, complex anions containing copper have been shown to be present, and to these the hypothetical formula $CuCl_4''$ has been assigned. Other complex ions, in which one, two, or three of the water molecules of the tetrahydrated copper-ion have been replaced by chlorine atoms, are assumed to be present in solutions of intermediate concentrations. A study of the absorption spectra of the metal ammines has shown that substitution of a chlorine atom for a water molecule in a complex ion causes a displacement of the minimum in the absorption curve toward the red end of the spectrum. Increase in concentration, or the addition of colourless chlorides, is shown to displace the absorption minimum of $0.8443M$ cupric chloride toward the red end of the spectrum. The cause of the observed displacement of the absorption minimum is believed to be the same as in the case of the metal ammines, namely, the successive replacement of water molecules by chlorine atoms in complex ions.

J. F. S.

Absorption of Light by Solutions of Cupric Lithium Chloride. FREDERICK H. GETMAN (*J. Physical Chem.*, 1922, 26, 377—383).—The absorption of light by solutions of cupric lithium chloride ($CuCl_2 \cdot LiCl \cdot 2H_2O$) has been examined spectrophotometrically, and the resulting absorption curves have been compared with corresponding curves for cupric chloride. The minima in the absorption curves were found to lie nearer the red end of the spectrum than the corresponding minima in the curves obtained with solutions of cupric chloride. In dilute solutions, the absorption curves of cupric lithium chloride and cupric chloride were found to be identical. From a comparison of the conductivities of solutions of cupric lithium chloride with the sum of the conductivities of cupric chloride and lithium chloride at the

same dilutions, it is found that the double salt, when dissolved in water, undergoes almost complete dissociation into the two component salts. The possibility suggested by Donnan that the solid salt may undergo dissociation as indicated by the equation $\text{CuCl}_2 \cdot \text{LiCl} \cdot 2\text{H}_2\text{O} \rightleftharpoons (\text{Li}2\text{H}_2\text{O})^+ + (\text{Cu}3\text{Cl})^-$ (A., 1905, ii, 806) is emphasised as offering a satisfactory explanation of the fact that the colour of the compound is widely divergent from that characteristic of copper salts. J. F. S.

Absorption Spectra of Glasses of Various Composition containing Didymium. F. WEIDERT (*Z. wiss. Photochem.*, 1922, 21, 254—264).—A spectrographic comparison of the absorption spectrum of didymium present as a solid solution in various glasses with that of aqueous solutions of the nitrate of didymium and other rare earths, and an investigation of the effect of the composition of the glass on the absorption spectrum. Eight of the glasses investigated contained various amounts of four or five of the oxides of silicon, boron, arsenic, lead, aluminium, calcium, potassium, and sodium, together with a mixture of the oxides of neodymium, praseodymium, samarium, cerium, and lanthanum. The remaining glass contained pure neodymium oxide. The aqueous solutions employed for comparison included, not only a solution of the mixture referred to, but also solutions containing respectively the equivalent of 1.37 gram of neodymium oxide, 0.76 gram of praseodidymium oxide, and 0.42 gram of samarium oxide per litre. The absorption bands characteristic of the glasses were broader and less sharp than the corresponding bands afforded by the aqueous solutions. The presence of boron in the glass increased the want of sharpness of the bands. Lead-potash glasses afforded the sharpest bands. Reproductions of certain of the absorption spectra are given, and the paper discusses the shift of the bands in various cases. J. S. G. T.

The Absorption of Colouring Matters of the Flavone Group.
II. Absorption Spectra of Phenyl Styryl Ketone and its Derivatives. YŪJI SHIBATA and WILLY NAGAI (*J. Chem. Soc. Japan*, 1922, 43, 101—122).—To determine the effect of the hydroxyl group on the absorption of light in compounds intimately related to the flavone group, the authors have studied the absorption spectrum of phenyl styryl ketone and its hydroxyl derivatives. Phenyl styryl ketone in 0.0001*N*-alcoholic solution shows a large absorption band in the ultra-violet (the centre being λ 3.300). The absorption of flavone, therefore, is more hypsochromic than that of phenyl styryl ketone in the same concentration (cf. Shibata and Kimotsuke, *J. Chem. Soc. Tokyo*, 1918, 39, 771). The effect on the absorption of light of the introduction of the hydroxyl group into phenyl styryl ketone is more complex than in the case of flavone. The effect of the introduction of the hydroxyl group into the phenyl group is very small; whilst in the styryl group it is distinct. In the latter case, it is bathochromic and accompanies the appearance of one or two new absorption bands. By introducing the hydroxyl group into both the phenyl and styryl groups

at the same time, the band is enlarged, and is bathochromic. When two hydroxyl groups are introduced into the group, the effect is additive, except in some cases of ortho-replacement. From the point of view of light absorption, natural naringenin is not shown to be a derivative of phenyl styryl ketone. K. K.

Spectrographic Detection of Change in Blood Pigment due to certain Organic and Inorganic Poisons, and the Characteristic Spectra of Yolk of Egg and Urobilin. L. LEWIN and E. STENGER (*Z. wiss. Photochem.*, 1922, **21**, 221—226; cf. A., 1908, ii, 1048).—In continuation of previous work, the authors have investigated photographically the effect of hydrocyanic acid, phenylhydrazine, acetylene, hydrogen phosphide, and sulphurous acid on the absorption bands of blood, both when the poison was added to blood withdrawn from an animal and when the poison was injected into the living animal. Only in the case of addition of phenylhydrazine did any appreciable shift of the absorption bands occur. In the case of blood derived from a rabbit after injection of phenylhydrazine, absorption bands occurred at $\mu\mu$ 629, 609, 581, 557, and 402, compared with absorption bands at $\mu\mu$ 577, 537, and 415 for normal blood. In the case of hydrocyanic acid, whilst no appreciable shift of the bands occurs, the sharpness of the bands diminishes, at first slowly, as the percentage of hydrocyanic acid increases. The absorption spectrum of yolk of egg showed bands at $\mu\mu$ 482, 453, 429, 401, and 380. The absorption spectrum of preparations of urobilin showed a band in the region $\mu\mu$ 494. By addition of an alcoholic solution of zinc chloride and ammonia, the maximum intensity in the band moves to $\mu\mu$ 509 and the solution fluoresces. J. S. G. T.

Optical Rotatory Dispersion. II. Tartaric Acid and the Tartarates. THOMAS MARTIN LOWRY and PERCY CORLETT AUSTIN (*Phil. Trans.*, 1922, [A], **222**, 249—308).—Bakerian lecture. The rotatory power of tartaric acid for a series of nine wave-lengths has been determined in aqueous solutions of eleven different concentrations ranging from 5 to 55% by weight, and also for twenty-one and twenty-six wave-lengths, respectively, at two other concentrations. The optical rotatory power of tartaric acid, like those of its methyl and ethyl esters, is expressed to a close degree of approximation by the formula $\alpha = k_1/(\lambda^2 - \lambda_1^2) - k_2/(\lambda^2 - \lambda_1'^2)$. The rotatory power of sodium tartrate agrees very closely with Biot's law, $\alpha = k/\lambda^2$, but requires for its exact expression a two-term formula similar to that used for tartaric acid. Potassium and ammonium tartrate and Rochelle salt give similar dispersion curves, but deviate more widely from Biot's law. A number of solutions which give negative rotations have been examined for a range of wave-lengths and the corresponding dispersion curves have been plotted. In the presence of an excess of boric acid, the rotatory dispersion of tartaric acid is no longer complex but simple, and may be expressed over a wide range of wave-lengths by the equation $\alpha = k/\lambda_2^2 - \lambda_0^2$. Tartar emetic also gives a simple dispersion curve. When tartar emetic is dissolved in an excess of potassium hydroxide,

or when a corresponding solution is prepared with bismuth in place of antimony, strongly lævorotatory solutions are obtained, but these again are characterised by a simple rotatory dispersion. It is suggested that tartaric acid, like nitrocamphor, exists in solution in two labile isomeric forms, and that the anomalous dispersion of the acid and of many of its derivatives is due to the presence of two isomeric compounds of opposite rotatory power and unequal dispersion. Derivatives which give simple rotatory dispersion are assumed (like salts of nitrocamphor) to be fixed in one of these forms. J. F. S.

The Inversion of the Rotatory Power in Anisotropic Liquids. L. ROYER (*Compt. rend.*, 1922, **174**, 1182—1185).—Cholesteryl cinnamate shows inversion of its rotatory power. The wave-length at which this inversion occurs varies with the temperature, the wave-length increasing as the temperature decreases. The wave-length of the reflected light varies with the temperature in the same manner, and it would appear that these two wave-lengths are identical. W. G.

Phototropy of Inorganic Salts. Cuprous Chloride and Bromide. GOPAL SINGH (T., 1922, **122**, 782—785).

Conversion of Energy in Photochemical Processes. A. BYK (*Z. wiss. Photochem.*, 1922, **21**, 197—199).—The contributions of Grothius and of Draper to the theory of photochemical processes are briefly reviewed, and attention is directed to outstanding ambiguities in the application of Einstein's quantum photochemical law to such processes. J. S. G. T.

Velocity of Reaction in the Photochemical Dissociation of Ferric Chloride. E. PUXEDDU and F. L. VODRET (*Gazzetta*, 1922, **52**, i, 229—234; cf. A., 1920, ii, 406).—The velocity of decomposition of ferric chloride in ethereal solution according to the equation $\text{FeCl}_3 = \text{FeCl}_2 + \text{Cl}$ has been measured under various conditions, both sunlight and electric arc light being used to effect the reaction. The course of the reaction was followed by titrating the ferrous salt with permanganate in presence of a few c.c. of Zimmermann's solution. As far as a certain stage in the reaction, the latter follows the equation for unimolecular reactions. The change proceeds more slowly in arc light than in sunlight, and yields a dense, highly transparent precipitate of ferrous chloride. T. H. P.

An Attempt to Detect Induced Radioactivity resulting from α -Ray Bombardment. A. G. SHENSTONE (*Phil. Mag.*, 1922, [vi], **43**, 938—943).—It is shown that the violent dismemberment of a molecule by an α -particle does not give rise to unstable nuclei, capable of emitting mass particles of a range greater than 2.0 mm. Also no cumulative effect is observable after a heavy bombardment by the α -particles. These negative results do not preclude the possibility of radioactive disintegrations taking place which involve the emission of β -particles or γ -radiation. W. E. G.

The Production of β -Ray Spectra by Radioactive Substances. LISE MEITNER (*Z. Physik*, 1922, 9, 131—144).—Experiments on the β -ray spectra of thorium-*B* have shown that it is possible to distinguish between a primary β -ray emitted from the nucleus and a secondary β -spectrum from the *K* and *L* rings of electrons. The primary β -rays are supposed to be converted into γ -rays in the nucleus and these set free electrons from the envelope of the atom. The source of the secondary β -rays was ascertained by allowing the γ -rays from thorium-*B* to set free electrons from an isotopic element, namely, lead, and comparing the velocities of these electrons with those emitted from the radioactive element. Two groups of β -rays were emitted identical with those from thorium-*B*. The energy of the γ -rays calculated from the energy of the secondary electrons, and the work required to separate these electrons from the nucleus, were found to agree with a wave-length $\lambda_\gamma = 5.2 \times 10^{-10}$ cm. and with a velocity for the primary β -ray of 73.9%. This β -ray was found to be present in the spectra emitted from thorium-*B*. The intensity was, however, very small, so that the primary β -ray emission is almost entirely converted into γ -rays. Evidence of the presence of electrons from the *K*, *L*₁, and *L*₂ rings was found. Similar conclusions are drawn for other elements, but the β -spectra of radium and radiothorium are entirely secondary in origin. The velocity of the primary β -ray, the atomic weight, and the life period of the isotopes of lead, radium-*B*, thorium-*B*, and radium-*D* are shown to be intimately related.

W. E. G.

The Relationship between β - and γ -Rays. LISE MEITNER (*Z. Physik*, 1922, 9, 145—152; see preceding abstract).—Arguments are adduced for the conclusion that γ -rays from radioactive substances have their origin in the nucleus. From the behaviour of uranium-*X* and radium-*C*, it is concluded that the primary β -ray is intense only when the γ -ray emission is small. The results of Ellis (*A.*, 1921, ii, 422) on radium-*B* preparations are explained on the assumption that there are three γ -ray frequencies emitted from the nucleus, two of which correspond with two different primary β -rays. The middle γ -ray could be accounted for if the most rapid β -ray under certain conditions gave up part of its energy and left the nucleus with the remainder.

W. E. G.

Reflection of X-Rays from Imperfect Crystals. C. G. DARWIN (*Phil. Mag.*, 1922, [vi], 43, 800—829).—In the recent work of Bragg, James, and Bosanquet (*A.*, 1921, ii, 477) on the reflection of X-rays from crystals, use was made of the theoretical formulæ of the author. The position of the electrons in a crystal can be inferred from a study of the intensity with which the various faces of a crystal reflect a given wave-length. The problem falls into two stages, the first from crystal to molecule and the second from molecule to electron. The formulæ are, however, falsified by the phenomenon of extinction. Extinction is shown to lead to two effects, primary and secondary. The primary diminishes the reflection from a perfect crystal below the amount given by the

simpler theory. This is, however, negligible for crystals invisible under a high-power microscope. The reflection from a small, perfect crystal, a conglomerate composed of a large number of small crystals oriented in nearly the same direction, and crystal powders is examined, and formulæ are worked out for Q , a quantity which is, approximately, the amplitude of the wave scattered by all the electrons in a single atom in the direction of the reflected beam.

W. E. G.

Positive Ray Analysis of Lithium and Magnesium. A. J. DEMPSTER (*Physical Rev.*, 1921, **18**, 415—422; cf. *ibid.*, 1918, **11**, 316; *Science*, 1920, **52**, 559).—Lithium has two isotopes with atomic weights 6 and 7, respectively, the relative proportions of which vary with the conditions. A suggested possible explanation is that the rates of evaporation of the two isotopes vary with the surface conditions of the metal. Magnesium has three isotopes with atomic weights 24, 25, and 26, the relative proportions being 7 : 1 : 1. These ratios give a mean atomic weight of 24.336.

A. A. E.

The Disappearance of Gas in the Electric Discharge. IV. THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LONDON (*Phil. Mag.*, 1922, [vi], **43**, 914—937; cf. A., 1920, ii, 730; 1921, ii, 369, 533).—A further account of experiments on the disappearance of gas in the presence of phosphorus vapour. The decrease in pressure was measured by use of a lamp filament as the hot wire of a Pirani gauge and by determining whether the pressure is above or below the value at which the glow potential is equal to the applied potential. The amounts of hydrogen adsorbed increase with increase in the phosphorus introduced. A marked step in the adsorption, however, occurs for 0.09 to 0.27 mg. of phosphorus. Sodium fluoride and phosphorus together exert a greater effect than either substance singly; spluttered tungsten is also effective. The adsorption of gases takes place in two stages; the first is practically instantaneous and is impossible to control.

The solid films on the walls are possibly in an electrically polar condition, and it is suggested that gaseous ions enter into combination with the surface by virtue of their charges. The very small adsorption of inactive gases, which do not form negative ions, suggests that it is the negative ions which are adsorbed by this layer.

W. E. G.

The Potential of the Iodine Electrode and the Activity of the Iodide Ion at 25°. A. MCKEOWN (*Trans. Faraday Soc.*, 1922, **17**, 517—521).—*E.M.F.* measurements have been made for cells of the type $\text{Pt} + \text{I}_2 | \text{KI solution sat. with I}_2 | \text{sat. KCl} | N \text{ calomel electrode}$, the concentration of potassium iodide being varied between wide limits. From the results, the activities of the iodide-ion and the tri-iodide-ion in the various solutions have been calculated. It was found that the activities of both ions increased much less rapidly than their concentrations. The potential of the normal

(saturated) iodine electrode has been deduced in terms of the activity of the iodide-ion. The value found is +0.2454 volt, the normal calomel electrode being taken as zero.

W. T.

The Effect of Telluric Acid on the Potential of a Silver Anode. FRANZ JIRSA (*Z. Elektrochem.*, 1922, 28, 186—191).—The author has determined the effect of halogen ions on the potential of a silver anode, and has investigated the nature of the depolarisation effected by telluric acid. In general, the halogens depolarise a silver anode in an alkaline electrolyte and reduce the value of the decomposition voltage. Apart from the fluorine-ion, which exerts no depolarising effect in an alkaline electrolyte, the maximum depolarisation is effected by the iodine-ion, the minimum by the chlorine-ion. Fluorine-ions accelerate the appearance and evolution of oxygen at the anode. When the polarisation of a silver anode in an alkaline electrolyte containing halogen ions is a maximum, the dioxide, Ag_2O_2 , alone is formed. The monoxide, Ag_2O , is produced when a silver anode is polarised to +1.40 volts in an alkaline electrolyte containing telluric acid. The following reactions occur: $\text{Ag}_2\text{O} + \text{K}_2\text{TeO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{Ag}_2\text{TeO}_4 + 2\text{KOH}$; $2\text{Ag}_2\text{O}_2 + 2\text{K}_2\text{TeO}_4 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{Ag}_2\text{TeO}_4 + 4\text{KOH} + \text{O}_2$. The potential of the electrode $\text{Pt}/\text{Ag}_2\text{O}_3$ in an alkaline electrolyte containing telluric acid is constant and equal to 1.57 volts.

J. S. G. T.

Effect of Changing the Hydrogen-ion Concentration on the Potential of the Zinc Electrode. THEODORE W. RICHARDS and THEODORE DUNHAM, jun. (*J. Amer. Chem. Soc.*, 1922, 44, 678—683).—Measurements of the potential of zinc in acid solutions of zinc sulphate, of various concentrations, measured at 18° against the calomel electrode, through a sodium sulphate bridge, and also directly against a zinc electrode containing pure *N*-zinc sulphate solution, showed marked rise in potential as the acid concentration was increased. The magnitude of this rise in potential indicated that it must be due partly to the liquid junction potential, owing to the presence of the hydrogen-ion. Equal concentrations of the sulphate-ion in the form of alkali sulphates added to the zinc sulphate solution gave smaller elevations in the potential, which elevations were in the order of the transport numbers of the kations concerned. It is assumed that the change in liquid junction potential produced by sodium sulphate is small and therefore it may be inferred that about two-thirds of the change produced by sulphuric acid is due to solution junction potential and the remaining third to a real increase in the single electrode potential of zinc, due, presumably, to the depression of the electrolytic dissociation of zinc sulphate.

J. F. S.

Variations in the Conductivity of Solid Electrolytes. P. VAILLANT (*J. Phys. Radium*, 1922, 3, 87—100; cf. A., 1912, ii, 419; 1920, ii, 722).—The changes in conductivity of solid electrolytes with temperature are due to two independently varying phenomena; the first of these occurs instantaneously, whilst the second is a slow change, frequently in an opposite direction to the first. These

progressive changes in the conductivity at constant temperature are not related to phosphorescence, being shown by many types of salts. The polarisation which occurs on passing the current is maintained indefinitely unless the crystals are short-circuited. The conductivity during the initial period is given by the relation : $\log C_T = a + bT$ or $\log C_T = \alpha - \beta/T$. In the second phase, the changes in conductivity follow different laws, being manifested by a series of oscillations of decreasing amplitude. W. E. G.

Abnormality of Strong Electrolytes and the Ionisation Theory of Ghosh. JAMES KENDALL (*J. Amer. Chem. Soc.*, 1922, **44**, 717—738).—The ionisation hypothesis put forward by Ghosh to explain the abnormality of strong electrolytes (T., 1918, **113**, 449, 627, 707, 790; 1920, **117**, 823, 1390) has been critically analysed and the following conclusions have been drawn. The second and third postulates are absolutely incompatible, for if the particles of a salt in solution possess a definite space-lattice arrangement, as in the crystalline state, then the combination of two oppositely charged particles to form a salt molecule or a completely saturated electrical doublet is impossible. Ghosh's calculation of the electrical work required to separate the component radicles of a gram-molecule of a dissolved salt is erroneous. The value actually derived, assuming a cubic space lattice arrangement, exceeds that obtained by Ghosh by 75%. The experimental conductivity data for potassium chloride solutions are not in agreement with the equation which Ghosh obtains from his postulates, or with various corrected forms of this equation. The agreement claimed by Ghosh to exist between his equations and the experimental results of previous investigators is largely fictitious. The remarkable coincidence of calculated and observed values in many tables is due to far too frequent errors of calculation and transcription. In other cases, the only legitimate deduction is that the equations tested serve very well as interpolation equations over a restricted range. No confirmation of the theory of Ghosh is afforded by the experimental data for (a) the variation of equivalent conductivity with dilution for salts in aqueous solution, (b) the temperature coefficient of the ratio μ_v/μ_∞ , (c) the electrical conductivity of non-aqueous solutions, (d) the molecular number i and the Clausius theorem, (e) the ionisation of strong acids, (f) the ionisation of weak acids, (g) the ionisation of transition acids, (h) the electrical conductivity of pure salts in the solid and fused states, (i) the conductivity of salts in mixtures of pyridine and water, (j) the ionisation of salts in solvents of low dielectric constant, (k) the partition of a salt between an ionising and a non-ionising solvent, and (l) the vapour pressure of the hydrogen haloids in aqueous solution. The rôle of the solvent in ionisation, which is ignored altogether by Ghosh, must be taken into account in any complete hypothesis of conducting solutions. In its present form, the ionisation hypothesis of Ghosh is unacceptable, and certain of the postulates on which it is based must be either modified or rejected.

J. F. S.

Ionic Equilibria of Strong Electrolytes. ALLEN E. STEARN (*J. Amer. Chem. Soc.*, 1922, **44**, 670—678).—The equivalent conductivities of the haloids of sodium and potassium of varying weight normal concentrations (0.1—4.0*N*) have been determined at 25°. A series of similar determinations has also been made for mixtures of a sodium and a potassium haloid. The observed values for the mixed salt solutions have been compared with those calculated from the values for the pure salt solutions at equivalent total concentrations on the basis of the isohydric principle. The differences between the calculated and observed values were found to be positive and to increase with the total salt concentration and with the numerical value of the ratio of sodium to potassium salt in the mixture, but to decrease generally from chloride to iodide. In general, the results are to be explained on the basis of complex formation, although at present no explanation is offered for the seeming decrease in complex formation on proceeding from chlorides to iodides. Tables of the specific gravities and the relative viscosities of all solutions measured are given in the paper. J. F. S.

Influence of the Solvent on Ionisation and the Accompanying Heat Effect. SIDNEY MAURICE NEALE (*Trans. Faraday Soc.*, 1922, **17**, 505—516).—In passing from pure water as solvent to 93.8% acetone, the ionisation constant of picric acid falls from about 0.2 to 0.002, but even in the latter case the deviation from Ostwald's dilution law still manifests itself, and, to a similar extent, the value of *k* decreasing by about 50% on increasing the dilution from 32 to 1024 litres. In anhydrous acetone, the ionisation constant for picric acid has fallen to the order of 10⁻⁶, and Ostwald's dilution law is obeyed. This indicates that the anomaly of strong electrolytes is to be referred to some property of the system solute plus solvent, rather than to high degree of dissociation. The heat of ionisation of picric acid varies largely with the nature of the solvent, passing through a minimum at about 70% acetone. In the case of *p*-nitrobenzoic acid, the heat of ionisation is practically zero. In 44.35% acetone, the ionisation constant has fallen one-twentieth of its value in pure water, but the heat of ionisation is still zero. W. T.

The Hydrolysis of a Salt formed from a Weak Acid and a Weak Base. R. O. GRIFFITH (*Trans. Faraday Soc.*, 1922, **17**, 525—527).—A theoretical paper. The author points out that it is necessary to state more exactly what is meant by the "degree of hydrolysis" in the case of a salt of a weak acid and a weak base at great dilution. He shows in the case of aniline acetate that at a dilution of 5000 litres the concentration of undissociated acid is not equal to the concentration of undissociated base, that is, the degree of hydrolysis differs for each ion. The calculation also shows that the hydrogen-ion concentration, whilst practically constant down to *v*=500 (the limit of Tizard's measurements (*T.*, 1910, **97**, 2494), should not be independent of the concentration between *v*=500 and *v*=5000, but should fall with increasing dilution. W. T.

[**Biochemical and Electrochemical Oxidation of Organic Compounds.**] A. NATHANSON (Z. *Elektrochem.*, 1922, **28**, 129—130).—A criticism of the views put forward and the interpretation of the author's work (*Koll. Chem. Beihefte*, 1919, **11**, 261) by Fichter in a paper under the same title (this vol., ii, 23).

J. F. S.

Simple Formula for the Calculation of the Specific Heats of Solids. H. J. KRASE (*J. Amer. Chem. Soc.*, 1922, **44**, 784—786).—A simple form of the specific heat equation of Lewis and Gibson (A., 1918, ii, 29), $C_v = f(T/\theta)$ has been obtained which fits the experimental facts. This equation has the form $C_v = 2.91 + 2.89 \tan h 2.95 \log T/\theta$. Since the entropy equation is obtained by integration of the specific heat equation $S_v = \int (2.91 + 2.89 \tan h 2.95 \log T/\theta) d \log_e T/\theta$, and on evaluating the integration constant by putting the entropy equal to the Lewis-Gibson value 1.62 when $\log T/\theta = 0$, $S_v = 6.70 \log T/\theta + 5.18 \cos h 2.95 \log T/\theta + 1.62$.

J. F. S.

Polymerisation at the Critical Temperature. WILLIAM R. FIELDING (*Chem. News*, 1922, **124**, 182—184, 198—199, 215—217; cf. A., 1920, ii, 732; A., 1921, ii, 487).—Calculations are made of the polymerisation factor at the critical temperature for a large number of volatile organic and inorganic compounds.

W. E. G.

Cinnamic Acid in Cryoscopy. P. FALCIOLA (*Gazzetta*, 1922, **52**, i, 175—179).—The results furnished by anthracene, naphthalene, *o*-, *m*-, and *p*-nitrobenzaldehydes, and phenylpropionic and phenylpropionic acids differ somewhat from those obtained by Mathews (A., 1917, ii, 356) and show that the value of the cryoscopic constant for cinnamic acid is about 100. The fact that phenylpropionic acid, when dissolved in cinnamic acid, produces almost normal depressions of the freezing point confirms Bruni's conclusion (A., 1899, ii, 731; 1900, ii, 714) that there is no tendency to the formation of solid solutions when saturated compounds are dissolved in unsaturated ones, although such tendency is exhibited in the inverse case (cf. also Mascarelli and Pestalozza, A., 1907, ii, 936; 1908, i, 527).

T. H. P.

A Micro-method for the Determination of Molecular Weight in a Melting-point Apparatus. KARL RAST (*Ber.*, 1922, **55**, [B], 1051—1054).—The freezing point of camphor is depressed to such an unusual extent by the presence of dissolved substances that the effects can be measured with sufficient accuracy for the determination of molecular weight by means of an ordinary thermometer and with minute amounts of material.

The substance under investigation and the camphor are weighed into a small tube which is subsequently closed with a cork carrying a pointed needle. The substances are melted together, well mixed, allowed to solidify, and withdrawn by means of the needle. A portion of the mixture is transferred to a melting-point tube the

bottom of which must be semi-spherical; it is pressed firmly together, giving a compact column not exceeding 1 mm. in height. The tube is heated in the usual melting-point apparatus. The mixture rapidly assumes the appearance of melting ice and is later converted into a cloudy liquid in which the presence of a delicate crystalline skeleton can be sharply detected by means of a lens. As the temperature rises, the latter disappears from above downwards, and the point at which the last trace vanishes is recorded as the melting point. Since the readings required are differential, the use of normal thermometers and the correction for the exposed part of the thread are unnecessary. H. W.

Orientation of Molecules in Surfaces. VII. Vaporisation in Steps as Related to Surface Formation. WILLIAM D. HARKINS and LATHROP E. ROBERTS (*J. Amer. Chem. Soc.*, 1922, **44**, 653—670; cf. A., 1921, ii, 242).—An account is given of the amount of energy involved in the various steps in the process of vaporisation, based on the assumption that the surface through which the vaporisation occurs is not highly curved. The results are expressed in *micri-ergs* as unit which is defined as 10^{-14} ergs. The relationships found at a corresponding temperature of 0.7° are tabulated for oxygen, nitrogen, ethyl ether, ethyl acetate, carbon tetrachloride, benzene, chlorobenzene, methyl alcohol, and ethyl alcohol, and the data indicate that, at a definite corresponding temperature, in the case of non-associated liquids the molecules of which are symmetrical, the molecular values for the latent heat of surface formation, l , the total surface energy, e , the energy of thermal emission, j , and the internal heat of vaporisation, λ_i , are nearly proportional to the critical temperatures of the liquids. The same relation seems to hold for the free surface energy, γ , provided that the temperature range is not too great. Thus the free surface energy of ethyl ether at a corresponding temperature of 0.7 is 4.0 as calculated from the value for carbon tetrachloride, and 3.9 as calculated from the value for chlorobenzene, whilst the experimental value is 4.0 . This statement, as applied to the latent heat of vaporisation alone, is somewhat similar to Trouton's law, which is known to be not entirely exact. Since the principle expressed above is much more general in its application, it is to be expected that it will prove to be somewhat less exact. The energy values for ethyl ether are lower than those for carbon tetrachloride, and this is a consequence of the lower critical temperature of the ether. The effect of a lack of symmetry in the molecule, especially when marked, is to lower the molecular free surface energy, latent heat of surface formation, and total surface energy and to increase the energy of thermal emission. Values are calculated for ethyl alcohol from the critical temperature on the assumption of a symmetrical molecule, using the values of carbon tetrachloride as a basis, and from the actual results it is evident that the molecular free surface energy, the total surface energy, and more markedly the latent heat of surface formation are considerably lowered by the dissymmetry of the molecule. The most striking

effect is, however, the very great increase in the energy of thermal emission. The symmetry considered is that of the electro-magnetic forces round the molecule rather than a symmetry with respect to mass. The substitution of the slightly polar chlorine atom for hydrogen in benzene gives almost exactly the calculated value for a symmetrical molecule except in the case of the thermal emission, which is considerably increased, since it is the most sensitive of all the quantities to changes of molecular symmetry. Since e is decreased and j increased by increasing dissymmetry of the molecule, the ratio e/j serves as a remarkably sensitive index of molecular symmetry. The ratio e/λ , which is equal to $e/(e+j)$, varies in the same way, but not to so large an extent. According to Stefan's law, the ratio of the total energy necessary to carry a molecule from the interior of a liquid into the surface to its total heat or energy of vaporisation, e/λ , is equal to $1/2$. This is shown not to be the case. Not only is this an increasing function with increasing symmetry of the molecule, but also with increasing corresponding temperature. Its value appears to approach unity as the corresponding temperature approaches unity. Thus a molecule in the surface at a high corresponding temperature is, in terms of relative energy, very much more nearly in the vapour phase than when the corresponding temperature is low. The relationships noted above are just those indicated by the hypothesis that molecules in the surface are oriented, the orientation increasing with increasing dissymmetry, and decreasing with increasing thermal agitation. The effect of thermal agitation is illustrated in the case of the alcohols; compounds of the polar-non-polar type. It is shown for these compounds that the molecular surface energy increases with the temperature. The effect of increased agitation is to overcome the orientation partly, and to throw the more polar groups into the outer surface, thus increasing the surface energy.

J. F. S.

Vapour Pressure of Sulphur Dioxide and Ammonia. F. W. BERGSTROM (*J. Physical Chem.*, 1922, **26**, 358—376).—The vapour pressure of ammonia and sulphur dioxide has been determined at temperatures from slightly above the normal boiling point to the freezing point. An improved form of apparatus is described which is capable of giving vapour pressure measurements below 900 mm. at low temperatures. The measurements are compared with those of Burrell and Robertson (A., 1916, i, 6; ii, 81) and of Brill (A., 1906, 847), and it is found that the author's results are in keeping with the Ramsay-Young relationship, whilst those of Brill and of Burrell are not. It has been shown experimentally that Burrell's vapour pressure measurements for ammonia are erroneous. The triple point of ammonia has been found to lie at -77.9° at a pressure of 45.5 mm. The value found by Cragoe, Meyers, and Taylor (A., 1920, ii, 370) is -77.70 at 44.9 mm.

J. F. S.

Binary Liquid Mixtures. O. FAUST (*Z. physikal. Chem.*, 1922, **101**, 94—103).—A theoretical paper in which, for the purpose

of comparing the relative efficiency and accuracy of the static and dynamic methods of determining the vapour pressure of liquid mixtures, the author has recalculated the results obtained by Schmidt (this vol., ii, 119), Beckmann and Faust (A., 1915, ii, 143), and von Zawidzki (A., 1901, ii, 6) for the vapour pressure of mixtures of acetone and chloroform. Curves are constructed and the shape of the curves discussed in connexion with Dolezalek's theory of liquid mixtures. J. F. S.

Vapour Pressures of Binary Mixtures. H. CASSEL (*Z. physikal. Chem.*, 1922, **101**, 104—108).—A theoretical paper in which the author criticises mathematically the assertion of Schmidt (this vol., ii, 119) that Dolezalek's theory of liquid mixtures cannot be maintained. The author shows that the measurements of Schmidt for mixtures of benzene and toluene show divergences from a straight line curve which vary between 1.0 and 2.4%. It is shown that the simplicity of Dolezalek's theory in comparison with the complicated expressions of van der Waals and Jahn has justified itself in numerous cases, so that its heuristic significance as a usable working hypothesis cannot be denied (cf. preceding abstract). J. F. S.

Binary Liquid Mixtures. ALFRED SCHULZE (*Z. physikal. Chem.*, 1922, **101**, 109—116).—A theoretical paper in which the author criticises the assertions of Schmidt (this vol., ii, 119) and shows that his statements in connexion with Dolezalek's theory of liquid mixtures cannot be maintained. Further, the results on which Schmidt bases his assertions are a confirmation of the theory (cf. preceding abstracts). J. F. S.

A Continuous Flow Calorimeter, and the Determination of the Heat of Neutralisation of a Solution of Hydrochloric Acid by One of Sodium Hydroxide. FREDERICK G. KEYES, LOUIS J. GILLESPIE, and SHINROKU MITSUKURI (*J. Amer. Chem. Soc.*, 1922, **44**, 707—717).—A continuous flow calorimeter has been so developed that measurement of the rise of temperature for ten different rates of flow leads to a value of the heat of neutralisation, which is associated with an error, as calculated by the method of least squares, which is less than 0.1% of the heat change itself. It is shown that a few slight modifications in the calorimeter will probably increase the precision. For the heat of neutralisation resulting in the formation of $\text{NaCl} \cdot 521\text{H}_2\text{O}$ (about 0.107N-sodium chloride) at 32.3°, the value 13280 cal./mol. is found. In the calculation, the specific heat data of Richards and Rowe were used, so that the unit is the 18° calorie (equivalent to 4.18 joules). It is held that this value is accurate within about 0.3%, although it is 2.6% higher than the corresponding point on Wörmann's curve for the same neutralisation (*Ann. Physik*, 1905, [iv], **18**, 775). The present value leads to a value for the heat of ionisation which is about 0.5% lower than the corresponding point on Noyes, Kato, and Sosman's curve (A., 1910, ii, 257). In the opinion of the authors, the 1% difference in the heat change when potassium

hydroxide is substituted for sodium hydroxide in the neutralisation is questionable, because no correction was applied for the carbonate present. J. F. S.

Heats of Neutralisation of Potassium, Sodium, and Lithium Hydroxides with Hydrochloric, Hydrobromic, Hydriodic, and Nitric Acids at various Dilutions. THEODORE W. RICHARDS and ALLAN W. ROWE (*J. Amer. Chem. Soc.*, 1922, **44**, 684—707).—The heat of neutralisation of the four acids by the three bases mentioned in the title have been determined at a series of dilutions. It is shown that the most serious errors in work of this kind are due to irregularity of mixing, presence of carbonates in the hydroxides, and inadequate avoidance of loss of heat by cooling. The solutions neutralised were molecular quantities in 100 gram-molecules of water, and they were combined in all possible pairs over two ranges of temperature not far apart, and the results were interpolated to exactly 20°. The values of the heat of neutralisation obtained ranged from 137500 to 14085, sodium hydroxide giving the lowest values among the bases and hydriodic acid among the acids. With the help of the heats of dilution, of factors and products, previously determined, the heats of neutralisation at other concentrations have been determined, and these have been extrapolated in two ways through a short range to infinite dilution. The heat of formation of water from its ions at 20° is found by this short extrapolation to be probably not greater than 13.69 Cal._{20°} or 57.22 kilojoules and possibly not smaller than 13.62 Cal._{20°} or 56.93 kilojoules.

J. F. S.

Pressure Volume Relation of Superheated Liquids. K. L. WISMER (*J. Physical Chem.*, 1922, **26**, 301—315).—A number of experiments are described, designed to obtain actual *PV* curves at high temperatures to see whether the curve shows any tendency to bend more sharply as the limit of superheating is approached, and to find what degree of superheating may be attained. Experiments were made with ethyl ether, ethyl chloride, and isopentane, which were subjected to a pressure of 20 atmospheres, heated to various temperatures, and the pressure then reduced to 1 atmosphere. The time before explosion occurred was then noted. In this way, the highest temperature to which the liquids may be superheated at ordinary pressures was obtained. The values found are ethyl ether 143°, isopentane 136°, and ethyl chloride 126°. The minimum pressures which can be reached with liquid ether at temperatures above 143° increase with the temperature, the points lying approximately on a straight line joining the critical point with the -72 atmospheres' point of J. Meyer ("Kenntnis des negativen Druckes in Flüssigkeiten," 1911). The pressure-volume relations have been determined experimentally for liquid ethyl ether at 121.5°, 127.9°, and 133.8°, and for liquid ethyl chloride at 99.6°, 109.7°, and 117.4°, at pressures down to 1 atmosphere. The pressure-volume relation under these conditions is almost linear. There is no tendency shown by the *PV* curves to bend more sharply at low pressures as

the limit of superheating is reached. The actual experiments showed a marked departure from van der Waals's curve.

J. F. S.

The Corresponding States : The Halogenated Derivatives of Benzene. MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1922, [iv], **31**, 295—299).—In the system of measurements of relativity constituted by the reduced values of the temperature, pressure, and density, the values obtained for the four monohalogenated derivatives of benzene are identical. The properties of the halogens are thus completely masked in such compounds.

For this series of compounds, the relation $M = AD_cT_c/P_c$ holds good independently of the halogen present. M is the molecular weight and A is a constant of value 21.65 for this series. W. G.

The Determination of Surface Tension from the Maximum Pressure in Bubbles. SAMUEL SUGDEN (*T.*, 1922, **121**, 858—866).

Method of Calculating Fluidity, Surface Tension, and Reaction (Equilibrium) Pressure. HENRY JERMAIN MAUDE CREIGHTON (*J. Franklin Inst.*, 1922, **193**, 647—655).—A theoretical paper in which it is shown that by means of a formula similar to the Ramsay and Young vapour-pressure equation, it is possible to calculate the fluidity (viscosity) of liquids, the equilibrium pressure of chemical reactions, and the surface tension of liquids. The expression has the form $R' = R + c(T_B - T_B')$, where R and R' are the ratios of the absolute temperatures at which two substances have the same value for any of the properties mentioned, T_B' and T_B the temperatures of one of the substances corresponding with the two values of the property chosen, and c is a small constant. The equations have been tested and shown to be in very good agreement with facts. J. F. S.

The Calculation of Adsorption of Vapours at Different Temperatures. L. BERÉNYI (*Z. angew. Chem.*, 1922, **35**, 237—238).—On the basis of Polányi's theory of adsorption, a formula has been evolved, by which the equation of state of the adsorbed substance within certain limits of pressure may be approximately calculated. The results for a range of temperatures which extends, for substances boiling between 170° abs. and 400° abs., from 0.06 to 1.4 times the boiling point in degrees abs. show no greater error than that of experimental determination. The formula applies to the reversible and physical adsorption of chemically homogeneous vapours, alone, or from a mixture of comparatively inert gases. From the observed data, p_1 , or the pressure of the gas, and x_1 , the quantity adsorbed at a temperature T_1 , the amount of gas adsorbed at the temperature T_2 , or x_2 , may be calculated by the formula: $x_2 = x_1 \times (1 + F_2 - F_1/100)$. $F_2 - F_1 = F$ is a correction factor which takes into account the thermal expansion and the compression of the adsorbed layer. The means by which the value F is determined, with relation to absolute temperature and the variation of the vapour from the law of gases, is given. H. M.

Electro-adsorption as a Purely Chemical Process. WOLFGANG OSTWALD (*Kolloid Z.*, 1922, 30, 254—260).—A theoretical paper in which the author discusses and criticises a paper under the same title by Kolthoff (this vol., ii, 197). It is shown that chemical adsorption, that is, the concentration of a dissolved substance on the surface in consequence of the chemical energy potential existing there, is quite possible. Therefore the hypothesis put forward by Kolthoff (*loc. cit.*) is not a purely chemical hypothesis, but a combination of chemical and electrical hypotheses. The deduction of the well-known adsorption formula by means of the law of mass action leads to concrete practically applicable formulæ only when instead of the stoichiometric weight concentration of the adsorbing substance the actual reacting mass of this substance is employed. The active quantity corresponds with the sum of the chemically reacting surface layers of the adsorbing substance. The stoichiometric weight concentration must therefore be multiplied by a factor which connects the actual reacting mass with the total mass. The demand of Kolthoff's hypothesis, that the value of the index must be the same for equivalent adsorbents whilst for electrolytes of different valencies the values stand in a simple relationship to one another, is not in keeping with experimental results. The cases quoted by Kolthoff are accidental or exceptions. In other cases, the hypothesis is in no way confirmed.
J. F. S.

Diffusion in Porous Vessels. A. L. HERRERA (*Mem. rev. soc. cient. "Antonio Alzate,"* 1921, 39, 343—347).—When solutions of reactive salts are allowed to diffuse very slowly together, the precipitates or crystals formed show analogies to natural cells. A solution of potassium silicate, d 1.5 or more, containing potassium carbonate not in excess of normality, is placed inside an unglazed porcelain cup, and the latter placed in calcium chloride of d 1.0068. After twenty-four hours, numerous very fine tubes of calcium silicate are formed on the outside of the porous cup, bearing on their surface microscopic cells, and in some cases are formed entirely of the latter.
CHEMICAL ABSTRACTS.

An Application of the Optical Method of Determining the Solubility of One Liquid in Another. C. CHÉNEVEAU (*Compt. rend.*, 1922, 174, 1019—1021; cf. this vol., ii, 355).—In the case of inorganic or organic salts which are without action on and insoluble in aniline, when their aqueous solutions are in contact with aniline the ratio of the lowering of the refractive index of the aniline to the quantity of water dissolved is constant and the same for equimolecular solutions. The lowering of the refractive index by unit mass is the same for all salts which fulfil the above conditions.
W. G.

Le Chatelier's "New" Geometrical Representation. ERNST JÄNECKE (*Chem. Ztg.*, 1922, 46, 361).—A claim for priority against Le Chatelier with regard to the method of geometrical representation of solutions of reciprocal pairs of salts (cf. Jänecke, A., 1906, ii, 833; Le Chatelier, A., 1921, ii, 248).
H. W.

The Partial Miscibility of Liquid Couples. Applications to Reactions between Dissolved Substances. RENÉ DUBRISAY (*Ann. Chim.*, 1922, [ix], **17**, 222—256).—A more detailed account of work already published (A., 1919, i, 73; ii, 78; 1920, ii, 508, 756; 1921, i, 535; ii, 282, 344).
W. G.

Sizes of Atoms in Crystals. ROBERT N. PEASE (*J. Amer. Chem. Soc.*, 1922, **44**, 769—774).—A theoretical paper in which, as an alternative to Bragg's view that the distances between atoms in crystals can be expressed in terms of atomic radii characteristic only of the element concerned, it is suggested that the particular element is of secondary importance for elements the atoms of which are of the same rare-gas type, and that the contribution of an atom to the distance between it and another atom in a crystal depends on the number and arrangement of electrons about its positive nucleus, on the type of lattice at least as far as this affects the latter, and, ordinarily, on the magnitude of the charge carried by the atom. The interatomic distances in substances crystallising in the diamond type of lattice have been analysed from this point of view. The following values are recorded: diamond 1.54 (1.54), silicon 2.30 (2.35), grey tin 2.80 (2.80), silicon carbide 1.92 (1.95), zinc sulphide 2.41 (2.35), cuprous chloride 2.41 (2.43), cuprous bromide 2.52 (2.57), cuprous iodide 2.66 (2.78), and silver iodide 2.80 (3.18). The values in brackets are due to Bragg, and the present values generally agree better with the observed values than do those of Bragg.
J. F. S.

Transition from Crystalloid to Colloid Properties within Homologous Series. EDGAR J. WITZEMANN (*J. Physical Chem.*, 1922, **26**, 201—216).—A theoretical paper in which an attempt is made to answer the question "How do such systems as constitute living organisms come into existence?" It is shown that the emulsoid structure of biocolloids (lipoids, carbohydrates, and proteins) constitutes a gross heterogeneity which is also present in a much less conspicuous form in the lower crystalloid members of the same homologous series. In this way, it follows that the particular properties of biocolloids arise from the cumulative effect of certain groups in the molecule. This effect of chemical constitution may be easily traced with soaps, but less easily with the carbohydrates and proteins. Associated with the material heterogeneity there is a well-known heterogeneity of energy. It is shown that such heterogeneities may arise spontaneously on releasing one system into another. The best known energy differentiation under these conditions is the surface energy. It appears that the surface energy phenomena in solutions are energy differentiations definitely associated with material differentiations and these in turn are due to chemical constitution, and that changes in the latter necessarily involve the whole series of effects. In connexion with biological phenomena, these two heterogeneities have been regarded as associated with a vital force, and even now they are frequently thought to be maintained in organisms by a constant expenditure of energy obtained from chemical reactions in the

organism. It is now shown that certainly part of the heterogeneity occurring in the structure of organisms arises from a predisposition on the part of the component substances themselves to give rise to these effects. Such colloidal systems as those prepared from simple biocolloids are self-reproducing from the components; they arise spontaneously and require no unusual outlay of energy for their construction and maintenance. It is shown that the quantitative statement of Le Chatelier's principle may be easily discovered in the phenomena of true and colloidal solutions so fundamentally involved in biological phenomena. J. F. S.

Cataphoresis of Colloidal Carbon. STEPHANIE GOLDBERG (*Kolloid Z.*, 1922, **30**, 230—234).—Colloidal carbon prepared by Sabbatani's method (A., 1914, i, 357; ii, 198) has been thoroughly dialysed to remove sulphuric acid and the influence of various factors on the rate of cataphoresis examined. The sols examined had a specific conductivity at 18° of 22.5×10^{-6} reciprocal ohms, and had various migration velocities toward the anode from 18.3×10^{-5} to 13.5×10^{-5} cm./volt sec. Dilution of the solution increases the velocity slightly to a maximum value, whilst filtration also causes an increase from 18.8×10^{-5} to 22.2×10^{-5} cm./volt sec. The addition of acids, irrespective of their nature, causes a decrease in the velocity; thus 0.001*M*-sulphuric acid decreases the velocity from 13×10^{-5} to 11×10^{-5} , and 0.002*M* reduces it to 8×10^{-5} cm./volt sec. Bases have a similar action, and in one case with ammonia the velocity was reduced from 19×10^{-5} to 13×10^{-5} cm./volt sec. Acids and bases change the colour of colloidal carbon, but the original colour may be regained by neutralisation. In the case of salts, only those of aluminium have any action on the velocity of migration, and in this case the velocity increases to a maximum with 1/500000*M*-aluminium sulphate and then falls with greater concentrations. The addition of colloidal ferric hydroxide generally coagulates the colloidal carbon, but if so much colloidal ferric hydroxide is added that no coagulation takes place, then the velocity is reduced about 20%. Dyes, such as crystal-violet, auramine, and methylene-blue, in small concentrations, reduce the velocity to zero and with increasing concentrations then increase it. J. F. S.

Ionic Synergism. II. Investigation of Mastic Sols. L. MICHAELIS and N. HIRABAYASHI (*Kolloid Z.*, 1922, **30**, 209—215; cf. A., 1921, ii, 682).—The limiting concentrations of hydrochloric, acetic, sulphuric, nitric, and sulphasalicylic acids, by which precipitation of mastic sols may be brought about, have been determined and the P_H value of the solutions has been measured. The effect of adding lithium chloride, rubidium chloride, sodium carbonate, sodium citrate, calcium chloride, sodium chloride, and potassium sulphate to mastic sols in the presence of measured concentrations of hydrogen-ions has also been investigated. The results show that the anion is not entirely without influence on the precipitation of electro-negative mastic sols; certain anions (sulphasalicylic acid) are strongly antagonistic to the cations, but

the more common anions have so small a specific action that as a first approximation they may be neglected in the investigation of the synergism of the hydrogen-ion and the metallic kations. The results therefore furnish an approximate confirmation of the rules established in the case of congo-rubin (*loc. cit.*) both for the univalent alkali-ions and for the bivalent calcium-ion. From the results, it follows that the relationship of the activity of a uni- and a bi-valent ion cannot be given in absolute terms, but only with reference to the P_H value, and only with increasing value of P_H does the relationship approach an absolute limiting value. Changes in the concentration of the hydrogen- and hydroxyl-ions are only without effect on the condition of a mastic sol when P_H is greater than about seven or eight.

J. F. S.

Soaps and Proteins. I. Colloidal Chemistry of Soaps and the Manufacture of Soap. MARTIN H. FISCHER, GEORGE D. McLAUGHLIN, and MARIAN O. HOOKER (*Koll. Chem. Beihefte*, 1922, 15, 3—102).—A general account of the preparation of soaps, and a consideration, with experimental results of the systems soap-water, soap-alcohol and soap- X , where X is one of a long series of organic liquids. Definitions of a number of terms in their colloid-chemical significance are given; these include hysteresis, swelling, liquefaction, power of gelatinisation, and solvation, syneresis, and sol. The behaviour of soaps towards indicators and many other properties of soaps are considered. Reproductions of twenty-nine photographs are included in the paper, illustrating the behaviour and properties treated.

J. F. S.

Non-, Uni-, and Bi-variant Equilibria. XXI. F. A. H. SCHREINEMAKERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, 23, 1151—1160; cf. A., 1920, ii, 361).—A theoretical paper in which the author considers the equilibria of n components in n phases, where the quantity of one of the phases approaches zero. The influence of a new substance on an invariant P or T equilibrium is discussed.

J. F. S.

Heterogeneous Equilibria: The Ternary System Sodium Sulphate-Sodium Carbonate-Water. ALFRED ERNEST DAWKINS (T., 1922, 122, 776—781).

Nature of Secondary Valency. V. Partition Coefficients in Systems containing Water as one Component, with Special Reference to the Absolute Values of the Series Constants. HOMER W. SMITH (*J. Physical Chem.*, 1922, 26, 256—271; cf. this vol., ii, 270).—A continuation of previous work in which the series constants of the partition of organic acids and bases between water and various organic liquids have been derived from data largely taken from the literature. It is shown that in each of these systems the series constants for the various dissolved substances are related to each other in a simple proportion. The series constants for twelve systems in which water is one component have been tentatively formulated by the study of diethylamine. In all twenty of the systems studied, the series constants

for the various systems are related to each other in simple proportion. In every system in which water is one component, the amines differ from the acids in the value of their series constants by a constant amount. It is concluded that the intermolecular forces concerned in the solvent powers of various molecular species differ in intensity by discrete and simply-related amounts.

J. F. S.

Nature of Secondary Valency. VI. HOMER W. SMITH (*J. Physical Chem.*, 1922, **26**, 349—357; cf. A., 1921, i, 324; ii, 315; this vol., ii, 270).—The results of the preceding papers are summarised and discussed. It is shown from the examination of twelve hundred determinations of the partition coefficient in twenty-one systems of two immiscible liquids that all may be covered by an equation of the form $100P = V_m/60.00 \pm a$, where V_m is the molecular volume at the boiling point and a is a constant. It is found that a limited number of values of a are required to cover the behaviour of all substances in any one system. All substances covered by any one value of a in any system have been termed a series, and the value of a a series constant. The various values of a in any one system are related to one another in simple proportion.

J. F. S.

Kinetics of Reactions in Heterogeneous Solutions. The Reduction and Oxidation Actions of Alternating Currents.

OSCAR COLLEBERG and SVEN BODFORSS (*Z. physikal. Chem.*, 1922, **101**, 117—149).—The action of metallic iron, copper, zinc, tin, and cadmium on a 4% solution of ferric alum has been investigated by studying the rate of solution of the metals. The results show that the solution of the metals takes place in accordance with Nernst's hypothesis, and the velocity of solution is in keeping with the laws of unimolecular reactions in heterogeneous systems. Apart from zinc, the reaction constant for the individual metals, despite their electrochemical dissimilarity, are very similar. The similarity becomes more apparent when the quantities of the metals dissolved in a given time are compared in terms of equivalents. Using the above metals as electrodes, the electrolysis of ferric alum has been carried out by means of alternating currents of various periodicity; it is shown that the current brings about no fundamental difference in the course of the reaction beyond an increase in the total yield. The influence of the periodicity is very small.

J. F. S.

Thermal Dissociation of Ammonia with Special Reference to Coke Oven Conditions. G. E. FOXWELL (*J. Soc. Chem. Ind.*, 1922, **41**, 114—125).—The thermal decomposition of ammonia diluted with coal gas in silica tubes packed with porous material such as coke or firebrick has been investigated at temperatures between 520° and 850°. It is shown that when an excess solid surface is present the decomposition is bimolecular. The velocity of decomposition, when the tube is filled with coke, increases slowly with increasing temperature, the temperature coefficient being

1.136. The value of the velocity constant, k , may be expressed by the Arrhenius formula $k_2 = k_1 e^{[A(C/T_1 - 1/T_2)]}$, where A is 13300. For tubes with a radius less than 0.5 cm., $k \propto 1/r^2$, but it is probable that for wider tubes $k \propto 1/r$. When gases containing ammonia are passed through porous material, the amount of decomposition in unit time varies directly as the square of the radius of the pores; hence it is the size of the pores rather than the total porosity that is of importance. Silica bricks have considerably less decomposing effect than siliceous (80% SiO_2) bricks, whilst the presence of iron is very deleterious. The composition of the ash of the coke has an important bearing on the rate of decomposition. Rutile and orthoclase have very little, if any, action; iron pyrites is converted into ferrous sulphide during carbonisation, and this increases the velocity of decomposition to some extent. Iron oxide, which is converted into metallic iron, enormously increases the rate of decomposition and the same is true, although to a less extent, of lime. The value of k for coke is found to be 0.00200 at 755° .
J. F. S.

Decomposition of Nitrous Acid. ALFONS KLEMENC and FRIEDRICH POLLAK (*Z. physikal. Chem.*, 1922, **101**, 150—171).—The velocity of decomposition of nitrous acid in dilute acid solutions (acetic, nitric, sulphuric) has been determined. The reaction mixture was stirred continuously by a stream of nitrogen to remove the nitric oxide from the solution. It is shown that the velocity of decomposition, according to the equation $3\text{HNO}_2 = \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$, as measured by the decreasing permanganate titre, depends on the velocity with which the nitric oxide is removed from the solution. This process is determinative of the velocity. The velocity also depends on the pressure of nitric oxide above the solution. It is assumed that undissociated nitrous acid possesses a considerable pressure of nitric oxide and in consequence the velocity of decomposition is proportional to the concentration of undissociated nitrous acid. This fact has been confirmed under the most widely varying conditions. On the basis of the "invasion" and "evasion" coefficients for carbonic acid measured by Bohr, it has been shown that the concentration of free nitric oxide in aqueous solution may be regarded as approximately the same as that of the undissociated nitrous acid. When nitrogen is led through a solution of nitrous acid the velocity of decomposition is increased, and the velocity constant increases with the increasing velocity at which the nitrogen is passed through. The velocity of the direct decomposition of nitrous acid cannot be determined by the method adopted, and is in all probability immeasurably rapid. Nitrous acid decomposes spontaneously into nitric oxide and the hydroxyl radicle and its transitory existence in aqueous solution is due to a mutual action between it and the solvent. The temperature coefficient of the reaction is in keeping with the quantities which define the solubility of a gas. The presence of mineral acids increases the velocity of decomposition.
J. F. S.

Thermal Decomposition of Nitrogen Pentoxide in Solution.

ROGER H. LUECK (*J. Amer. Chem. Soc.*, 1922, **44**, 757—769).—The velocity of decomposition of nitrogen pentoxide in carbon tetrachloride and in chloroform solutions has been determined gasometrically at temperatures between 25° and 55°. It is shown that such systems are of special value in considering the newer hypotheses concerning the relationships of radiant energy to chemical action. The fact that the velocity constants obtained in solution so closely approximate to those obtained in the gas phase by Daniels and Johnston (*A.*, 1921, ii, 249) is of particular importance because of the wide variation of conditions under which the measurement has been made. The experimental facts show the energy of activation or the critical increment to be practically independent of the temperature. It has also been shown that, in accordance with a necessary deduction from the Perrin-Lewis radiation theory, a change in reaction velocity brought about by temperature effects or the influence of solvent diminishes as the magnitude of the velocity constant increases. A comparison has been made between the values of the velocity constant experimentally obtained and those calculated from the critical increment, by means of the equation recently put forward by Dushman (*A.*, 1921, ii, 315), and although the agreement is not exact, it is far better than can be obtained by means of the older equations developed by Trautz and Lewis. The nitrogen peroxide formed in the reaction has been shown to exert an autocatalytic effect on the thermal decomposition of the nitrogen pentoxide.

J. F. S.

The Velocity of Absorption of Carbon Dioxide by Alkaline Solutions.

PAUL RIOU (*Compt. rend.*, 1922, **174**, 1017—1019).—A study of the absorption of carbon dioxide by solutions of sodium carbonate. For a given area of absorbing surface the velocity of absorption of carbon dioxide diminishes as the concentration of the sodium carbonate increases. It is also diminished by the presence of increasing amounts of sodium chloride or hydrogen carbonate. The velocity of absorption is markedly increased by agitation or rise in temperature of the liquid. It is diminished by diluting the carbon dioxide with air.

W. G.

The Speed of Sulphonation of Phenols. I. The Effect of Temperature and the Methyl Group.

ARTHUR FRED CAMPBELL (*T.*, 1922, **121**, 847—857).

Formation and Hydrolysis of Lactones. II.

ANTON KAILAN and EMANUEL FRANZ NEUMANN (*Z. physikal. Chem.*, 1922, **101**, 63—93; cf. *A.*, 1920, ii, 606).—The velocity of lactone formation in aqueous and ethyl-alcoholic solutions in the case of hydroxybutyric acid and hydroxyvaleric acid has been determined both in the absence of catalysts and in the presence of hydrochloric, hydriodic, sulphuric, chloroacetic, and *n*-butyric acids. All experiments were carried out at 25°, and in some cases an addition of potassium chloride or sodium chloroacetate was made to the

reaction mixtures. The rate of hydrolysis of butyrolactone and valerolactone in the presence of hydrochloric acid has also been determined. It is shown that the autocatalysis of the lactone formation in aqueous solution is practically proportional to the hydrogen-ion concentration alone, and that consequently the results of Henry (A., 1892, ii, 1303), which differ from this result, must be attributed to the presence of the silver salt of the hydroxy-acid in his solutions. Lactone formation in the presence of chloroacetic acid also depends on the concentration of the hydrogen-ion. When hydrochloric acid is used as catalyst in concentrations up to $N/5$, the velocity of lactone formation is proportional to the total concentration of this acid, and if the view be held that the undissociated hydrochloric acid exerts a specific catalytic action, then in this case it must be the same as that of the hydrogen-ion ($k_m = k_H$). With larger concentrations of hydrochloric acid, the velocity of reaction increases much more rapidly than the hydrogen-ion concentration, but more slowly than the total acid concentration, so that in these concentrations the action of the undissociated hydrochloric acid molecule must be decidedly less than that of the hydrogen-ion. This difficulty is removed if the hydrogen-ion is regarded as the only independent catalyst in this reaction, and the divergences from the proportionality between concentration and velocity as due to an increase in the activity of the hydrogen-ion brought about by the addition of hydrochloric acid exactly as is the case on the addition of neutral salts. The increase in the velocity of reaction which occurs on the addition of potassium chloride to hydrochloric acid is not to be attributed to a driving back of the dissociation alone, as was assumed by Taylor and Close (A., 1917, ii, 253), and consequently the deduction of the ratio k_m/k_H from this is not permissible. No connexion could be found between the velocity of reaction and Noyes's activity constants. The velocity of lactone formation in 99% alcohol, by volume, in the case of γ -hydroxyvaleric acid, both in the presence and absence of hydrochloric acid or other catalysts, takes place much more rapidly than in water. Water exerts a greater retardation on the velocity of lactone formation by hydrochloric acid than it does in the case of esterification by the same acid. The gradual addition of water causes the velocity of lactone formation to fall gradually to a point below that obtained in pure water, after which it gradually rises to that obtained in pure water. In the autocatalytic lactone formation in 99% alcohol, only a part of the observed velocity is to be explained by the concentration of the hydrogen-ions.

J. F. S.

The Alkaline Hydrolysis of the Esters of the Two Ethylenedicarboxylic Acids. ANTON SKRABAL and EMMY RATH (*Monatsh.*, 1921, 42, 245—249).—The study of the hydrolysis of tartaric esters (A., 1920, ii, 239) and succinic esters and their homologues (A., 1921, ii, 34) has been extended to the investigation of the alkaline hydrolysis of the methyl esters of fumaric and maleic acids. The experiments were conducted at 25° in aqueous

solution containing a molecular proportion each of sodium carbonate and sodium hydrogen carbonate, the dilution being necessarily high on account of the low solubility in water of both esters. Referred to $[\text{OH}'] = 1$, the constants for the two stages of the hydrolysis are, for the fumaric ester, $k_1 = 414$, $k_2 = 19$, ratio $n = 22$; for the maleic ester, $k_1 = 48$, $k_2 = 0.72$, $n = 67$. Comparing these values with the first and second dissociation constants of the acids, which are: fumaric acid 1.0×10^{-3} and 3.2×10^{-5} ; maleic acid, 1.4×10^{-2} and 2.6×10^{-7} , fumaric acid falls into line with the saturated, straight chain dicarboxylic acids in that the acid strength and rate of hydrolysis of the esters are symbatic. Maleic acid, however, is abnormal, the first hydrolysis constant being unexpectedly low compared with the high value of the first dissociation constant. The observation may have an important bearing on the question whether there may not be a structural as well as a spatial difference between the two acids.

E. H. R.

Kinetics of the Reaction between Ammonia and Aromatic Aldehydes. FRIEDRICH DOBLER (*Z. physikal. Chem.*, 1922, **101**, 1—33).—The velocity of the reaction of ammonia and alcoholic solutions of benzaldehyde, *p*-tolualdehyde, *m*-xylyl-aldehyde, anisaldehyde, cinnamaldehyde, *p*-chlorobenzaldehyde, and *o*-, *m*-, and *p*-nitrobenzaldehydes has been investigated. The method of investigation depends on the fact that ammonia may be estimated in the presence of hydrobenzamide by titration with hydrochloric acid, using hæmatoxylin as indicator. The formation of hydrobenzamide at 20° is shown to be strictly bimolecular, and the corresponding hydramides formed from the other aldehydes are also in most cases formed according to the bimolecular formula. In the case of benzaldehyde and *p*-tolualdehyde, the dependence of the velocity constant on temperature has been determined; it is found that k is nearly doubled by raising the temperature 10° and trebled by raising the temperature 20° , thus: for benzaldehyde, $k_{20} = 0.233$, $k_{30} = 0.400$ and $k_{40} = 0.627$, the two latter values are not very constant. It is found that, on the one hand, an equilibrium is set up between aldehyde and ammonia, and, on the other, between hydramide and water. The influence of temperature on the equilibrium has been investigated, and it is shown that with increasing temperature the equilibrium is displaced so that less hydramide is formed; thus in the case of benzaldehyde at 20° , 48.4% of the ammonia has been converted into hydramide, at 30° , 43.8%; 40° , 36.3% and 50° , 23.2%. An addition of 0.01*N*-benzoic acid practically doubles the reaction velocity in the case of benzaldehyde; small additions of ammonium chloride effect a large increase in the velocity of hydramide formation, in one case this amounted to an increase in the k value from 0.233 to 2.325. Ammonium sulphate has no effect on the specific reaction velocity, whilst sodium hydroxide reduces the k value from 0.233 to 0.028. These changes in velocity are shown to be due to the same cause, namely, changes in the dissociation of ammonium hydroxide. A decrease in the hydroxyl-ion con-

centration increases the specific reaction velocity, and an increase decreases the velocity. Double bonds and chlorine in the para-position in the nucleus of the aldehyde increase the reaction velocity respectively six and three times. The introduction of a methyl group in the para-position, for example, *p*-tolualdehyde, increases the velocity, whilst a second methyl group in the ortho-position, *m*-xylyl-aldehyde, reduces the value somewhat, but it is still greater than that of the original benzaldehyde. The methoxyl group in anisaldehyde reduces the velocity to about one-half. The substitution of a nitro-group in the meta-position increases the velocity, but in the ortho- and para-positions it reduces the velocity, the para-substitution causing the greater reduction. The ionic concentration of the reaction mixtures does not change during the hydramide formation at 0° and 20°, as is shown by the constant value of the electrical conductivity.

J. F. S.

Catalysts and Chemical Equilibrium. J. CLARENS (*Bull. Soc. chim.*, 1922, [iv], 31, 299—307).—From a study of the action of glass wool and cupric chloride respectively as catalysts of the reversible reaction $4\text{HCl} + \text{O}_2 \rightleftharpoons 2\text{H}_2\text{O} + 2\text{Cl}_2$, it is shown that the action of the catalyst is different for each of the inverse reactions which determine the equilibrium. In general, it is considered that there is no reason to suppose that a catalyst modifies equally the velocity of two inverse reactions.

W. G.

The Influencing of the Catalysis of Hydrogen Peroxide with Platinum by Röntgen Rays. ROBERT SCHWARZ and WALTER FRIEDRICH [with H. WUNNERLICH] (*Ber.*, 1922, 55, [B], 1040—1051).—The catalytic decomposition of hydrogen peroxide in the presence of colloidal platinum is retarded by Röntgen rays, the effect being observed when the mixture of the substances is exposed to the radiation or when the platinum sol is treated in this manner separately and added shortly afterwards to the hydrogen peroxide; the latter alone does not undergo an appreciable change under the influence of Röntgen rays. The maximal value of the retardation is 77% (calculated on the percentage of hydrogen peroxide) and the highest values are observed in the sixth and seventh hours of the experiments. The cause of the phenomenon does not appear to lie in coagulation, diminution in the degree of dispersivity, or alteration in the charge of the particles, as is shown by special experiments, and is rendered improbable by the further observation that the illuminated sol recovers its activity completely within about sixteen hours. It appears probable, therefore, that the platinum sol suffers a reversible change at its surface which must be attributed to the presence of water. Since the action of the Röntgen rays is accompanied by an emission of β -rays from the platinum particles which are able to decompose water, it is possible that an oxide of platinum is formed or that hydrogen is adsorbed by the sol. If, however, it is assumed with Haber that the platinum catalysis of hydrogen peroxide is conditioned by the presence of dissolved or combined oxygen in the catalyst, the formation of an oxide would in all probability accelerate the

change. It is therefore more likely that the first stage of the catalysis is delayed because the platinum charged with hydrogen is not immediately able to form the intermediate product, Pt_2O_9 . The first stage of the action therefore consists in the combustion of the dissolved hydrogen by oxygen derived from the peroxide after which catalysis can take place in the sense of Haber's theory. The recovery of the platinum sol within sixteen hours is attributed to the gradual decomposition of the platinum hydrogen alloy, and this hypothesis is supported by the known complete instability of the product at 100° . It is also possible that the removal of hydrogen is effected by dissolved atmospheric oxygen, but direct experiments in the absence of oxygen do not lend support to this view, although their interpretation is hampered by the extreme difficulty of excluding oxygen completely in such observations. Pure water is not altered by exposure to Röntgen rays in such a manner as to give rise to contact poisons.

Catalase, also, is altered in such a manner by Röntgen rays that its power to catalyse the decomposition of hydrogen peroxide is lessened; as with the platinum sol, the enzyme recovers its activity completely after several hours. A satisfactory explanation of the phenomena cannot yet be given.

H. W.

The Catalytic Activity of Copper. W. G. PALMER (*Proc. Roy. Soc.*, 1922, [A], **101**, 175—186; cf. A., 1920, ii, 609; 1921, ii, 542).—This communication describes the effect on the dehydrogenating activity of copper of the addition of magnesium oxide, ferric oxide, zinc oxide, manganous oxide, and sodium carbonate. The presence of small amounts of sodium carbonate completely destroys the activity. The addition of 1% or less of an oxide reduces the activity considerably, but with higher concentrations, owing to the separation of two phases, an increase in the catalytic effect is observed. The pure oxides are usually less active than pure copper, and hence must be deficient in the density of radiation of about 1.0μ wave-length (cf. previous papers). They, however, adsorb water and probably alcohol to a greater extent than metals, but this increase may be counteracted by the opacity of the oxide film to radiation from the copper core. Increased adsorption thus increases the activity, provided the oxide films are transparent to the radiation of the main catalyst.

W. E. G.

A Defined Organic Catalyst with a Hydrogen-ion Optimum. ERIK WIDMARK and CARL ALEX JEPSSON (*Skand. Arch. Physiol.*, 1922, **42**, 43—61; from *Physiol. Abstr.*, 1922, **7**, 6; cf. A., 1921, ii, 183).—The kinetics of the catalysis of acetoacetic acid into acetone and carbon dioxide is investigated in detail. It is found to have a reaction optimum at P_{H} 4.09, and this corresponds exactly with the optimum reaction calculated on the assumption that only undissociated molecules of catalyst and of substrate enter into the reaction. For this calculation from the dissociation constants, the original must be consulted. The conclusion is drawn that only the undissociated aniline molecule is effective,

and acts only on the undissociated molecule of acetoacetic acid. The conclusion cannot be generalised: for example, alanine has its optimum at P_H 8, at which reaction acetoacetic acid is almost completely ionised. The suggestive comparison with the behaviour of enzymes is indicated.

W. O. K.

The Bôhr Atom. The Lagrange Theorem applied to Electronic Orbits. MARCEL BRILLOUIN (*J. Phys. Radium*, 1922, 3, 65—73).—A mathematical paper emphasising the exclusively spectroscopic character of Bôhr's theory.

W. E. G.

Atoms and Molecules. II. ALBERT C. CREHORE (*Phil. Mag.*, [vi], 43, 886—914; cf. A., 1921, ii, 632).—A theory of the structure of atoms is presented which is in conformity with the Saha form of the electromagnetic theory. In the models given, the negative electron is assumed to be an oblate spheroid with a ratio of axes about three to one and the hydrogen atom consists of a positive charge of two units with very small dimensions situated in between two negative electrons. A structure is suggested for nitrogen and oxygen, which indicates that the heavier products of disintegration found by Rutherford may possess a mass 12 and a charge of 5.

It is also sought to compute the known distances between the atoms forming a molecule. The shape of the negative electron is a most important factor in determining the equilibrium distance, and hence it is a universal distance. Only electrostatic forces are considered, and it is shown that equilibrium is possible between the attractive and repulsive forces of the atoms and electrons when the eccentricity of the electron lies between the limits 0.9 and 1.0. This agrees with the value found in the previous paper. It is shown that helium and neon atoms will not form compounds and must be monatomic.

W. E. G.

Unsymmetrical Addition to the Double Bond. I. A Theory of the Reaction Mechanism of the Direct Union. GRANVILLE A. PERKINS (*Philippine J. Sci.*, 1921, 19, 645—660; cf. this vol., A., ii, 138).—A theory of the mechanism of chemical reaction based on the Langmuir octet theory of valence. Diagrams are given showing the relationships between the forces of attraction and repulsion for two types of reaction, (a) a direct addition reaction, where an interpenetration of the outer shells of electrons occurs, and (b) a dissociation addition reaction where only secondary valence comes into play. These two types are illustrated by double bond reactions.

W. E. G.

The Dissociation of Hexaphenylethane from the Point of View of the Octet Theory of Valence. HOWARD IRVING COLE (*Philippine J. Sci.*, 1921, 19, 681—690).—A historical survey of the previous investigations on the dissociation of hexaphenylethane is given and the Lewis-Langmuir octet theory of valence applied to this problem on the lines suggested by Perkins (this vol., A., ii, 138). On this theory hexaphenylethane cannot possibly dissociate without a rearrangement of one or more of the phenyl

groups. Symmetrical dissociation occurs in non-ionising solvents such as benzene, giving the quinoid modification as in Gomberg's

formula, $(\text{C}_6\text{H}_5)_2\text{C}=\text{C}=\text{C}_6\text{H}_5$, which contains a para-carbon atom in a tervalent condition. In an ionising solvent such as sulphur dioxide, which contains unshared electrons, the dissociation occurs unsymmetrically. An unstable union with a solvent molecule takes place, which supplies two electrons to the shell of one of the carbon atoms in a phenyl group. In this manner is obtained a colourless negative ion, $(\text{C}_6\text{H}_5)_3\text{C}^-$, and a coloured positive ion, $(\text{C}_6\text{H}_5)_2\text{C}=\text{C}=\text{C}_6\text{H}_5^+$; the latter exists only in combination

with a solvent molecule. These two ions can combine to give $(\text{C}_6\text{H}_5)_3\text{C}=\text{C}=\text{C}_6\text{H}_5$. These modifications are essentially

the same as those of Gomberg, except that, on this view, colourless triphenylmethyl can exist only in the form of a negative ion. The physical and chemical properties appear to support this theory. The oxidation of triphenylmethyl to form a peroxide is explained by the formation of intermediate positive and negative ions. An oxygen molecule is added to the positively charged ion, which then combines with the negative ion to give the peroxide.

W. E. G.

A Proposed Laboratory Test of the Theory of Relativity.

HAROLD S. KING (*Nature*, 1922, 109, 582—583).—Since it is impossible to conceive of the annihilation of mass, such as appears in the synthesis of an atom of helium from four hydrogen atoms, it must be supposed that mass is electromagnetic in origin, loss of mass being ascribed to overlapping of fields. According to the theory of relativity, 1 gram of matter is equivalent to 9×10^{20} ergs, or 2.1×10^{13} calories; moreover, 1 gram of radium in disintegrating to lead evolves 3.7×10^9 cal. Thus, it is possible to calculate the atomic weight of radium (226.038) by addition of 1 gram atom of radium-*G* (206.000), 5 gram atoms of helium (20.000), 4 gram electrons (0.0005) [?], and 3.7×10^9 cal. (0.038). If Hönigschmid's value (225.97) for the atomic weight of radium is accepted, it would therefore appear that radium-*G* has an atomic weight less than 206 (the lowest experimental figures being 206.08 and 206.05, due respectively to Richards and Hönigschmid), that energy is derived from outside sources as suggested by Perrin, or that the equation connecting mass and energy is not correct. It is therefore suggested that an extension of the method of positive ray analysis to the determination of the atomic weights of radium, radium-*G*, and helium to an accuracy of 1 part in 10,000 not only would be of intrinsic value, but also would show whether the relation of mass and energy, based on the theory of relativity, holds.

A. A. E.

Inorganic Chemistry.

A Simple Hydrogen Generator for Use in making Hydrogen-ion Determinations. P. H. CATHCART (*J. Ind. Eng. Chem.*, 1922, **14**, 278).—The hydrogen is generated electrolytically in a bell jar inverted in a cylinder containing 10% sodium hydroxide. The outer vessel consists of a large glass precipitating jar, the hydrogen reservoir being a large inverted percolator with its mouth resting on a support about 1 inch from the bottom of the precipitating jar. A rubber stopper in the top of the hydrogen reservoir carries the cathode (which consists of an iron disk suspended from an iron wire) and a glass tube with stop-cock. The inner vessel is held down by four rubber-covered wires. The anode is similar to the cathode, of about 4 sq. in. area, and so adjusted in the annular space between the two vessels that it just touches the liquid when all gas has been withdrawn from the reservoir. The cathode just projects below the lower rim of the reservoir. A 110 volt D.C. circuit was used for generating the hydrogen, with a switch so arranged that the current is automatically cut off when the reservoir becomes full. A diagram of the apparatus is given. H. C. R.

Rectilinear Diameter of Hydrogen. E. MATHIAS, C. A. CROMMELIN, and H. KAMERLINGH ONNES (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **23**, 1175—1184; cf. A., 1921, ii, 256).—The density of liquid and gaseous hydrogen has been determined in grams/c.c. at temperatures from -240.57° to -249.89° . The critical density is calculated from the results and the value 0.03102 obtained, a figure which is considerably smaller than the corresponding figure for any other substance. The equation of the diameter of the form $y=a+bt$ is considered, and the values of the coefficient are evaluated from the experimental data. The values obtained are $a=-0.063510$ and $b=-0.00039402$. The value of the slope of the diameter b is the smallest observed for any substance.

J. F. S.

The Crystal Structure of Ice. (SIR) W. H. BRAGG (*Proc. Physical Soc.*, 1922, **34**, 98—103).—This is derived independently of direct X-ray analysis on certain suppositions connected with the low density of ice. St. John (*Proc. Nat. Acad. Sci.*, 1918, **4**, 193) and Debye (*Physical Rev.*, 1921, **17**, 20) have applied the methods of X-ray analysis and both refer the structure to a lattice composed of four right triangular prisms but disagree as to the dimensions. In the present paper it is assumed that ice belongs to that class of crystals in which the molecules are broken up into positive and negative ions, the hydrogens having given up their valency electrons to the oxygens. The density of ice is so low that the most economical spacing is adopted; the atoms are arranged in a hexagonal lattice with each oxygen surrounded by four hydrogens and each hydrogen by two oxygens. The distance between the

centres of two oxygen atoms is 2.76, the distance between consecutive basal planes is 3.67, and the distance between two atoms in the same plane is 4.52. The structure is extremely empty and a loose arrangement of water molecules would occupy less space. The hydrogen atom has apparently a larger diameter than the oxygen atom if oxygen has the value 1.30. These results agree exactly with the *X*-ray analysis of Dennison and the conclusions are supported by a comparison between the calculated and observed intensities of reflection.

W. E. G.

The Variations in the Chemical Composition of Sea-water and the Evaluation of the Saline Content. GABRIEL BERTRAND, FREUNDLER, and (Mlle) MÉNAGER (*Compt. rend.*, 1922, **174**, 1251—1253).—The authors have determined the total halogens and the calcium and magnesium in the water from the Atlantic ocean and the Mediterranean sea. The halogens being calculated as chlorine, the ratio of chlorine to calcium and magnesium respectively in the two samples of water was by no means the same. Thus the method of evaluating the saline content of sea-water from the density or chlorine content by means of Knudsen's tables can only be considered as at the best an approximation.

W. G.

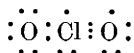
The Dissociation of Chlorine. H. VON WARTENBERG and F. A. HENGLEIN (*Ber.*, 1922, **55**, [B], 1003—1006).—Difficulties are experienced in attempting to measure the dissociation of active gases such as chlorine by observation of the abnormal increase of pressure when they are heated owing to the impossibility of finding a completely resistant material for the construction of the apparatus. Since, however, the dissociation of binary compounds is dependent on the total pressure, it is possible to effect such measurements at temperatures which silica vessels will withstand if an extremely low pressure is used. In this manner, preliminary measurements of the dissociation of chlorine at 10^{-3} mm. pressure have been made. The apparatus consists of a quartz bulb surrounded by a quartz mantle, the space between the two being continuously evacuated. The bulb is connected with a 2 mm. wide quartz capillary which leads to a quartz thread manometer and mercury seal cooled to -30° and thence to a Volmer pump. The chlorine is generated by heating auric chloride in a glass capillary which is subsequently sealed off. The bulb is surrounded by platinum foil and heated in a Heraeus furnace, the temperature measurements being accurate to $\pm 2^{\circ}$. The temperature interval ranges from 985° to 1151° absolute.

It is certain that the heat of dissociation of chlorine is considerably lower than the value 106,000 cal. usually adopted and for $T=0$ is about 70,000 cal.

H. W.

The Structure of Chlorine Dioxide and Related Compounds. GRANVILLE A. PERKINS (*Philippine J. Sci.*, 1921, **19**, 729—740; cf. this vol., ii, 138).—A discussion of the constitutional formulæ of some of the oxides of chlorine and nitrogen. In the Langmuir theory no place is given to bonds consisting of

one, three, or five electrons. The suggestion is made that in exceptional cases an odd number of electrons may form a chemical bond. In chlorine dioxide, five electrons are shared between the three atoms as in the formula :



On this view chlorine dioxide contains a three electron bond. An odd electron is also shared in nitric oxide and nitrogen peroxide. The electron binding strength of atoms and its variation with the covalence is discussed.

W. E. G.

Hydroxylamine. I. Simple Method of Preparation of Free Hydroxylamine. HANS LECHER and JOSEF HOFMANN (*Ber.*, 1922, 55, [B], 912—919).—The method adopted is essentially a modification of that of Lobry de Bruyn, its most important feature being the avoidance of the final distillation of the product.

The apparatus consists of a Brühl receiver in which the reaction vessel is placed. The lower tubulus (generally used for evacuation) is provided with a calcium chloride tube whilst the upper tubulus is fitted with a stopper carrying two dropping funnels, the ends of which are placed above the reaction vessel. The tubulus of the lid serves for the introduction of a very efficient stirrer, which is provided with the customary mercury seal. The finely divided hydroxylamine hydrochloride is suspended in absolute ethyl alcohol in the reaction vessel and a small quantity of solid phenolphthalein is added. A solution of sodium ethoxide in absolute ethyl alcohol is introduced slowly from one of the dropping funnels into the well-stirred suspension, the rate of addition being so controlled that the red coloration which occurs as each drop enters the suspension disappears instantaneously. Should ultimately a pale pink coloration persist, it is removed by cautious addition of a solution of hydroxylamine hydrochloride in ethyl alcohol from the second dropping funnel. The precipitated sodium chloride is removed and the filtrate allowed to remain undisturbed in a freezing mixture of ice and salt until it attains a temperature of -18° . The large crystals of hydroxylamine thus produced are filtered, washed with absolute ether, and brought into a desiccator which is immediately exhausted. In this manner, there is no loss of hydroxylamine by decomposition during the preparation, but about 5.4% of it is retained by the precipitated sodium chloride. The yield of solid hydroxylamine is about 40% of that theoretically possible, but the remainder can be readily recovered as the hydrochloride from the alcoholic mother-liquor. The product contains about 97% of hydroxylamine, the remainder being water. It has m. p. $32-35^{\circ}$, $d^{10}_{4} 1.335$, $d^{14}_{4} 1.334$. It is distinguished from Lobry de Bruyn's purest specimens by its greater instability; after twenty-four hours it smells of ammonia and after four days it is completely liquefied and contains only 42.55% of hydroxylamine. Hydroxylamine crystallises in the rhombic system; the crystals obtained from ethyl alcohol and by the solidification of the molten substance are identical.

H. W.

Behaviour of Carbon at High Temperatures. F. SAUERWALD (*Z. Elektrochem.*, 1922, **28**, 183—185).—Continuing the work of Ryschkewitsch (A., 1921, ii, 258, 586, 696) and Münch (A., 1921, ii, 586), the author heated rods of carbon and graphite to various temperatures, attaining finally the temperature of the positive crater of the arc. The heating was effected by passing a current through the rods in an atmosphere of hydrogen. The ends of the rods were copper-plated. Small globules appeared on the surface of the Acheson graphite employed, and these are attributed to the distillation of impurities from the hotter interior of the rod to the surface. This was confirmed by a determination of the respective ash contents of the rod and of the globules. The conclusion is not in agreement with that of Ryschkewitsch, who found similar globules to be composed of pure graphite. J. S. G. T.

Behaviour of Carbon at High Temperatures. EUGEN RYSCHKEWITSCH (*Z. Elektrochem.*, 1922, **28**, 185—186).—The author contends that the experimental conditions employed by Sauerwald (see preceding abstract), differ so materially from his own, that the results obtained in the two cases are not comparable. He remarks more particularly on the different atmospheres and current densities employed in the two cases, and on the possibility of impurities being derived, in Sauerwald's experiments, from the heated metallic connexions employed. J. S. G. T.

Preferential Catalytic Combustion of Carbon Monoxide in Hydrogen. ARTHUR B. LAMB, CHARLES C. SCALIONE, and GRAHAM EDGAR (*J. Amer. Chem. Soc.*, 1922, **44**, 738—757).—With the object of finding a method of removing small quantities of carbon monoxide from hydrogen before its use in the synthetic production of ammonia, a number of experiments have been carried out on the preferential combustion of carbon monoxide in mixtures containing air, hydrogen, carbon monoxide, and carbon dioxide by means of a catalyst termed "hopcalite," which is a mixture of metallic oxides and in the present experiments was composed of 60% of manganese dioxide and 40% of cupric oxide. It is shown that "hopcalite," which oxidises carbon monoxide in air rapidly and catalytically at the ordinary temperature, does not affect hydrogen in air under the same conditions, and that by its means carbon monoxide can be completely and continuously removed from a dry mixture containing, for example, 0.5% of carbon monoxide, 89.50% of hydrogen, and 10% of air without any noticeable action on the hydrogen. A similar mixture containing 1% of carbon monoxide, on the other hand, liberates so much heat that under these conditions oxidation of the hydrogen sets in, and the catalyst is soon heated to incandescence and is destroyed. It is also shown that moist mixtures of carbon monoxide and air and of hydrogen and air require much higher temperatures for oxidation. In the presence of water vapour at a pressure of 50 mm. of mercury, carbon monoxide in a 0.5% mixture with air is completely oxidised at a temperature of 90° or lower. Hydrogen, on the other hand, mixed with air, does not begin to be oxidised under these conditions

until a temperature of 120—125° is reached. It is possible, therefore, to remove carbon monoxide completely and continuously from a mixture having, for example, the composition 0.5% of carbon monoxide, 0.5% of oxygen, 24.75% of nitrogen, and 74.25% of hydrogen and containing water vapour at a pressure of 50 mm. of mercury without any considerable oxidation of hydrogen. On the other hand, in a similar 1% carbon monoxide mixture, the hydrogen soon takes fire and the catalyst becomes incandescent. The effect of space velocity, carbon dioxide, hydrogen sulphide, and the concentration of carbon monoxide on the efficiency of the catalyst have been investigated. Formulæ for the temperature rise in the catalyst, and the factor limiting the permissible concentration of carbon monoxide have been derived and verified at different space velocities in tubes of various diameters, and on the basis of these results the proper conditions for the technical application of this method of removing carbon monoxide from hydrogen have been outlined. The present results are in agreement with those of Rideal (T., 1919, **115**, 993). J. F. S.

Preparation of Bright Metallic Sodium and Potassium, or their Alloys, in Nitrogen. G. BORNEMANN (*Z. angew. Chem.*, 1922, **35**, 227).—A glass tube of 15—20 mm. diameter is drawn out into a short constriction of 3—4 mm. diameter about 20 cm. from one end which is sealed up. A fine wire gauze thimble is fitted tightly into the tube above the constriction and the required amount of metal introduced into the open end of the tube, which is then sealed. The tube is then placed in a horizontal position and the metal melted, whereby the oxygen, moisture, and carbon dioxide are removed, leaving an atmosphere of nitrogen. On now placing the tube vertically and carefully remelting the metal it flows through the gauze and the constriction into the lower portion of the tube as perfectly bright untarnished metal, all impurities remaining behind on the gauze filter. The tube is then drawn off and sealed at the constriction. G. F. M.

Sodium Silicate. A. ERDENBRECHER (*Mikrokosmos*, 1921, **15**, 55—60).—The addition of not more than 40 grams of sodium hydroxide to 100 c.c. of the solution obtained when 20—25 grams of the salt $\text{Na}_2\text{SiO}_3 \cdot 9\text{—}10\text{H}_2\text{O}$ are dissolved in 40 c.c. of water yields the hydrate $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, rhombic, m. p. 47°. Sixty grams of sodium hydroxide similarly yield the hydrate $\text{Na}_2\text{SiO}_3 \cdot 6\text{H}_2\text{O}$, monoclinic, m. p. 63.5°, whilst larger amounts yield the hydrate $\text{Na}_2\text{SiO}_3 \cdot 4\text{H}_2\text{O}$, hexagonal, m. p. 83—85°. Other hydrates of sodium metasilicate mentioned in the literature are probably mixtures of these, as changes in the composition of the mother-liquor cause changes in the degree of hydration.

CHEMICAL ABSTRACTS.

Preparation of Ammonium Chloride. P. MONDAIN MONVAL (*Compt. rend.*, 1922, **174**, 1014—1017).—A study of the conditions governing the crystallisation of ammonium chloride from solution at 15° when in solution alone or in the presence of one or more of

the salts, sodium chloride, sodium carbonate, and ammonium carbonate. A Le Chatelier diagram showing the surfaces of saturation is given. Commercially in the ammonia-soda process the salt is not crystallised out from the liquid from which the sodium hydrogen carbonate has been extracted, but ammonia is first added to convert the hydrogen carbonates into normal carbonates. W. G.

The Melting Point of Normal Ammonium Sulphate. R. KATTWINKEL (*Ber.*, 1922, **55**, [B], 874).—Contrary to the statement of Caspar (A., 1920, ii, 431), a definite melting point cannot be assigned to normal ammonium sulphate; with increasing temperature it suffers loss of ammonia, decomposition being complete at 365°. H. W.

Conditions of Formation and Stability of Ammonium Carbamate. C. MATIGNON and M. FRÉJACQUES (*Bull. Soc. chim.*, 1922, [iv], **31**, 307—316).—A more detailed account of work already published (A., 1920, ii, 250). W. G.

Liquid Crystals of Calcium Phosphate. P. GAUBERT (*Compt. rend.*, 1922, **174**, 1115—1117).—When the rhombohedra obtained by crushing calcite are ignited, they retain their shape and if then they are submitted to the action of phosphoric acid certain optical phenomena are observed due to the formation of liquid or soft crystals of calcium phosphate. These are described in detail. W. G.

Action of Nitrogen on Mixtures of Barium Oxide and Carbon at High Temperatures. PAUL ASKENASY and FRITHJOF GRUDE (*Z. Elektrochem.*, 1922, **28**, 130—151).—The rate of combination of compressed mixtures of barium carbonate and wood charcoal or graphite with nitrogen has been investigated up to 1600°. It is shown that the reaction proceeds with a practicable velocity at 1400°, and in fifteen minutes 60% of the barium has been converted into a mixture of cyanide and cyanamide when an excess of nitrogen is present. In agreement with Caro and in opposition to Ewan and Napier, the primary reaction is the formation of barium carbide, and from this much cyanide is formed which then undergoes a secondary reaction to form barium cyanamide. The formation of cyanide at comparatively low temperatures (1300—1400°) reaches a maximum of 65% in fifteen to thirty minutes, which is not increased at 1600°. With increasing temperature, the formation of the cyanamide rapidly increases. There is no evidence that a basic cyanide is first formed, nor is there any evidence of a sublimation of barium cyanide at the lower temperatures. The reproducibility of the combination of nitrogen is best achieved in the presence of an excess of carbon. When there is a shortage of carbon it is the cyanamide formation, and not that of the cyanide, which is effected. It is shown that the reaction proceeds more rapidly when compressed materials are used. Impurities in the carbon, such as silica or alumina, retard the reaction, whilst iron, in opposition to previous statements, accelerates it, but disturbs the reproducibility. A mixture of barium oxide and carbon takes up the same amount of

nitrogen as an equivalent quantity of 55% barium carbide, and the relative amounts of barium cyanide and cyanamide formed are the same in both cases. A very long list of references on this subject, with comments, precedes the paper.

J. F. S.

Electro-deposition of Lead from Mathers's Perchlorate Bath. I. Structure of the Deposit. W. E. HUGHES (*J. Physical Chem.*, 1922, **26**, 316—323).—The author has made a macroscopic and microscopic examination of the structure of lead deposited from Mathers's perchlorate bath (U.S. Pat. 931944, 1909; A., 1911, ii, 113). The specimens were etched by using them as anodes in the electrolysis of 30 c.c. of 30% perchloric acid in 270 c.c. of water for various periods with a current density of 9—10 amperes/sq. dm. and a voltage of 1.5. The etched surface was much worn, cindery, and dull and light grey in colour with no crystalline appearance. Where the outside surface of the lead was directed toward the cathode during etching, a thin, skin-like substance is formed, which after a while detaches itself and comes away in flakes; no such action occurs when the inside surface is directed to the cathode. The term inside surface indicates the lead surface which was in contact with the cathode during the deposition. When examined microscopically (125 diameters) the deposit is seen to consist of irregular cells with lustrous, slightly yellow walls. The interior of each cell appeared to be made up of a mosaic of small bright and dark particles. The author deduces from the observations that the structure of the lead is ordered, and not amorphous; the size of the grain is reduced by the colloid (peptone) contained in the bath and that the colloid separates from solution with the lead, not in any haphazard fashion, but in continuous layers in the deposit.

J. F. S.

Amalgams. III. Colloidal Copper Amalgam. C. PAAL and HERMANN STEYER (*Kolloid Z.*, 1922, **30**, 215—228; cf. A., 1919, ii, 69, 516).—Hydrosols of copper amalgam may be prepared by (a) shaking copper hydrosol with mercury, (b) keeping copper hydrosol in contact with mercury without shaking, (c) mixing either red or blue copper hydrosol with mercury hydrosol. The preparations were all effected in an atmosphere of hydrogen, and the amalgam sols possess colours which differ markedly from those of the original copper sols. In the first preparation, sols of an amalgam represented by the formula $\text{CuHg}_{0.02}$ may be obtained, in the second preparation the composition of the amalgam is given by the formula $\text{CuHg}_{0.34}$, and in the third preparation, using the red copper hydrosol, the amalgam has the composition $\text{CuHg}_{1.35}$. The copper amalgam sols are less stable and more easily oxidised than the gold amalgam hydrosols previously described (*loc. cit.*), and require a larger concentration of protecting colloid (sodium lysalbate or sodium protalbate) to stabilise them than the corresponding gold amalgam sols.

J. F. S.

Copper Sulphide. W. GLUUD (*Ber.*, 1922, **55**, [B], 952—953).—The oxidation of copper sulphide by air at the atmospheric

pressure proceeds rapidly in ammoniacal suspension with the production of a mixture of sulphate and thiosulphate; cuprous sulphide is similarly but more slowly oxidised. In neutral or acid solution, the change is slower and necessitates the use of compressed air at temperatures up to 160° ; copper sulphate is formed. In certain circumstances the sulphur is deposited in the elementary state; the chief conditions are that the copper solution should not be precipitated completely, that the oxidation should be effected immediately, and that the solution should contain, in addition to ammonia, considerable amounts of dissolved salts, preferably ammonium compounds. H. W.

Mechanism of the Dehydration of Crystalline Aluminium Hydroxide and of the Adsorption of Water by the Resulting Alumina. LOWELL H. MILLIGAN (*J. Physical Chem.*, 1922, 26, 247—255).—Crystalline aluminium hydroxide in air at atmospheric pressure and humidity is not affected by temperatures below 145° , and remains constant in composition as the normal hydroxide, $\text{Al}(\text{OH})_3$, up to this temperature. The decomposition and evolution of water commences just above 145° , and as far as the evolution of the chemically combined water of the hydroxide is concerned, is practically complete at 200° . Slight irregularities are observed in the drying curve between 145° and 196° , which are attributed to the very slow rate at which equilibrium is reached at these particular temperatures and the resultant experimental errors. All the water is not driven off at 200° , but an amount equal to about 8% of the original aluminium hydroxide is retained at this temperature, and is driven off slowly as the ignition temperature is increased, very much higher temperatures being required for complete dehydration. Above 200° , the curve has the general form of an adsorption curve, and the 8% of water, which is retained at 200° , appears to be practically adsorbed by the highly porous aluminium oxide. There is no evidence of the existence of hydrates formed by step-wise dehydration. When alumina, produced by drying aluminium hydroxide at temperatures as low as 275° , is allowed to take up water, this water is simply adsorbed, and does not recombine chemically with the alumina. This is established by the fact that the drying curve after "rehydration" bears no resemblance to the original dehydration curve of aluminium hydroxide. The higher the ignition temperature at which alumina is prepared the smaller is the amount of water which it is capable of adsorbing under a given set of conditions.

[With W. J. MEAD.]—The original aluminium hydroxide, the alumina prepared by its ignition, and the alumina after "rehydration" have been subjected to an X-ray examination. It is shown that the X-ray pattern produced by the original crystalline aluminium hydroxide is identical with that of the mineral gibbsite, which is a definitely crystalline chemical compound. Alumina prepared by calcining the crystalline hydroxide at 325° gives no trace of the hydroxide structure, neither is it similar to the mineral diaspore, $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, nor to corundum, Al_2O_3 . It shows a set of

lines which indicate a crystalline structure. The adsorption of water does not alter its structure. Alumina prepared by calcination at 600° shows a faint pattern similar to the preceding specimen, but the bulk of the material is probably amorphous. When calcination temperatures somewhat above 1000° are employed, the product gives a faint corundum pattern, and still higher temperatures increase the intensity of this pattern until it becomes that of pure corundum.

J. F. S.

Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. I. Reaction between [Potassium] Permanganate and Formic Acid in Slightly Acid Solution.

JOSEF HOLLUTA (*Z. physikal. Chem.*, 1922, **101**, 34—53).—The velocity of the reduction of potassium permanganate by formic acid in faintly acid solutions has been investigated at 22° , 25.1° , 24.7° , and 15.3° . The results are discussed in connexion with previously published work of Schilov (A., 1903, ii, 720) and of Skrabal (A., 1905, ii, 17, 18; 1906, ii, 658), and it is shown that the reduction takes place in the following stages: (1) $2(\text{MnO}_4' + \text{HCO}_2' = \text{MnO}_4''' + \text{H}^* + \text{CO}_2)$ (measurably slow); (2) $2\text{MnO}_4'' + 8\text{H}^* + 5\text{HCO}_2' = \text{MnO}_4' + \text{Mn}(\text{HCO}_2)_5'' + 4\text{H}_2\text{O}$ (instantaneous); (3) $\text{Mn}(\text{HCO}_2)_5'' = \text{Mn}^{***} + 5\text{HCO}_2'$ (equilibrium); (4) $2\text{Mn}^{***} + \text{HCO}_2' = 2\text{Mn}^{**} + \text{H}^* + \text{CO}_2$ (more rapid than 1); (5) $2(2\text{Mn}^{***} + 4\text{H}_2\text{O} = \text{Mn}^{**} + \text{Mn}(\text{OH})_4 + 4\text{H}^*)$ (immeasurably fast); (6) $\text{MnO}_4' + 4\text{Mn}^{**} + 8\text{H}^* = 5\text{Mn}^{***} + 4\text{H}_2\text{O}$ (immeasurably fast); (7) $2(\text{Mn}[\text{OH}]_4 + 4\text{H}^* = \text{Mn}^{***} + 4\text{H}_2\text{O})$ (equilibrium), and (8) $2\text{Mn}^{***} + \text{HCO}_2' = \text{Mn}^{**} + \text{H}^* + \text{CO}_2$ (very slow). These partial equations give a total equation for the reaction which has the form $2\text{MnO}_4' + 11\text{H}^* + 5\text{HCO}_2' = 2\text{Mn}^{**} + 5\text{CO}_2 + 8\text{H}_2\text{O}$. The measured temperature coefficient for 10° is 1.86.

J. F. S.

Mixed Crystal Formation in Ternary Systems containing Water, Ammonium Chloride, and Ferrous, Cobaltous, or Nickel Chloride. FREDERICK WILLIAM JEFFREY CLENDINNEN (T., 1922, **121**, 801—805).

Complex Nitrites of Nickel. V. CUTTICA (*Gazzetta*, 1922, **52**, i, 210—215).—In consequence of the slight tendency to dissociate exhibited by nickel nitrite, the latter is able to form complexes, double nickel nitrites occupying a position between true complex compounds and double salts and possessing the constant co-ordination number of the former and the great mobility of the component simple ions in solution shown by the latter. Cryoscopic measurements of aqueous solutions of nickel thallium nitrite, $4\text{TlNO}_2 \cdot \text{Ni}(\text{NO}_2)_2$, give a molecular weight of 107—111, the calculated value being 1050; hence rather more than nine of the eleven simple ions are manifest in solution. Since thallium nitrite is completely dissociated in the experimental conditions employed, the nickel nitrite is only partly dissociated.

Owing to the markedly "imperfect" nature of double nickel nitrites it is necessary, in the preparation of triple nickel nitrites, that the active masses of the component ions be high in order

that undissociated molecules of the complex may be formed and that the solubility product may be exceeded. The failure of Przibylla (A., 1898, ii, 162; 1899, ii, 222) and of Reichard (A., 1904, ii, 488, 741) to obtain triple nickel cadmium nitrites was probably due to neglect of this condition. The author has prepared *nickel cadmium potassium nitrite*, $\text{Ni}(\text{NO}_2)_2 \cdot 2\text{Cd}(\text{NO}_2)_2 \cdot 4\text{KNO}_2$, which is pale yellow; *nickel cadmium thallium nitrite*, of analogous formula, which is brick red, and *nickel cadmium ammonium nitrite*, $\text{Ni}(\text{NO}_2)_2 \cdot \text{Cd}(\text{NO}_2)_2 \cdot 2\text{NH}_4\text{NO}_2$, which is pale flesh-coloured. These three compounds are profoundly disgregated by the dissociating action of water, the nickel and cadmium nitrites undergoing only limited dissociation.

Many of the triple nickel nitrites known may be represented by the general scheme for the double nickel nitrites, for example, $[\text{Ni}(\text{NO}_2)_6]_{\text{K}_2} \text{Ba}(\text{Ca}, \text{Sr}, \text{Pb})$, $[\text{Ni}(\text{NO}_2)_6]_{(\text{NH}_4)_2} \text{Cd}$, the nickel in these exhibiting analogy to iron and cobalt. In the case of nickel cadmium potassium and nickel cadmium thallium nitrites, which do not correspond with this scheme, if the fundamental co-ordinating action capable of functioning in two concentric spheres is attributed to the nickel, it may be assumed that in the inner sphere are co-ordinated six nitrous residues in the same ion as occurs in the other nickel nitrites and that in the second sphere two whole cadmium nitrite molecules remain bound. This supposition, expressed by the formula $[\text{Ni}(\text{NO}_2)_6]_{\text{K}(\text{Tl})_4} [\text{Cd}(\text{NO}_2)_2]_2$, is in accord with the similarity in colour between these compounds and the double and certain other triple nickel nitrites. T. H. P.

Complex Chlorides containing Gold. I. Pollard's Ammonium Silver Auric Chloride. HORACE L. WELLS (*Amer. J. Sci.*, 1922, 3, [v], (16), 257—259).—The triple chloride examined by Pollard (T., 1920, 117, 99) was investigated. It was found that when solutions somewhat similar to the one recommended by Pollard were diluted with an equal volume or more of 1:1, or stronger, hydrochloric acid better products for analysis were obtained. The results of analysis suggest the formula $(\text{NH}_4)_6\text{Ag}_2\text{Au}_3\text{Cl}_{17}$ for the triple salt against $(\text{NH}_4)_8\text{Ag}_3\text{Au}_4\text{Cl}_{23}$ put forward by Pollard. The corresponding potassium salt could not be obtained, but a triple salt of caesium was prepared and is being investigated. W. T.

Complex Chlorides containing Gold. II. Caesium Triple Salts. HORACE L. WELLS (*Amer. J. Sci.*, 1922, 3, [v], 315—326).—Five new triple chlorides of caesium have been prepared. $\text{Cs}_4\text{Ag}_2\text{Au}'''_2\text{Cl}_{12}$, very black, opaque, powder black. $\text{Cs}_4\text{ZnAu}'''_2\text{Cl}_{12}$, yellow (sometimes red), transparent, powder pale yellow. $\text{Cs}_4\text{HgAu}'''_2\text{Cl}_{12}$, orange, transparent, powder yellow. $\text{Cs}_4\text{CuAu}'''_2\text{Cl}_{12}$, crystals black, powder pale brown. $\text{Cs}_4\text{Au}_2'\text{Au}'''_2\text{Cl}_{12}$, very black, opaque, powder black. These triple salts are apparently isomorphous, an interesting case of isomorphous replacement of two univalent atoms by one bivalent atom. Caesium calcium auric

chloride could not be prepared. These cæsium triple salts do not correspond with the ammonium triple chloride (Wells, preceding abstract). In preparing these triple chlorides a large excess of cæsium chloride over the theoretical quantity is desirable, but the solutions should be very dilute in respect to gold in order to avoid the deposition of the sparingly soluble cæsium auric chloride. Presence of concentrated hydrochloric acid is favourable.

W. T.

Mineralogical Chemistry.

Cristobalite in Basalt from Washington. EARL V. SHANNON (*J. Washington Acad. Sci.*, 1922, **12**, 195—196).—Minute, white crystals of cristobalite (SiO_2) occur with plagioclase, magnetite, opal, etc., in the steam-cavities of basalt at Spokane; they have the form of cubo-octahedra. L. J. S.

Becquerelite, a New Radioactive Mineral. ALFRED SCHOEP (*Compt. rend.*, 1922, **174**, 1240—1242).—This mineral occurs as canary- to orange-yellow, crystalline crusts on pitchblende from the Kasolo mine, Katanga, Belgian Congo. Minute crystals are orthorhombic with perfect (001) and (110) cleavages. The acute negative bisectrix emerges through (001). The mean of two analyses on material dried at 100° gave:

UO_3 .	Fe_2O_3 .	PbO .	SiO_2 .	SO_3 .	H_2O .	Total.
86.51	0.54	5.25	0.83	1.01	5.82	99.96

Needles of anglesite and crystals of curite (this vol., ii, 77) and soddite (this vol., ii, 451) are present; and microchemical tests of the canary-yellow material show only traces of lead. Deducting lead, etc., and adding water (4.21%) lost at 100° , the formula is deduced as $\text{UO}_3 \cdot 2\text{H}_2\text{O}$. L. J. S.

Sincosite, a New Mineral. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1922, **12**, 195).—This forms green, rectangular plates, which are optically uniaxial (sometimes biaxial) and negative, in black carbonaceous shale near Sincos, Peru. Analysis:

CaO .	V_2O_4	P_2O_5 .	H_2O .	Insol.	Total.
12.1	36.3	31.7	19.9	0.3	100.3

gives the formula $\text{CaO} \cdot \text{V}_2\text{O}_4 \cdot \text{P}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$. Since the mineral belongs to the uranite group (autunite, torbernite, etc.), the "equivalent valency" of quadrivalent vanadyl-vanadium with sexavalent uranic-uranium is suggested. L. J. S.

Optical-crystallographic Properties of Calcium Oxalate Monohydrate. EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1922, **12**, 196—200).—The crystallographic and optical constants

hitherto determined for the mineral whewellite are tabulated, and the relation of the optical orientation to the various habits of the crystals is pointed out. Fragments of the mineral, crystals from plant tissues, and crystalline precipitates (prepared by boiling together solutions of the constituent ions) were examined microscopically. Refractive indices, α 1.490, β 1.555, γ 1.650.

L. J. S.

The Chemical Constitution of Felspars. Analysis of Two Microclines. M. E. DENAEYER (*Bull. Soc. chim. Belg.*, 1922, **31**, 131—147).—Theories of the constitution of complex silicates (W. and D. Asch, "Die Silicate," Berlin, 1911; P. Erculisse, "Classification chimique des silicates naturels," Brussels, 1920; J. Jakob, A., 1920, ii, 754) are discussed, and an attempt is made to apply Werner's co-ordination theory to the problem. Some formulæ based on the latter theory are given and a pseudo-phase rule diagram based on these is used to suggest the mutual relationship of quartz, orthose, plagioclases, micas, and spinels. The connexion between the views put forward by Jakob and by F. W. Clarke is briefly discussed.

The analysis of two microclines (triclinic potash-soda felspars) is considered to indicate that they are built up of three separate components in solid solution, and a study of results of analyses carried out by other workers tends to confirm this view.

H. J. E.

Soddite, a New Radioactive Mineral. ALFRED SCHOEP (*Compt. rend.*, 1922, **174**, 1066—1067).—This forms with curite (A., 1922, ii, 77) fine-grained crystalline aggregates at Kasolo, Katanga, Belgian Congo. In veins in this material minute prismatic crystals were found which from their optical characters are orthorhombic. H 3—4, d^{17} 4.627. Heated in a bulb-tube the mineral gives off water and oxygen and turns black, and it is infusible before the blow-pipe. The mean of several partial analyses is:

SiO ₂ .	UO ₃ .	Fe ₂ O ₃ .	H ₂ O.
7.83	85.33	0.40	6.23

agreeing with the formula $12\text{UO}_3, 5\text{SiO}_2, 14\text{H}_2\text{O}$.

L. J. S.

Ore Deposits and their Genesis in Relation to Geographical Distribution. A Lecture Delivered before the Chemical Society on December 8th, 1921. JOHN WALTER GREGORY (T., 1922, **121**, 750—772).

Meteoric Iron from Odessa, Ector Co., Texas. GEORGE P. MERRILL (*Amer. J. Sci.*, 1922, [v], **3**, 335—337).—The much rusted fragment of 1120 grams as received was stated to be from a larger mass found near Odessa. The etched surface shows a coarse octahedral structure. Analysis by E. V. SHANNON gave:

Fe.	Ni.	Co.	Cu.	Pt.	Cr.	Mn.	C.	P.	S.	Total.
90.69	7.25	0.74	0.02	nil	trace	nil	0.35	0.23	0.03	99.31

L. J. S.

Meteoric Irons from Alpine, Texas, and Signal Mountain, Lower California. GEORGE P. MERRILL (*Proc. U.S. Nat. Mus.*, 1922, **61**, art. 4, 1—4).—A fragment of a mass, said to weigh two tons, from Alpine shows the finely granular structure of an ataxite, and gave anal. I by J. E. WHITFIELD. A fragment from a mass, said to have been observed to fall at Signal Mountain several years ago, gave II. The medium octahedrite structure grades into a finely granular structure at the exterior of the mass, the latter structure having evidently resulted by the heating during flight through the earth's atmosphere.

	Fe.	Ni.	Co.	Cu.	S.	P.	C.	Si.	Total.
I	93.60	5.62	0.43	0.016	0.012	0.328	0.008	0.015	100.029
II	91.47	7.86	0.60	0.015	0.002	0.041	—	0.004	99.992

A pallasite from Cold Bay, Alaska, is also briefly described.

L. J. S.

Analytical Chemistry.

The Application of Conductometric Methods to Precipitation Analysis. I. M. KOLTHOFF (*Z. anal. Chem.*, 1922, **61**, 171—180).—The author discusses the conditions necessary for obtaining good results by conductometric methods in precipitation analysis and details the possible sources of error under three headings: errors in the determination of the conductivity, errors due to the solubility of the precipitate being too great, and errors due to the composition of the precipitate not being constant. In the first case, the analysis is more exact the slower the rate of migration of the ions taking the place of those precipitated, whilst the end-point is sharper the greater the speed of the anion which is precipitated and the greater the degree of dissociation of the salt. The speed of the ions present which take no part in the reaction is immaterial, but, as the presence of indifferent electrolytes decreases the accuracy of the method, they should be kept as low as possible and the reagent used for precipitation must be a strong electrolyte. The solubility of the precipitate must, at the most, not exceed a normality corresponding with one-twentieth of the normality of the solution from which it is produced. Errors may arise owing to the slow rate at which the precipitate forms or to adsorption of salts by the precipitate; the former may be overcome by the addition of alcohol to the solution. A. R. P.

Estimation of Hydrogen-ion Concentration in Urine with Indicators. ADOLF SILBERSTEIN (*Biochem. Z.*, 1922, **128**, 534—539).—The colorimetric estimation of the P_H of coloured liquids like urine is simplified by removing the natural colouring matter by shaking with charcoal, for instance, "Carbo medic," Merck. There is no change of P_H after this treatment of urine. H. K.

Reaction between Thiosulphuric and Nitrous Ions. P. FALCIOLA (*Gazzetta*, 1922, **52**, i, 179—182).—If sodium thiosulphate, even in very dilute solution, is treated with dilute sodium or potassium nitrite solution and the liquid is then acidified with either an inorganic or organic acid or a salt, such as alum, giving an acid solution, more or less marked effervescence occurs and the solution assumes a yellow colour which, according to the amounts of the substances used, may at first be green or orange-brown. The reaction is equally sensitive in aqueous alcoholic solution and is shown distinctly by 0.0001*N*-sodium thiosulphate solution, which does not readily yield sulphur when treated with a mineral acid or give a coloration with ferric chloride. Only excessive proportions and concentrations of sulphurous acid prevent the reaction with traces of thiosulphate. The nitrous ion in presence of the nitric ion may be detected by means of the reaction (cf. Bodnár, A., 1914, ii, 67).
T. H. P.

The Volumetric Estimation of Dithionates. A. FISCHER and W. CLASSEN (*Z. angew. Chem.*, 1922, **35**, 198—199).—Sodium dithionate is not attacked by cold alkaline or neutral oxidising agents and but little in acid solution. On heating with acid, evolution of sulphur dioxide commences and oxidation follows. Attempts to devise a direct titration with an acid oxidising agent were unsuccessful either through loss of sulphur dioxide or through secondary reactions. A method was therefore adopted of distilling the sulphur dioxide into a known volume of an oxidising agent. Potassium permanganate and dichromate proving unsuitable, iodine solution was employed. The sodium dithionate is weighed into a flask, distilled hydrochloric acid free from chlorine added, and a stream of carbon dioxide passed through the apparatus. The flask is then heated and at the end of the reaction carbon dioxide is again passed through the apparatus. The results are in close agreement with those of gravimetric analysis. The method may be applied to mixtures of dithionates with other sulphur salts, most of which are decomposed by cold hydrochloric acid or oxidised by alkaline hydrogen peroxide.
C. I.

Estimation of Ammonia in Urine by Schloesing's Bell-glass Method. W. MESTREZAT and (MLLE) M.-P. JANET (*Bull. Soc. Chim. Biol.*, 1922, **4**, 154—164).—Schloesing's method is modified and used for the estimation of ammonia in urine. To 20 c.c. of urine contained in a desiccator are added a few drops of sulphuric acid to dissolve any ammonium magnesium phosphate, and five drops of a 10% solution of mercuric cyanide to prevent bacterial decomposition of urea. Ten c.c. of 20% milk of lime are then added, after which a basin containing 10 c.c. of 0.1*N*-sulphuric acid is rapidly placed on a tripod in the desiccator and the latter closed. After remaining for three days at a room temperature of 15—20°, the excess of acid is titrated. No appreciable quantity of ammonia is evolved from nitrogenous organic substances present in the urine.
E. S.

The Estimation of Ammoniacal Nitrogen in Nitrogenous Organic Substances, and particularly in Proteins and their Products of Decomposition. J. FROIDEVAUX (*Compt. rend.*, 1922, **174**, 1238—1240).—To 15 c.c. of the solution under examination 35 c.c. of 60% aqueous sodium hydroxide are added and air, carefully freed from ammonia, is bubbled through at the ordinary temperature at the rate of 150—200 bubbles per minute. The issuing air is passed through a known volume of standard acid. The acid is replaced from time to time and titrated. The ammonia absorbed is plotted against the time. The resulting curve consists of a line sharply inclined to the time axis and a line slightly inclined to the same axis, these being joined by a curved portion. The first line corresponds with ammoniacal nitrogen and the second line with ammoniacal nitrogen coming from the slow decomposition of protein or amino-acids. The curved portion is a combination of the two. The two lines are produced to meet and their junction represents the total ammoniacal nitrogen originally present as such in the sample. W. G.

The Analysis of Liquid Nitrogen Peroxide. A. SANFOURCHE (*Bull. Soc. chim.*, 1922, [iv], **31**, 316—319).—The sampling is done by means of a Durand washing flask, the central tube of which is drawn out to a fine orifice, the flask being kept immersed in ice.

For the estimation of nitric acid in the sample, 10 c.c. of the liquid are measured out into a cylindrical gas-drying tube, which is then surrounded with ice, and air is bubbled through the liquid until the whole of the nitrogen peroxide has evaporated. The residual nitric acid, which should not evolve nitrous vapours when warmed by the hand, is diluted with water and titrated with *N*-sodium hydroxide.

For the estimation of nitrogen peroxide and nitrous anhydride, a known volume of the sample is dissolved in 20 c.c. of concentrated sulphuric acid cooled in ice, and aliquot portions of the solution are titrated with *N*/10-permanganate, and analysed in a Lunge nitrometer, respectively. From these results it is possible to calculate the percentages of nitrogen peroxide and nitrous anhydride respectively in the sample. W. G.

Estimation of Nitrates in Drinking Water by Mayrhofer's Method. A. REUSS (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 174—183).—The consumption of indigotin solution is considerably increased in the presence of sodium chloride, the reaction between small quantities of nitrates and the indigotin being facilitated by this substance. If only small quantities of nitrates and small quantities of chlorides are present in the water, it is advisable to add sufficient sodium chloride to bring the concentration up to 1 gram per litre. The indigotin solution must then be standardised against a nitrate solution containing 1 gram of sodium chloride per litre. Mayrhofer's tables can then be used. The indigotin solution must not have the slightest sediment or its titre will be variable. It is best filtered through asbestos without suction until no suspended particles are visible with a lens. The solution should

be added at a rate of 2—3 drops per second, the last drops being added at a somewhat slower rate. Care must be taken that the whole of the 5 c.c. of sulphuric acid actually reach the liquid in the flask. The acid used must be of the same composition as that used in standardising the indigotin solution which should be prepared as described by Lehmann in an appendix to the paper.

H. C. R.

The Estimation of Inorganic Phosphorus in Blood Plasma by Bell and Doisy's Method. BURTON A. MYERS and MARIAN C. SHEVKY (*J. Lab. Clin. Med.*, 1921, 7, 176—180; cf. A., 1920, ii, 769).—Phosphorus was not recovered quantitatively from plasma by Bell and Doisy's method, when added in known quantity. The only solution correctly measured was one which was weaker than the standard; all stronger than the standard showed considerable minus errors. This difficulty was obviated by using a series of standards of such strength that one might be chosen containing approximately 0.25 mg. per 100 c.c. more phosphorus than the unknown. A small series of estimations thus made gave an error ranging from 2.3 to 10% with an average of 5.8%. In many rabbit plasmas and some human plasmas larger amounts of molybdic acid and quinol solutions than prescribed in the original directions must be used to develop the proper colour. 1.5 c.c. of molybdic acid and 3 c.c. of quinol for each 5 c.c. of plasma filtrate (1 : 5 dilution) are recommended.

CHEMICAL ABSTRACTS.

Qualitative Reactions for Arsenic. I. M. KOLTHOFF (*Pharm. Weekblad*, 1922, 59, 334—350).—The reactions of Mayençon and Bergeret (this Journal, 1874, 1008; reduction to arsine and detection with mercuric chloride paper), Bougault (reduction to free arsenic by use of hypophosphite), Bettendorf (reduction to arsenic, using stannous chloride), and Reinsch have been examined. The most suitable is the first, which under the conditions recommended will detect one-millionth of a gram (1 μ .g.) in 1 c.c. To 1 c.c. of the neutral solution are added 1 c.c. of 22% hydrochloric acid containing 1% of stannous chloride, and 0.1 gram of finely divided aluminium foil. The gas is led through cotton-wool on to a strip of paper 4 mm. wide prepared by saturating filter-paper in 5% aqueous mercuric chloride solution. After one hour the colour of the paper is examined. Antimony must be removed by treating the paper with hydrochloric acid or potassium iodide.

Mercury salts interfere strongly, copper salts moderately; salts of other metals do not seriously affect the test.

Bougault's reaction will detect 2 mg. of arsenic per litre. Two c.c. of the solution, admixed with 1 c.c. of the reagent, and 4 c.c. of strong hydrochloric acid, are heated in the water-bath for thirty minutes. A brown colour shows presence of arsenic. The solution may be filtered, a stain remaining on the paper. S. I. L.

Aluminium for the Arsenic Reaction. G. ROMIJN (*Chem. Weekblad*, 1922, 19, 177—179).—The author agrees with Kolthoff

(preceding abstract) that aluminium is to be preferred to zinc, which he had formerly recommended (Romijn, *Pharm. Weekblad*, 1917, **54**, 1216), in the Mayençon and Bergeret reaction. He details some improvements in the apparatus which allow of the detection of 0.5 μ .g. of arsenic with a reaction time of two to five minutes. He suggests that in presence of formaldehyde hexamethylene-tetrarsine may be formed. S. I. L.

Estimation of Volatile Matter in a Coal. A. DESSEMOND (*Rev. ind. min.*, 1921, **1**, 451—456).—The essential analytical operations for estimating the volatile substances and ash of a coal by desiccation, distillation, and incineration are discussed. In the formula $V=v/(100-c)$, where c =% ash, v =% volatile substances in the crude coal, and V =% volatile substances exclusive of the ash, calculations show that the percentage of V increases as the percentage of ash increases and becomes infinite when the ash becomes 100. A general investigation of the formula and of the errors usual in the procedures has led to the proposal of a simple formula expressing the content of volatile substances in a coal exclusive of the ash: $V=[v-(c/n)]/(100-c)$, where n is a variable coefficient depending on the impurities. Numerous samples of coal are given, and it is suggested that the value $n=10$ be adopted as a sufficiently accurate approximation for most coals. CHEMICAL ABSTRACTS.

The Separation of Zinc by Means of Ammonium Phosphate. G. LUFF (*Chem. Zeit.*, 1922, **46**, 365—366).—Magnesium and manganese may be separated quantitatively from zinc by precipitation with ammonium phosphate in solutions containing at least one-fifth of their bulk of ammonia (d 0.923), whilst iron and aluminium may be precipitated as phosphates free from zinc by addition of ammonium phosphate to the solution containing at least one-fifth of its bulk of glacial acetic acid. The zinc is recovered from the filtrate by rendering it neutral to litmus, in the first case with hydrochloric acid, and in the second case with ammonia. The separation of manganese and zinc must be carried out in an atmosphere of hydrogen to prevent precipitation of manganese dioxide. [Cf. *J. Soc. Chem. Ind.*, 1922, June.] A. R. P.

An Electro-volumetric Method for Lead. D. A. MACINNES and ERIC B. TOWNSEND (*J. Ind. Eng. Chem.*, 1922, **14**, 420—421).—The solution containing the lead as nitrate together with free nitric acid is electrolysed with a current of 13 amperes for thirty to forty-five minutes in a platinum dish, 9 cm. in diameter and roughened on the inside, which acts as anode whilst the cathode consists of a small platinum disk rotated at 600 revolutions per minute. The deposit is washed with cold water and dissolved in an excess of standard oxalic acid and 5 c.c. of nitric acid heated at 80°. The solution is rinsed into a beaker, a few c.c. of sulphuric acid are added, and the excess of oxalic acid is estimated by titration with permanganate. The results prove that the deposit consists entirely of lead dioxide with variable amounts of water, and that, contrary to previous statements, it contains no higher oxides.

The method described is more exact than that of weighing the deposit and calculating the lead by using an empirical factor, as the amount of water in the deposit varies with its weight.

A. R. P.

Red Coloration of Sodium Hypochlorite Solutions. TEALDI MARIO (*Boll. Chim. Farm.*, 1922, **61**, 165—166).—Sodium hypochlorite prepared from chemically pure calcium hypochlorite and sodium hydrogen carbonate develops no red coloration, and the presence of manganese in the glass of the containing vessel neither induces the coloration nor enhances the intensity of solutions already reddened. If commercial reagents are used in its preparation the salt at once turns red, irrespective of the presence of manganese in the reaction vessel. The coloration is not modified by addition of an iron salt, but is destroyed by sodium thiosulphate. The conclusion is drawn that the red colour is due to salts of permanganic acid derived from the manganese in the reagents used.

T. H. P.

Chemical Analysis with Membrane Filters. III. Their Application to Volumetric Analysis. GERHART JANDER (*Z. anal. Chem.*, 1922, **61**, 145—171).—Membrane filters are particularly suited to volumetric work involving precipitation of a definite compound followed by solution of the precipitate and titration, owing to the ease with which the precipitate can be removed from the filter simply by spraying water over it. The estimation of calcium by precipitation and titration of the oxalate with permanganate, of manganese by precipitation of the sulphide followed by solution of the latter in standard acid and titration of the excess acid with alkali, and of chromic acid in the presence of other oxidising acids is described in detail.

The estimation of manganese is carried out by treating the solution, 70 c.c., containing not more than about 0.25 gram of metal with 30 c.c. of 10% ammonium chloride solution, a few c.c. of ammonia and, after boiling, a large excess of freshly prepared ammonium sulphide solution. Boiling is continued for ten minutes to change the precipitate into the green modification, more ammonium sulphide is added, and the solution is cooled and filtered on a "30—60 second" membrane filter. The precipitate is washed first with water containing ammonium sulphide, then with neutral 2% sodium sulphate solution, rinsed off the filter with cold water, and dissolved in 60 c.c. of *N*/5-sulphuric acid. The solution is boiled to expel hydrogen sulphide, cooled, and titrated with *N*/5-sodium carbonate solution, using methyl-orange as indicator.

The volumetric estimation of chromium as chromate in solutions containing other oxidising substances, for example, chlorates or bromates derived from the oxidation of trivalent chromium to the sexavalent form in alkaline solution by means of chlorine or bromine, is carried out as follows: the solution is just acidified with acetic acid, 20 c.c. of *N*-sodium acetate solution are added, and the chromic acid is precipitated from the boiling solution by the addition, drop by drop, of a slight excess of *N*/10-lead acetate

solution. After cooling, the precipitate is collected on a membrane filter, washed with cold water, rinsed back into the beaker, and dissolved in 100 c.c. of *N*-hydrochloric acid. An excess of a standard solution of ferrous sulphate is added and the excess is estimated by titration with potassium dichromate as usual.

A. R. P.

The Estimation of Cobalt in Steel. ALOIS EDER (*Chem. Ztg.*, 1922, 46, 430).—The method depends on the separation of the iron from a weakly acid sulphate solution by means of an emulsion of zinc oxide and precipitation of the cobalt in an aliquot part of the filtrate after acidification with hydrochloric acid by means of an excess of a solution of nitroso- β -naphthol in 50% acetic acid, followed by ignition of the precipitate mixed with oxalic acid to the oxide Co_3O_4 , which is weighed. [Cf. *J. Soc. Chem. Ind.*, 1922, June.]

A. R. P.

Detection and Estimation of Small Quantities of Nickel and Cobalt in Silicate Rocks. O. HACKL (*Chem. Ztg.*, 1922, 46, 385—386).—A large quantity of the sample is digested with aqua regia, the filtered solution is evaporated to expel nitric acid, the residue digested with hydrochloric acid, the solution diluted with water, treated with hydrogen sulphide, filtered, and the filtrate made ammoniacal and saturated again with hydrogen sulphide. A large excess of 5% hydrochloric acid is added, the solution set aside until the precipitate has settled, and then filtered, the precipitate being washed with dilute hydrochloric acid solution saturated with hydrogen sulphide. It is dissolved in aqua regia and the solution divided into two parts, one of which is tested for nickel by means of α -dimethylglyoxime in weakly ammoniacal tartaric acid solution, and the other for cobalt, after removing the trace of iron present by any suitable method, by Vogel's thiocyanate reaction or by means of nitroso- β -naphthol. The quantitative estimation of the metals is made in the same way, except that the sulphide precipitate after dissolving in aqua regia is freed from iron by triple precipitation of the solution with ammonia or by precipitation with barium carbonate. Nickel and cobalt are again precipitated as sulphides in the filtrate from the iron, the sulphides are ignited to oxides, and these reduced to and weighed as metals. Either the nickel or the cobalt is then estimated and the other found by difference. In all cases, the insoluble residue from the original aqua regia treatment of the ore must be tested for the presence of nickel and cobalt by dissolving it in hydrofluoric acid and testing the solution as described above.

A. R. P.

A Modified Reaction of Tin. HANS HELLER (*Z. anal. Chem.*, 1922, 61, 180—182).—The following modification of the iodide method for the detection of tin gives more trustworthy results than that recommended by Mazuir (*A.*, 1920, ii, 197). One c.c. of the solution containing only a little hydrochloric acid is mixed with 0.5 c.c. of 5% potassium iodide solution and 0.5 c.c. of strong

sulphuric acid is introduced, by means of a pipette, below the surface of the liquid. If tin is present an immediate precipitate of yellow iodide forms at the surface between the two liquids. The precipitate dissolves readily on addition of hydrochloric acid and careful shaking. Arsenic and antimony interfere with the test.

A. R. P.

The Volumetric Estimation of Titanium Dioxide in Bauxite.

H. J. WINCH and V. L. CHANDRATREYA (*Chem. News*, 1922, **124**, 231—232).—0.3 Gram of the sample is dissolved by fusion with 3 grams of potassium pyrosulphate and the fused mass is dissolved in hydrochloric acid. The solution is boiled with 0.15 gram of tin powder and 5 grams of ammonium chloride until all the tin has dissolved. Cold water is added to the liquid followed by 50 c.c. of 4% mercuric chloride solution to destroy excess of stannous chloride (titanous chloride is not oxidised by mercuric chloride in the cold) and 5 c.c. of ferric chloride solution containing 10 grams of iron per litre. The liquid is then titrated with potassium dichromate as usual. The iron is determined in a separate sample by reduction with stannous chloride followed by titration with the same dichromate solution. The difference in the two readings corresponds with the titanium dioxide present.

A. R. P.

Detection and Estimation of Vanadium in Steels. GEORGES MISSON (*Bull. Soc. chim. Belg.*, 1922, **31**, 123—126).—A colorimetric method of estimating vanadium is described, for which considerable accuracy is claimed. The steel is dissolved in nitric acid, any organic matter oxidised by means of permanganate, and, after oxidising any precipitated oxide of manganese with a solution of sodium peroxide in dilute nitric acid, a further quantity of the latter reagent is added in order to produce the colour for comparison. It is essential that all the reagents should be free from chlorine. Modifications are described which render the method applicable to steels containing tungsten, chromium, and nickel.

H. J. E.

Detection of Traces of Osmium by Means of Potassium Thiocyanate.

MAX HIRSCH (*Chem. Ztg.*, 1922, **46**, 390).—The metal to be tested for osmium is dissolved in fuming nitric acid or by fusion with sodium hydroxide and potassium nitrate or chlorate, followed by solution of the fused mass in water and acidification of the solution with nitric acid. In either case, the solution is distilled and the distillate collected in cold water. This solution is acidified, concentrated potassium thiocyanate solution added, and the whole shaken with ether or amyl alcohol. A blue colour in the ethereal layer indicates osmium. The colour is just perceptible at a dilution of 1 part of osmium per million parts of solution.

A. R. P.

The Clarification of Solutions containing Reducing Sugars by Basic Lead Acetate. The Effect of Different Deleading Agents. DUANE T. ENGLIS and CHUK YEE TSANG (*J. Amer. Chem. Soc.*, 1922, **44**, 865—867).—The removal of excess of basic

lead acetate, used as a clarifying agent from solutions of dextrose or l  vulose results in the loss of sugar. Of the agents tried, namely, potassium oxalate, disodium hydrogen phosphate, potassium sulphate, potassium sodium tartrate, and sodium carbonate, the least loss of sugar occurred when disodium phosphate was used. In general, the loss of l  vulose is much greater than that of dextrose. If the precipitate is washed, a much smaller loss is observed. W. G.

Detection of Lactic Acid in Organic Liquids. F. D'ARBELA (*Rend. accad. med.-fis. fiorentina; Sperim.*, 1921, **75**, 415—416).—Pittarelli's method (A., 1921, ii, 418) is not specific, as the coloration is given by many other substances. Uffelmann's reaction is preferred

CHEMICAL ABSTRACTS.

The Analysis of Solutions of Ammonium Citrate. C. S. ROBINSON and SELMA L. BANDEMAR (*J. Ind. Eng. Chem.*, 1922, **14**, 429—432).—The methods proposed for the determination of the ratio of ammonia to citric acid in ammonium citrate solutions have been examined and the results obtained are tabulated. The formaldehyde method invariably yields accurate results provided sufficient of the reagent is added to combine with all the ammonia and the addition of alkali is carried to the first permanent pink colour of the phenolphthalein. The only other method that gives accurate results is as follows: 50 c.c. of the solution are diluted to 500 c.c. and 10 c.c. trials are distilled with an excess of standard alkali to obtain the ammonia. The residue in the distillation flask is titrated with standard acid until the solution is distinctly acid to methyl-red; it is then boiled to expel carbon dioxide, a few drops of phenolphthalein are added, and the solution is titrated with standard alkali hydroxide until a permanent pink colour is obtained. The difference between the total alkali and acid used gives the amount of alkali used in neutralising the citric acid. A. R. P.

Golodetz's Reaction (The Benzoyl Peroxide Reaction). H. C. J. H. GELISSEN (*Rec. trav. chim.*, 1922, **41**, 224—227).—Golodetz's reaction (A., 1908, ii, 330) is not specific for benzoyl peroxide, but is given by all peroxides which, on treatment with concentrated sulphuric acid, yield phenolsulphonic acid. It may therefore be regarded as based on Hehner's reaction. Liebermann's test and Millon's test for phenol apply equally to benzoyl peroxide under the conditions indicated for Golodetz's reaction. A modification of Golodetz's procedure is recommended, as the test is considerably more sensitive if the sulphuric acid is cooled to -20° instead of being gently heated; the tests for phenol are also clearer at the lower temperature.

H. J. E.

Indican Reactions for the Detection of Urine in Stains. GIUSEPPE JEMMA (*Arch. Farm. speriment. Sci. aff.*, 1921, **32**, 193—194).—Replacement of thymol by α -naphthol in the application of Jolles's test (A., 1915, ii, 593, 655) to the detection of urine in stains (Latta, A., 1920, ii, 339) renders the reaction from two to four times more sensitive. The use of α -naphthol-*p*-sulphonic acid in this test leads, however, to unsatisfactory results. T. H. P.

General and Physical Chemistry.

Spectrum of Hydrogen. T. R. MERTON and S. BARRATT (Bakerian Lecture, *Phil. Trans.*, 1922, [A], 222, 369—400).—The wave-lengths of about 1200 lines in the secondary spectrum have been measured and classified into physically related groups according to the effects of the pressure of the gas, electrical excitation, and the presence of helium. This method of classification has been compared with the results of other investigators relating to the Stark and Zeeman effects and with the regularities observed by Fulcher. By means of a new method of measuring the widths of spectrum lines, it is shown that the secondary spectrum is due to hydrogen molecules. No evidence of the presence of secondary hydrogen has been found in the spectra of the sun. The effect of impurities and changes in the methods of electrical excitation on the relative intensities of the Balmer and secondary series is discussed, and it is shown that the greater the purity of the hydrogen the more prominent the secondary spectrum. The light from different portions of the capillary of the discharge tube varies in character with the nature of the discharge. With a condenser and spark gap in the electrical circuit, a mixture containing hydrogen and helium gives the hydrogen line at the two ends of the tube. Mercury lines and the lines of the heavier elements appear in the middle of the tube. On cutting out the condenser, this unequal distribution slowly changes. A partial separation of the gases in the discharge tube would explain these phenomena and the observation of Wood (cf. A., 1921, ii, 665) with long vacuum tubes, that the Balmer series are strongest in the middle of the tubes.

W. E. G.

Excitation of Gas-spectra during Chemical Reactions. F. HABER and W. ZISCH (*Z. Physik*, 1922, 9, 302—326).—A continuation of the work of Haber and Just (cf. A., 1911, ii, 954) on the emission of electrons in chemical reactions. The nature of the light emitted from flames of sodium and mercury burning in the halogens is investigated. Sodium vapour, diluted by nitrogen, is burnt in chlorine, bromine, iodine, or oxygen, the concentrations being so adjusted that the temperature of the flame is maintained below the limit at which temperature radiation becomes visible. With chlorine, a luminosity, greyish-green in appearance, is first observed at 350—360°. At higher temperatures, it becomes yellow, and at 473° is of sufficient intensity to make it possible to photograph the sodium doublet. The source of the *D*-line is the free sodium atom which is activated by collision with a freshly formed molecule, NaCl or NaCl₂, which has not yet dissipated its energy of combination. It is considered that the conductivity and luminosity of the inner cone of the Bunsen flame are partly chemical in origin and this view is supported by the intense colour of the inner cone when an alkali metal is added to the flame.

Mercury, burnt under similar conditions, gives a green cone with a band showing maxima between $595\ \mu\mu$ and $300\ \mu\mu$, whereas the wave-length, corresponding with the heat of formation of mercuric chloride, is $546\ \mu\mu$.

The conductivity of oxygen and potassium vapour at low pressures is considerable, so that electrically charged particles, possibly electrons, are liberated. New determinations of the vapour pressure of sodium vapour between 473° and 563° have been made. The relationship between light and electron emission during chemical reaction is discussed. In light emission, the excitation of the electron takes place from the normal state to the first quantum orbit, whereas in electron emission the electron is raised to an infinitely large orbit.

W. E. G.

Doublets in the Visible Spectrum. S. GOUDSMIT (*Arch. Néerland*, 1922, [iii], 6, 116—126).—Diverse empirical relationships have been found between the doublets in the visible spectrum. Sommerfeld gives $\Delta\nu=0.365\ (Z-z)^4$; where $\Delta\nu$ is the breadth of the doublet in cm^{-1} , Z is the nuclear charge or atomic number, and z is the number which indicates the "screening effect" of the electrons; Sommerfeld calls $(Z-z)$ the effective nuclear charge (Z_{eff}). From this equation he has deduced the effective nuclear charge from the L -doublets, the difference between this and the true nuclear charge gives the screening effect of the L -series, and the mean value 3.63 was obtained. It is here assumed that Z_{eff} has the same value at all points on the orbit of the electron, but whilst this may be true in the case of a circular orbit, it cannot hold when the orbit is an ellipse. Lithium gives a spectrum closely resembling that of hydrogen, the doublet $2p$ being almost of the same magnitude. The present author investigated whether this doublet and as a result all the doublets in the spectra have not the same origin as that of hydrogen, that is, that they were due to relativity. This point of view is contradictory to the well-established theory of Sommerfeld concerning the origin of the spectral series, but the results obtained were in good agreement. The objections to this method of treatment are discussed.

W. T.

The L -Series of the Elements Barium to Rubidium. D. COSTER (*Arch. Néerland*, 1922, [iii], 6, 76—91).—The author gives the wave-lengths and intensities of the L -series of these elements found by Hjalmar (A., 1921, ii, 145) and himself, using the method of Siegbahn. The values found differ somewhat from those found by Siegbahn. The results are discussed in detail on the basis of Bohr's new theory (this vol., ii, 277).

W. T.

Observations on the Rare Earths. XI. The Arc Spectrum of Yttrium. L. F. YNTEMA and B. S. HOPKINS (*J. Opt. Soc. Amer.*, 1922, 6, 121—134).—A determination of the emission spectrum of yttrium. The yttrium material which contained 0.005% of holmium was obtained in the work on atomic weights at the University of Illinois. The spectrum, however, showed

that other rare earth elements, erbium and dysprosium, and also magnesium and silicon, were present in small amounts. The yttrium material has a few lines in common with the eurosamarium of Eder. A comparison is made with the values previously obtained by Eder.

W. E. G.

The *L*-Series of Lutecium and Ytterbium and the Identification of Celtium with the Element of Atomic Number 72.

A. DAUVILLIER (*Compt. rend.*, 1922, **174**, 1347—1349).—By a modification of his previous technique (cf. A., 1921, ii, 421, 475, 669), the author has been able to make a detailed study of the *L*-series of lutecium and ytterbium in the form of their oxides. Twenty-six rays have been identified for lutecium, and the wave-lengths of these together with those for ytterbium are tabulated. In addition, the existence of some feeble lines indicated the presence of a trace of thulium. These lines were $\gamma_7=1272.1$; $\gamma_1=1311.3$; and $\beta_2=1456.3$. Further the existence of two very feeble lines, $\beta_2=1319.4$ and $\alpha_1=1561.8$, show the existence of a trace of celtium and assign to it the atomic number 72. This element had been discovered in the same preparation by Urbain (A., 1911, ii, 115) by the appearance of a group of unknown lines in the arc spectrum.

W. G.

The *N*-Series of Röntgen Spectra. V. DOLEJŠEK (*Z. Physik*, 1922, **10**, 129—136).—With the aid of the spectrograph of Siegbahn (*Z. Physik*, 1922, **9**, 68), determinations have been made of the *N*-series of uranium, thorium, and bismuth. All these lines were severely tested, to eliminate the *M* lines of higher order, by absorption through different thicknesses of aluminium and black paper and by a comparison of the spectra reflected from different crystals. A scheme of the *N* lines of the gas niton (86) shows the presence of seven *N*, five *O*, and three *P* levels in the atom. The various modes of transference of the electrons between these levels are also indicated. All the lines which have been found (λ 8,594— λ 13,255) agree with the theoretical expectations, and all possible lines, except that due to the transference between *N*₇ and *O*₄, have been observed. The *P*₁—*P*₂ and *O*₁—*O*₂ doublets have been separated for the first time. The hardest lines of the *N*-spectra for the three metals follow the Moseley frequency relation.

W. E. G.

X-Ray Spectra. WILLIAM DUANE and R. A. PATTERSON (*Proc. Nat. Acad. Sci.*, 1922, **8**, 85—90).—In view of certain criticisms of their previous work, the measurements of the *L*-absorption limits of platinum, gold, and bismuth (cf. A., 1920, ii, 407) have been repeated with increased accuracy. The absorption limits are found to possess somewhat shorter wave-lengths than the shortest emission lines associated with them. The authors have also measured the absorption spectrum for the *K*-series of molybdenum, and there are considerable discrepancies between their measurements and those of Overn (*Physical Rev.*, 1921, **17**, 350). The ratio of the intensities of α_1 to α_2 is given as 1.97 as

compared with 2.00 predicted by Bohr. The ratio of the intensities of β to γ in the first order is 6.3, and in the second order is 5.46.

W. E. G.

A Chromophore Grouping of Atoms in Inorganic Triple Salts and a General Theory for the Cause of the Colours of Substances. HORACE L. WELLS (*Amer. J. Sci.*, 1922, [v], 3, 417—422).—The author finds that complex salts containing the same metal in different states of valency are highly coloured, and he suggests that there is a constant exchange of electrons between the atoms of different valency and that this activity of electrons affects the passage of light, producing colours or opacity. An attempt is also made to extend this theory to explain the colours of substances in general by assuming spontaneous exchanges of electrons which affect the passage of light.

W. T.

The Labile Nature of the Halogen Atom in Organic Compounds. III. The Absorption Spectra of Bromomalonic Derivatives and Nitroparaffins, and their Bearing on the Question of an Oxygen-Halogen Linking. HUGH GRAHAM and ALEXANDER KILLEN MACBETH (*T.*, 1922, 121, 1109—1115).

The Relationship between Chemi- and Photo-luminescence in Unsaturated Silicon Compounds. H. KAUTSKY and H. ZOCHER (*Z. Physik*, 1922, 9, 267—284).—The compounds obtained by the action of acids on calcium silicide, for example, oxydisilin, silical hydroxide, and leucone (cf. A., 1921, ii, 505) have been further investigated. Chemiluminescence occurs when silicones, mixtures of oxydisilin, and silical hydroxide, are oxidised by chromic acid or potassium permanganate in acid solution. The colour of the silicones varies from pale yellow to deep red as the concentration of silical hydroxide increases, and the chemiluminescence follows identical colour changes. Oxidisilin gives only a feeble green light, and the dark red silical hydroxide a dark red light. Similar changes in colour occur for mixtures of silical hydroxide and leucone, and the latter, a white substance, shows no chemiluminescence. The photochemical oxidation of oxydisilin with ethyl iodide and water by short wave-lengths of light is accompanied by the emission of light of long wave-length. The intensity of the photoluminescence is dependent on the silical hydroxide concentration, and the change is apparently autocatalytic. Both chemi- and photo-luminescence are strengthened in liquid air, although the velocity of reaction is reduced. The substances in liquid air also exhibit phosphorescence with the same colour as that of the chemiluminescence. The emitted light is plane polarised.

W. E. G.

The Theory of Klein and Rosseland applied to Fluorescence, Photochemical Processes, and the Electron emission from Hot Substances. J. FRANCK (*Z. Physik*, 1922, 9, 259—266).—The theory proposed by Klein and Rosseland (cf. 1921, ii, 291) is extended to collisions between atoms and molecules. It is sought to determine the percentage of excited molecules which

undergo a change from the active into the normal condition after collision with a slow unexcited atom. The fluorescence of dilute iodine gas is shifted towards the red end of the spectrum by the addition of another gas. This result suggests that some of the excited molecules may transfer their rotation and vibration quanta to the colliding atoms without the emission of light. Observations of Wood and of the author on the resonance spectrum of the mercury line 2536.7 lead to the conclusion that the number of rayless transformations in the collision of excited atoms with slow moving atoms is not small compared with unity. In solids at high temperatures, the number of rayless quantum changes with liberation of electrons is large compared with the number of quantum changes taking place with the emission of light. W. E. G.

Photocatalysis. II. The Photosynthesis of Nitrogen Compounds from Nitrates and Carbon Dioxide. EDWARD CHARLES CYRIL BALY, ISIDOR MORRIS HEILBRON, and DONALD PRYCE HUDSON (T., 1922, 121, 1078—1088).

Photochemical Activity of the Triphenylmethanesulphonic Acids. EDWARD O. HOLMES, jun. (*J. Amer. Chem. Soc.*, 1922, 44, 1002—1008).—Solutions of magenta, malachite-green, methyl-violet, and crystal-violet which have been decolorised by sulphur dioxide when exposed to ultra-violet light of wave-length between 2200 Å.U. and 3300 Å.U. develop their original colours. Comparison of the absorption spectra of the original dyes and those which had regained the colour showed that the regained colour is due to the original dye, since the absorption spectrum is the same in both cases. It is shown that the reaction with sulphurous acid is reversible and consists of a decolorising action and a colorising action, the latter of which is photochemical. The large quanta of energy supplied by the ultra-violet light cause the photochemical action to increase and consequently a displacement of the position of equilibrium occurs. The equilibrium position can also be displaced by chemical and thermal means.

J. F. S.

A Determination of the Number of α -Particles per Second Emitted by Thorium-C of known γ -Ray Activity. ALLEN G. SHENSTONE and HERMAN SCHLUNDT (*Phil. Mag.*, 1922, [vi], 43, 1038—1047).—A direct comparison is made between the number of α -particles and the γ -ray activities of radium-C and thorium-C. α -Particles of ranges 8.6 cm. (thorium-C) and 6.96 cm. (radium-C) were counted by the wheel method devised by Rutherford, and accurate γ -ray measurements were made at the same time as the counts. The ratio $\alpha\text{Th-C}/\alpha\text{Ra-C}$ for equal γ -ray activities is not independent of the thickness of the wall of the γ -ray electroscope. Values of this ratio have been determined for thicknesses of lead ranging from 3.3 to 14.3 mm. For 3.3 mm., the ratio = 0.75. The γ -ray activities of thorium-C, radium-C, and a radium standard are given for the same range of thicknesses of lead. W. E. G.

The Interpretation of β -Ray and γ -Ray Spectra. C. D. ELLIS (*Proc. Camb. Phil. Soc.*, 1922, **21**, 121—128).—The researches of Rutherford and Chadwick have shown that the β -rays from a radioactive atom may be separated into a general and a magnetic line spectrum. The latter (cf. this vol., ii, 339) may be accounted for, if the γ -rays are the primary phenomena in the disintegration of the atom. The details of five different β -ray spectra (radium-B, radium-C, radium-D, thorium-B, thorium-D) lend support to this theory. The γ -rays are emitted during the movement of an electron from one stationary state in the nucleus to another. Some of these rays are absorbed in the electronic structure of the same atom and eject electrons with characteristic energies from the *K*, *L*, and *M* levels. When an electron arrives in a stationary state, in which it is not permanently stable, it is ejected from the nucleus. This electron, which has a variable kinetic energy, gives rise to the continuous or general spectrum. The numerical results obtained in this paper do not support the theory of Meitner (this vol., ii, 416), which affirms that the emission of a β -particle is the primary phenomenon in the disintegration of the atom.

W. E. G.

The Chemical Action of Penetrating Radium Rays. XIII. The Velocity of Formation and Equilibrium of Hydrogen Peroxide. ANTON KAILAN (*Monatsh.*, 1921, **42**, 387—398).—It is known that penetrating radium rays accelerate both the formation and decomposition of hydrogen peroxide (cf. A., 1912, ii, 10). Experiments have now been made to determine the equilibrium concentration of hydrogen peroxide in neutral solution and in solutions of varying degrees of acidity, since the stability of hydrogen peroxide is known to depend on the hydrogen-ion concentration. Experiments were made using the same samples of radium as in the previous work, at temperatures from 6° to 13°. No difference was found between Merck's perhydrol and ordinary hydrogen peroxide. At equilibrium the concentration of hydrogen peroxide, in gram equivalents per litre, was 0.005 and 0.001 when the hydrogen-ion concentration was 0.5 and 0.008 gram-ion per litre, respectively, whilst in neutral solution the equilibrium concentration was only 0.0006. Impurities present in ordinary distilled water lowered the equilibrium concentration in acid solution. The reaction velocity in either direction agrees with the equation $k=1/t \log a-b/a-b-y$, where *b* is the concentration at equilibrium, *a* the original concentration and *a-y* the concentration after time *t*. The values of *k* found at hydrogen-ion concentrations 10^{-7} , 0.008, and 0.5 were 7×10^{-3} , 0.7×10^{-3} , and 0.14×10^{-3} , respectively. The higher equilibrium concentration in acid solutions than in neutral solutions is due mainly to the retardation of decomposition of hydrogen peroxide in acid solution. It is calculated that for each primary β -particle, in neutral solution $3 \cdot 10^3$ and in acid solutions from 0.1 to 1.0*N*, $6 \cdot 10^3$ molecules of hydrogen peroxide are formed per second. A discrepancy between the velocity of formation found now and in 1911—1912 (*loc. cit.*) is discussed at length;

it may be due to physical changes in the glass apparatus brought about by prolonged exposure to radium rays.

The number of molecules of hydrogen peroxide formed is of the same order as the number of ion pairs from the total absorbed rays. This supports the view that there is a relation between ionisation and chemical action for β - and γ -rays as well as for α -rays. On the other hand, the ratio of hydrogen peroxide molecules decomposed to number of ion pairs is 1500:1 and the mechanism of decomposition appears to be different from that of formation. Some experiments on the decomposition of hydrogen peroxide in the light of a quartz mercury vapour lamp are also recorded. The velocity coefficient is much greater than with radium rays.

E. H. R.

Electrical Charges of Colloidal Particles and Anomalous Osmosis. II. Influence of the Radius of the Ion. JACQUES LOEB (*J. gen. Physiol.*, 1922, 4, 621—627; cf. this vol., ii, 354).—The rate of transport of water and the potential difference across a collodion-gelatin membrane separating solutions of the chlorides of potassium, sodium, and lithium from pure water, when the P_H is on the acid side of the isoelectric point of gelatin, vary inversely with the radius of the kations. At P_H 3.0 the influence of the three salts on the potential difference between the liquid and the membrane inside the pores of the gelatin is identical. The influence of the three salts on the potential difference across the membrane varies inversely as the relative mobilities of the kations, which suggests that this influence may be due to a diffusion potential.

C. R. H.

Effect of Hydrogen Pressure on the Electromotive Force of a Hydrogen-Calomel Cell. I. WILLIAM R. HAINSWORTH and DUNCAN A. MACINNES (*J. Amer. Chem. Soc.*, 1922, 44, 1021—1032).—The effect of pressure of hydrogen on the cell $H_2|HCl(0.1N)HgCl|Hg$ has been investigated at 25° for pressures up to 400 atmospheres, and the change of $E.M.F.$ by pressure calculated. The thermodynamic theory of the change of $E.M.F.$ has been investigated and the expression $\Delta E = 0.02958 \log p + 6.56 \times 10^{-6}(p-1) + 3.7 \times 10^{-10}(p^2-1)$ obtained for the change of $E.M.F.$ The calculated and the observed values have been compared and are as follows: 50 atmos. $\Delta E = 0.0504$ volt (0.0506), 100 atmos. $\Delta E = 0.0594$ (0.0598), 200 atmos. $\Delta E = 0.0688$ (0.0694), 300 atmos. $\Delta E = 0.0745$ (0.0753), and 400 atmos. $\Delta E = 0.0787$ (0.0797). The values in brackets are the calculated values. The values indicate that the thermodynamic theory as developed does not quite represent the measurements at higher pressures. This is probably due to the solubility of hydrogen, and it would appear that a correction to account for the solubility must be introduced.

J. F. S.

Carbon Monoxide-Oxygen Cell with Glass as Electrolyte. HARTMUT KALLMANN (*Z. Elektrochem.*, 1922, 28, 81—85).—The $E.M.F.$ of cells containing mixtures of carbon monoxide, carbon dioxide, and oxygen on one side of a glass wall and air on the other

side has been determined at 717° under various pressures from 920—800 mm. It is shown that the *E.M.F.* for such a cell is expressed by the equation $E = 1.118 - 0.0707 \log p_{\text{CO}_2}/p_{\text{CO}} \cdot p_{\text{O}_2}^{1/2}$. The experimental values agree with the values calculated by the equation to within 0.9%.

J. F. S.

Use of Phthalate Solutions for Hydrogen Electrode Standards. EARLE T. OAKES and HENRY M. SALISBURY (*J. Amer. Chem. Soc.*, 1922, **44**, 948—951).—The proposal recently made to replace the calomel electrode as a standard of *E.M.F.* measurement by a hydrogen electrode made up in alkaline solutions of phthalates has been investigated; and it is found that when such a phthalate solution, of P_{H} value 6.0 as measured by indicators, is measured against a calomel electrode, the *E.M.F.* slowly drifts in forty-eight and a half hours from about 0.57 to 0.66, that is, to a P_{H} value of 7.01. This change in the P_{H} value was confirmed by indicators. It is held that the change in the P_{H} value is due to a change in the phthalate itself, probably a reduction, and not to reduction of impurities, for the purification had been such as to exclude the large quantities of impurities necessary to bring about the observed change. If impurities are responsible for the change in *E.M.F.* their action must be that of catalysts reducing the phthalate. Hence, unless specially pure, phthalate solutions are unsuitable as standards for measuring hydrogen-ion concentrations.

J. F. S.

Instability of Phthalate Potentials. WM. MANSFIELD CLARK (*J. Amer. Chem. Soc.*, 1922, **44**, 1072—1073; cf. preceding abstract).—The author has re-examined some phthalate hydrogen electrodes over a period of twenty-four hours and has been unable to find a drift of more than 1.0 millivolt, and in the last fifteen hours of the observation the drift was less than 0.00005 volt. There was also no change in the Sørensen value. The author is therefore unable to explain the very large changes observed by Oakes and Salisbury (*loc. cit.*).

J. F. S.

New Conceptions of Electrolytes. III. The Hydration of the Hydrogen Ion. ERLING SCHREINER (*Z. anorg. Chem.*, 1922, **121**, 321—334; cf. A., 1921, ii, 425, 498).—The author measured the *E.M.F.* of the hydrogen ion in 0.001, 0.002, and 0.005 molar hydrochloric acid in potassium chloride solutions the concentration of which varied from 0.001 to 3.0 molar. The quinhydrone electrode was employed (cf. Büllmann, A., 1921, ii, 372). These measurements do not give the concentration of hydrogen ions, but the activity of these ions which is associated only with the non-hydrated ions. The author has given the method of calculation in a previous communication (A., 1921, ii, 425). The results obtained were fairly constant and showed that 8—9 molecules of water are on an average associated with each hydrogen ion, a result in good agreement with that found by Bjerrum (*Z. anorg. Chem.*, 1920, **109**, 275).

W. T.

Electrochemical Oxidation of Organic Compounds.

ERICH MÜLLER (*Z. Elektrochem.*, 1922, **28**, 101—106).—A theoretical paper in which the author discusses the views put forward by Fichter (this vol., ii, 23) and makes his own views clear. It is shown that the assertion of Fichter, that his views on electrochemical oxidation and those of the author are in agreement, is not true. Whilst the author assumes the discharge of anions, Fichter supports the view of a primary formation of oxygen and the accompanying purely chemical oxidation. Fichter assumes the intermediate formation of peroxides or peracids, the method of formation and decomposition of which is not explained, and consequently furnishes nothing toward the explanation of electrochemical processes. Such per-compounds may be prepared chemically, but their decomposition is to some extent different from what would be expected from the view that they are formed at the anode and from the products of electrolysis. The author accepts the formation of intermediate hydroxy-compounds, formed by the discharge of anions, which decompose in a manner in keeping with facts, and present a mechanism for both the chemical and electrochemical oxidation. The view of Fichter that the substitution of discharge processes at the anode by purely chemical oxidations contributes to the understanding of the course of electrolytic oxidations is incorrect.

J. F. S.

Magnetic Properties and Atomic Structure.

B. CABRERA (*Anal. Fis. Quím.*, 1922, **20**, 92—97).—A theoretical discussion of the relation between magnetic properties and atomic structure in the metals of the iron group. It is suggested that the N -electrons may be divided into two concentric subdivisions, the more superficial, N_2 , being the valency electrons and those beneath, N_1 , those with which magnetic properties are associated. It is supposed that the relation between magnetic moment and the number of N_1 electrons is periodic. The magnetic moment reaches a maximum for bivalent manganese and trivalent iron with five N_1 -electrons and diminishes to zero with increasing number of N_1 -electrons.

G. W. R.

Magnetism and Atomic Structure. II. The Constitution of the Hydrogen-Palladium System and other Similar Systems. A. E. OXLEY (*Proc. Roy. Soc.*, 1922, [A], **101**, 264—279; cf. A., 1921, ii, 82).—The specific magnetic susceptibility of palladium black, the value of which is $+64.6 \times 10^{-7}$, is considerably reduced by occluded hydrogen, the greatest reduction observed being about 75% to $+14.7 \times 10^{-7}$ when great care was taken to prevent loss of hydrogen after charging. The specific susceptibility gradually returns to its original value as the occluded hydrogen escapes. If the occluded hydrogen were in the atomic state, it would be expected to increase the specific susceptibility. On the other hand, molecular hydrogen, liquid or gaseous, being diamagnetic, should reduce the specific susceptibility by a calculable amount. The maximum reduction on this assumption would be 0.19×10^{-7} , an amount insufficient to account for the observed

reduction. The experimental results may be accounted for on the assumption that a loose compound is formed, possibly having the composition Pd_2H . That the presence of such a loose compound should lower the magnetic susceptibility is not surprising when it is remembered that the carbonyls of iron and of nickel are both diamagnetic. It is noteworthy that a loose compound of the composition PdH would form a system of two nuclei with an electronic system resembling that of silver, the atomic number of which exceeds that of palladium by one. Such a system would be expected to have a magnetic susceptibility very nearly equal to that of silver, -1.8×10^{-7} . If half the palladium atoms were in this form, its susceptibility would be reduced by about 50%. The difference between the occluding powers of amorphous and crystalline palladium is discussed. The slow diffusion of hydrogen into crystalline palladium can be understood when its face-centred cubic lattice is taken into account.

When manganese is fused in an atmosphere of hydrogen, or is deposited electrolytically, it becomes ferromagnetic with a specific susceptibility $+2000 \times 10^{-6}$, its normal value being $+11.0 \times 10^{-6}$. It may be supposed that the presence of hydrogen produces with the manganese, atomic number 25, a certain number of electron systems similar to that of iron, atomic number 26, and that these are the cause of the observed ferromagnetic properties. This suggestion is discussed in connexion with the Lewis-Langmuir theory.

E. H. R.

Determination of High Temperatures by Effusion of Gases.

YOHEI YAMAGUCHI (*J. Chem. Soc. Japan*, 1922, 43, 1—21).—The author has studied the relations between pressure and temperature on the passage of a gas through a capillary tube of quartz. (1) The increase of pressure necessary to pass the same quantity of air through a quartz capillary tube at various temperatures was investigated. A linear relation, $\log p = a \log T + b$, holds between the pressure (p) and the absolute temperature (T) within the range 17° to 1205° . This, however, cannot be applied to the measurement of temperature, owing to the complexity of the apparatus necessary, and the difficulty of regulating the pressure. (2) Using the same capillary, the relation between the effluent velocity of the transpired air and its temperature has been investigated, no simple linear relation being found for the temperature interval 20.5° to 1046° . (3) The relation was investigated between temperature and the effluent velocity of air as measured by its effusion through a small hole in the round bottom of a quartz tube. A linear relation, $t = a + b\sqrt{T}$, holds between the effluent time (t) and the absolute temperature (T) of the tube heated by an electric furnace at temperatures from 17° to 1125° which can be applied to the measurement of high temperatures.

K. K.

Considerations on Cooling and Heating Curves. R. ARIANO (*Gazzetta*, 1922, 52, i, 246—261).—The author considers the courses followed normally, that is, when no transformation occurs, during

cooling or heating, by: (1) the temperature-time curve, and (2) the curve representing the difference between the temperature of the substance examined, T , and that of a second substance, chosen for comparison, T_1 , as a function of the latter temperature, $T - T_1 = f(T_1)$.

As regards the temperature-time curve, it is first shown theoretically that Newton's law expresses, without appreciable error, the transference of heat between furnace and sample in the case of the cooling of metallic samples of small dimensions. Analogous reasoning applies in the case of heating curves. Cooling curves are exponential in form and are defined by equations of the type $T = k + Ae^{-a\theta/Pc}$, whilst heating curves are probably represented by equations of the form $T = k + Ae^{-a\theta/Pc} + f(\theta)$, θ being the time, a the product of the coefficient of external thermal conductivity and the surface, P the weight of the sample, and c its mean specific heat. The results of cooling and heating experiments with silver show that A in the former of the two above equations is sensibly identical with the temperature at the beginning of the cooling (t_1), k being consequently nearly zero in magnitude.

As regards the differential curve, $T - T_1 = f(T_1)$, it is shown theoretically and confirmed experimentally that, if the sample chosen for comparison undergoes no transformation in the interval of temperature chosen, this curve exhibits a maximum almost at the beginning of the cooling. In order that the normal course of the curve may be as nearly rectilinear as possible, the specific heats of the two samples and their mode of variation with temperature should be almost coincident; the same should hold for the values of the ratio, weight : surface, for the coefficients of linear expansion and their variation with temperature, and for the coefficients of external conductivity.

T. H. P.

Revision of the Entropies of the Elements. GILBERT N. LEWIS and W. M. LATIMER (*J. Amer. Chem. Soc.*, 1922, **44**, 1008—1017).—A theoretical paper in which on the basis of new determinations of the specific heats of many elements the entropy has been recalculated. By means of the equation $S = 3/2R \log_e W + 25.70$ the entropies of nitrogen, oxygen, fluorine, sodium, chlorine, potassium, calcium, zinc, bromine, cadmium, iodine, caesium, and mercury have been calculated in the state of monatomic gas. In four cases where the experimental values are of sufficient accuracy a comparison is made between the experimental values and the calculated values for 25° and 1 atm. The following are recorded where the values in brackets are those calculated: helium 29.2 (29.8), argon 36.4 (36.7), cadmium 40.0 (39.8), and mercury 41.3 (41.5). A table of entropies at 1 atm. and 25° has been drawn up and is appended to the paper.

J. F. S.

Electrically Heated Apparatus for the Determination of Melting Points. UYTENBOGAART, jun. (*Chem. Ztg.*, 1922, **46**, 493).—The apparatus consists of a circular glass tube at the bottom of which a platinum resistance is placed; it is filled with water, glycerol, or sulphuric acid (d 1.84). The liquid, warmed by the

platinum resistance, rises uniformly in the two limbs and the currents, joining at the top, pass down a central tube which contains the thermometer and substance, with a kind of whirlpool motion. For temperatures up to 75° , an ordinary 4-volt accumulator is sufficiently powerful, but for higher temperatures it is preferable to use the lighting current with a suitable resistance in the circuit.

H. W.

Binary Liquid Mixtures. GERHARD C. SCHMIDT (*Z. physikal. Chem.*, 1922, **101**, 286—291).—An answer to the criticisms of Faust (this vol., ii, 423), Cassel (this vol., ii, 424), and Schulze (this vol., ii, 424) on the views expressed by the author in connexion with Dolezalek's theory of binary liquid mixtures (this vol., ii, 119).

J. F. S.

Heat of Vaporisation and the Difference, $m'-m$, of the Specific Heats at the State of Saturation for Argon, Oxygen, Nitrogen, and Hydrogen. E. MATHIAS, C. A. CROMMELIN, and H. KAMERLINGH ONNES (*Compt. rend.*, 1922, **174**, 1395—1397; cf. A., 1921, ii, 256).—A mathematical paper in which formulæ are given for the four gases by means of which it is possible to calculate the latent heat and hence the reduced heat of vaporisation, and also the difference between the specific heats of the saturated vapour and the saturated liquid.

W. G.

The Vapour Pressure of Hydrogen and New Thermometric determinations in the Domain of Liquid Hydrogen. J. PALACIOS MARTINEZ and H. KAMERLINGH ONNES (*Arch. Néerland.*, 1922, [iii], **6**, 31—39).—Cath and Onnes (A., 1918, ii, 218) could not explain the disagreement of their results for the vapour pressure of hydrogen in the neighbourhood of its boiling point with the values found by Keesom and Onnes. The former authors determined the temperatures directly by means of a helium thermometer, whilst the latter employed a platinum resistance thermometer, the values obtained being reduced to the hydrogen and helium thermometers by Onnes and Holst. The present authors redetermined these measurements between the absolute temperatures $14\cdot10^{\circ}$ and $20\cdot63^{\circ}$, particular attention being directed to the boiling point of hydrogen, an important point on the temperature scale. The boiling point was found to be $20\cdot35^{\circ}$, a value agreeing with that found by Keesom and Onnes; for points immediately below the boiling point the results agreed with those of Cath and Onnes. All the results are given in a table. The calibration of platinum thermometers is also described.

W. T.

The Distillation of Greatly Frothing Liquids. KLÄNHARDT (*Chem. Ztg.*, 1922, **46**, 493).—The difficulty in effecting the distillation of foaming liquids, such as aqueous solutions of soap or saponins, can be easily overcome by passing a current of compressed gas (such as carbon dioxide) over the surface of the liquid. A suitable apparatus for the introduction of the gas is a tube terminating in a ball of 2 cm. diameter in which three series of holes about

1 mm. in diameter are blown. Distillations with steam can also be smoothly effected in this manner. H. W.

Maintenance of the Adiabatic Condition in Calorimetry.
FREDERICK BARRY (*J. Amer. Chem. Soc.*, 1922, **44**, 899—937; cf. A., 1920, ii, 734).—An extensive series of measurements is described, which were undertaken to establish a standard of accuracy for the calorimetry of slow processes. It is shown that to attain the accuracy defined by the loss or gain of 0.5 gram-calorie in ten hours, the following precautions are necessary and sufficient. A closed calorimetric system must be used which allows no measurable evaporation into the insulating air gaps, and these gaps must be dry. The outer environment must be thermostatically controlled, whenever there are conducting parts which pass directly from the calorimeter to the surrounding air, with a precision characteristic of the system employed. This is about $\pm 0.2^\circ$ when encased mercury thermometers are used. It is always advisable to keep the environmental temperature close to the calorimetric within the characteristic range of negligible direct leakage; and it is necessary to correct for fluctuation beyond this range. For this control, a constant temperature chamber is essential. A convenient structure for this purpose is described. With the usual system of about 1000 cal. heat capacity the air gaps should not be less than 40 mm. wide and there is no advantage in larger gaps. With a 40 mm. gap, when the temperature fluctuates within $\pm 0.01^\circ$ and the environment within 0.2° of the calorimetric temperature, the system is practically adiabatic within the error defined above, the total leakage being little more than three times that of a perfect vacuum gap. The leakage rate in such systems is the same in both directions and for heads below 0.1° is proportional to the head. Corrections for imperfect adiabaticity due to bath fluctuation may be made on this basis, since transmission lag has no measurable effect on the leakage. A calorimeter based on the above-named conditions is described. With this calorimeter, the initial conditions are perfectly adiabatic; and the total calorimetric lag for the temperature changes characteristic of long-continued operations is negligible. It is permissible and advantageous to stir the closed system reciprocally. In the system described, this may be done without significant loss of heat. The heat of stirring is developed identically in different assemblages and at the same rate for any one speed, whether stirring is intermittent or continuous. It may vary at low speeds with the fourth and higher powers of the speed. The continuous stirring necessary to ensure mixture in chemically reacting systems is productive of negligible error; and similar stirring at low speeds throughout determinations is shown to be practicable, although in very protracted operations intermittent stirring is better. Strictly uniform speeds are necessary for long, continuous stirring, but not for intermittent stirring, nor for continuous stirring during mixture if the approximate rates of heat production under different speeds be known for the system used. The open calorimeter is unavailable in protracted calori-

metry, since, even with an initially dry gap, evaporation leakage is inconstant as the result of uncontrollable variability in prior conditions. This is due in great part to the condensation of water vapour in the air gap on the walls of the calorimeter, which occurs on clean as well as on dirty surfaces, and is probably due to the simple adsorption of moisture, an effect which can be neither eliminated nor controlled even under approximately isothermal conditions. With change of temperature, its effects are greater and still more irregular, and in gaps saturated with water are complicated in the extreme. The close system is best for all types of calorimetry; but in the adiabatic measurement of swift reactions the open calorimeter may be safely used, either with dry surfaces in an initially dry gap, or with invisibly wetted surfaces in a saturated gap which holds no water, provided always that correction for aggregate thermal disturbances due to evaporation leakage be made by interpolation from the results of observations taken before and after the reaction period. The initially dry gap, with which leakage is less and more nearly uniform, is preferable in such measurements; but correction for imperfect adiabaticity is safer with the saturated gap. Under all heads less than 1° , the total leakage from a closed calorimeter system in a dry gap shows slight divergence from Newton's law, since the convection increases very slowly with increase in gap width, and varies as powers of the thermal head less than two except when the gap is unusually wide. Similar leakage from the open system is irregular, but yields itself to a rough analysis which gives some indication of the character of the thermal disturbances and the magnitude of the uncertainties characteristic of the merodiabatic measurements which have yielded the bulk of the present thermochemical data. J. F. S.

Calorimetric Researches : (I) The Standardisation of a Calorimetric System ; Comparison of the Heats of Combustion of the Substances Used for Standardisation : Benzoic Acid and Naphthalene. P. E. VERKADE, J. COOPS, jun., and H. HARTMAN (*Rec. trav. chim.*, 1922, **41**, 241—277).—A discussion of previous work on this subject and its bearing on the authors' experiments. Standardisation of the apparatus was effected as the result of thirty-seven experiments in the combustion of benzoic acid and thirty-six in the combustion of naphthalene. A detailed description is given of the apparatus used, the method of carrying out the experiments and the corrections applied to the results. Adiabatic calorimetry was discarded in favour of the ordinary methods for various reasons; there is little difference in the results obtained by the two methods (cf. Dickinson, A., 1914, ii, 802, and Swientoslawski, A., 1921, ii, 679). The ratio between the values obtained for the two substances used agrees with that of Dickinson, the figure given by Swientoslawski (A., 1918, ii, 32) is criticised on both theoretical and practical grounds. In order to carry out an absolute standardisation of a calorimetric system, a standard substance should be chosen the heat of combustion of which is known with the greatest possible accuracy. The results obtained

by the authors show that benzoic acid should be preferred to naphthalene, as it gives more constant results, is easily obtained pure, and is practically non-hygroscopic. Naphthalene, on the other hand, does not undergo complete combustion in many experiments, and also loses weight by evaporation; figures are given in illustration of the latter objection. Other substances suggested for the purpose are not so easily obtained pure as is benzoic acid. The value finally recommended as the standard ratio of the heats of combustion of naphthalene and benzoic acid is 1.5203. H. J. E.

Heat of Combustion of Lactic Acid. OTTO MEYERHOF (*Biochem. Z.*, 1922, **129**, 594—604).—The author has determined the heat of combustion of lactic acid (in dilute aqueous solution) from the heat of combustion of zinc lactate, the heat of dilution of lactic acid, the heat of neutralisation of zinc oxide and lactic acid, and the heat of solution of zinc lactate in water. The value found for 1 gram of lactic acid is 3615 cal. H. K.

Heat of Solution of Zinc in Hydrochloric Acid. THEODORE W. RICHARDS and THORBERGUR THORVALDSON (*J. Amer. Chem. Soc.*, 1922, **44**, 1051—1060).—A new apparatus is described, suitable for dissolving substances in a comparatively small excess of liquid and providing a conveniently large heat capacity for the reception of the heat. With this apparatus the heat of the reaction $\text{Zn} + 2(\text{HCl}, 200\text{H}_2\text{O}) = \text{ZnCl}_2, 400\text{H}_2\text{O} + \text{H}_2$ was found to be 36.32 Cal. (or 151.8 kilojoules) if the hydrogen is dry, and 36.07 Cal. (or 150.8 kilojoules) if the hydrogen is moist at 20°. The total energy change, U , of this reaction is therefore 36.90 Cal. (or 154.2 kilojoules) at 20°. The heats of dilution of factors and products needed for the calculation of the above results were determined experimentally. The temperature-coefficient of the heat of solution of zinc in concentrated hydrochloric acid is shown to be negative and of considerable magnitude; even with diluted acid it probably amounts to -30 cal. per degree. J. F. S.

Heat of Solution of Cadmium in Hydrochloric Acid. THEODORE W. RICHARDS and SETSURO TAMARU (*J. Amer. Chem. Soc.*, 1922, **44**, 1060—1066).—Using the apparatus previously described (cf. preceding abstract), the heat of the reaction $\text{Cd} + 2(\text{HCl}, 200\text{H}_2\text{O}) = \text{CdCl}_2, 400\text{H}_2\text{O} + (\text{H}_2)_p$ is found to be 17.23 Cal. (or 72.0 kilojoules) at 20° if the hydrogen is dry, and 16.98 Cal. (or 71.0 kilojoules) if the hydrogen is moist at 20° and 760 mm. The total energy change, U , of the reaction is therefore 17.81 Cal. (or 74.4 kilojoules) at 20°. The temperature-coefficient of the heat of solution of cadmium in concentrated hydrochloric acid is shown to be negative -71 cal. per degree, and probably with diluted acid it amounts to -30 cal. per degree. All the necessary factors used in the present calculation were determined experimentally. J. F. S.

Heat of Transformation of Austenite into Martensite and of Martensite into Pearlite. NOBUO YAMADA (*Sci. Rep. Tohoku Imp. Univ.*, 1922, **10**, 453—470).—The heat of dissolution of carbon

in iron and also the heat content of austenite and pearlite are determined in a series of carbon steels ranging from 0.38—1.74% carbon. The heat of dissolution of carbon in iron is shown to be a linear function of the carbon content of the steel and amounts to 1130 cal. per gram of carbon. By combining the results obtained with those of Meuthen (cf. A., 1913, ii, 385) for the total heat of transformation, the heat of allotropic transformation of austenite to martensite is calculated. It is a linear function of the carbon content and has a maximum value of 5.6 cal. per gram for eutectic steel. For a carbon content of 0.38% carbon, the value is 2.4 cal. and for 1.74% carbon 4.8 cal. Martensite has a definite heat content corresponding with the quantity of dissolved carbon, a definite crystalline form stable at ordinary temperatures, characteristic physical properties as compared with austenite or pearlite, and must therefore be considered as an independent phase. It is shown that troostite, sorbite, and pearlite have the same specific heats within the limits of experimental error. It is confirmed that the transformation of austenite into pearlite involves the intermediate production of martensite.

J. B. F.

Some Remarkable Properties of Gases. FRIEDRICH WÄCHTER (*Z. anorg. Chem.*, 1922, **121**, 225—239).—A theoretical paper which derives from Naumann's formula the lowest value for the molecular weight of gases to enable them to remain in the atmosphere of a planet. Hydrogen can exist in our atmosphere, but not in the atmosphere of the moon. In the atmosphere of the sun, a gas with a molecular weight 1/1864 can remain. The author identifies these imponderable molecules with the light ether, which he thus regards as a very light gas susceptible to the Lorenz contraction. He concludes from the above that the apparent mass of electrons as found by Kaufmann and Bucherer is merely a proof of the Lorenz contraction in the ether; thus the idea of apparent mass in the interior of the atom is not justified. Instead of the idea of β -particles or atoms of electricity, the author suggests the atoms of the lightest ponderable gas of invariable mass, and on this hypothesis finds that the enormous velocities in the inner atom such as Bohr calculated for the Rutherford atom are unnecessary. These results are also applied to the radioactive atoms. An earlier paper dealt with the astronomical implications, such as the Michelson's experiment, the abnormal motion of mercury, and the displacement of spectral lines (*Astron. Z.*, 1921, **4**, 62). W. T.

Specific Characters of Hydrolytic Decomposition. S. T. J. TROMP (*Rec. trav. chim.*, 1922, **41**, 278—295; cf. Schoorl, A., 1920, i, 531).—A study of the specific volume occupied by the molecule of water which is fixed in various reactions. An examination of esters, cyanides, carbylamines, nitro-compounds, anhydrides, ethers, oximes, amides, and acetals shows that the volume of the water taken up varies little in one type of reaction, but considerably from one type to another. This method of investigation shows that neither cyanides nor carbylamines should be regarded as esters of hydrocyanic acid and also provides a means of dis-

uishing between nitrites and nitro-compounds, also between nides and carbylamines. The values obtained for anisole and netole show that these substances are esters of phenol rather than ethers, and the view of saccharose as an ether is corroborated. Comparison of the specific refraction of fixed water with that of ether as such gives no such trustworthy data as the discrepancies considerable and numerous.

H. J. E.

Thin Films of Binary Mixtures (Glycerides). (MILLE) PAULET (*J. Phys. Radium*, 1922, [vi], 3, 128—132).—Mixtures of various glycerides in benzene solution are applied to the surface of water and determinations made of the surface covered. No definite relationships were found for binary mixtures, the curves always showing either maxima or minima. These maxima and minima appear to correspond with changes of physical state and with a simple ratio of the number of molecules of the two constituents. On the assumptions that all the molecules are associated the maximum and minimum value of the area covered and that the free molecules of the glycerides cannot exist side by side, it is possible to derive theoretical curves which are in good agreement with the experimental results.

W. E. G.

Examination of the Compression Equation of Liquids by means of the Data of Amagat and Bridgman. H. CARL (*Z. physikal. Chem.*, 1922, 101, 238—268).—The compression equation forwarded by Wohl (this vol., ii, 117) which has the form $e^{(v_0-v)/A} = (p-p_0)/(k+p_0)$; $v_0\alpha = A$; $k = b\tau - c$ has been tested by means of Amagat and Bridgman's isothermals for twelve liquids. In this expression, K is a pressure quantity for the internal pressure of liquids and α a constant, which expresses the influence of differential resistances and the distances of molecules and atoms in the liquid. Every normal liquid has a constant α value over the whole temperature range 0—80°, and the K value in the limit is sufficient for the case of normal liquids for rising temperature in the above relation. Water exhibits here the known anomaly in its volume change up to pressures of 2500 kg./cm.² At 50°, it shows first regular behaviour with increasing temperature. The constant α is constant over the whole range of temperature, but the K values do not, as is to be expected from the foregoing, be brought into a single equation, since from 50° downwards K decreases with increasing temperature. Similar anomalies are shown by ethyl alcohol for lower pressures, according to Amagat's data for 1—1000 mos., α is not constant over the temperature range 0—180°, and K does not decrease so regularly with increasing temperature, as is shown to be the case for all normal liquids. The agreement between the v value calculated by the above equations and those from Amagat's isothermals is excellent. A mean divergence of 0.2 units is found in the last place of decimals, the error of experiment being 6 units. Larger divergences have been shown from series of differences to be due to experimental errors. In the case of Bridgman's results for higher pressures, the agreement has a mean divergence of 0.5%. A reduced form of the equation, in

which the pressure values are expressed as fractions of p_k , has been obtained. By inserting $K/p_k = b\tau/p_k - c/p_k = 1/\beta(\tau - \gamma)$ the equation $(v_0 - v)/v_0 = \alpha \log_e[1 + \beta(\pi - \pi_0)/(\tau - \gamma - \pi_0/\beta)]$ is obtained, and on placing $p_0 = 0$ in this the simplified form $(v_0 - v)/v_0 = \alpha \log_e[1 + \beta\pi/(\tau - \gamma)]$ results. A table containing the values of α , β , and γ and the critical data of the substances examined is included in the paper.

J. F. S.

Negative Viscosity. ADOLPH I. RABINOVICH (*J. Amer. Chem. Soc.*, 1922, **44**, 954—964).—The term negative viscosity is applied to the viscosity of solutions which have lower viscosities than the solvents. With the object of explaining negative viscosity, the author discusses a large number of factors which may determine the viscosity of solutions. The factors considered are, (a) viscosity of the solvent, (b) viscosity of the solute, (c) solvation, (d) formation of complex ions and molecules, (e) the electric fields of the ions, (f) depolymerisation of associated solvents, (g) electrostriction, and (h) depolymerisation of the solute.

J. F. S.

Significance of Surface Tension Phenomena for the Dairy Practice. OTTO RAHN (*Kolloid Z.*, 1922, **30**, 341—346).—The author has studied the formation of the foam which accompanies the pouring of skim milk from the cream separator. It is shown that foaming is due to a reduction of the surface tension caused by the accumulation in the surface of an albuminous substance which passes into the walls of the foam. These walls are shown to contain a solid substance, and the drying of such material is shown to be similar to the drying of many albuminous substances inasmuch as it is irreversible. It is probable that this solid albuminoid is the main constituent of the skin which forms on the surface of milk which has been heated at 60° or above. On the basis of the foregoing, the formation of whipped cream is explained as follows: on whipping cream a network of foam is produced, which is stiffened by the solidified fat so that it does not fall like the foam but retains its form. A microscopic examination of whipped cream shows that it consists of a solid structure of albumin penetrated by layers of solid fat which has the same form as the foam. On warming whipped cream above the melting point of the fat, the structure collapses, but remains somewhat frothy because the albumin cannot melt. Butter formation is explained as follows: The cream contains much of the foam producing albumin; this surrounds the particles of fat. On churning, a large volume of air is entrapped by the cream, so that the surface is very much enlarged. The albumin passes into the walls of the foam and takes the fat with it, so that a foam rich in fat stands above a liquid poor in fat (buttermilk). The fat particles lie very close together in the foam walls and are compressed by the surface pressure to form conglomerates of fat particles. This causes the albumin in the walls to solidify and further churning breaks up the foam and mixes the fat conglomerates with the solid albumin to form lumps of butter. It is shown that butter may be formed at 34°, but not at 39°.

J. F. S.

Theory of Adsorption Processes. M. POLANYI (*Z. Elektrochem.*, 1922, **28**, 110—111).—A criticism of Eucken's paper (this vol., ii, 262) on the theory of adsorption processes. J. F. S.

The Adsorption Problem. Sorption of Vapours by Charcoal. BROR GUSTAFVER (*Koll. Chem. Beihefte*, 1922, **15**, 185—338).—The sorption isotherms for water, alcohol, and acetic acid vapours have been determined at 20°, 25°, 30°, and 35° with animal charcoal as adsorbent. These show that sorption is not a single process. The isotherms, which over the first portion are straight lines (water) or concave to the pressure axis (alcohol and acetic acid), show a well-defined inflexion at the point *O*. At this point the curve rises steeply and becomes convex to the pressure axis (water), or turns, and forms a wedge-shaped peak pointed outwards with respect to the pressure axis (alcohol and acetic acid). In the experiments, the vapours were added to the charcoal in small portions and the sorption equilibria were reached in all cases from both sides. The first part of the curves before the point *O* is reached represents a reversible process, since the points obtained by both methods lie on the same curve, whilst the equilibria points above the point *O* lie on parallel curves. Equilibrium is set up much more rapidly from below than from above. The experimental results are explained in much the same way as the sorption by gels. The sorption occurs first through adsorption and then from the point *O* mainly through condensation of liquid in the pores of the charcoal. The hysteresis observed is explained by the varying curvature of the meniscus during sorption and desorption. This depends on the fact that during sorption the walls of the charcoal pores are only slowly wetted, which in its turn is probably due to the presence of air. When the equilibrium is established from the under side, desorption, a rapid evaporation of the vapour from the charcoal, occurs, whereby the meniscus in the capillaries take on a greater curvature than previously and the equilibrium is rapidly stable. Sorption takes place slowly, because the radius of curvature of the meniscus decreases uninterruptedly while the walls are moist. Thereby a fresh condensation of vapour takes place and the establishment of equilibrium is delayed. The taking up of each portion of vapour added occurs at first by means of adsorption, and the adsorption equilibrium is established in about thirty seconds. Only in the case of charcoal which had been exhausted immediately before the experiment could the adsorption equilibrium be recognised. For this process the formula $k=1/tp_{\infty} \cdot [\log p/(p-p_{\infty}) - \log p_0/(p_0-p_{\infty})]$ is representative. The structure of charcoal has been discussed, and the radii of the capillaries have been calculated by means of the Trouton and Andersson formula. The taking up of alcohol and acetic acid vapour at 20° occurs in such a way that only capillaries of the same diameter are active. Approximately 75% of the total quantity is taken up at very low pressures, that is by capillaries of very small radius of the order $r < 6.2 \times 10^{-8}$ cm., which indicates that charcoal is possessed of an exceedingly fine structure. The

course of the taking up of water differs from that of the two other liquids inasmuch as the calculated radii are partly much greater and that the maximum volume is smaller. These two circumstances are explained by the smaller power of water to wet the charcoal and by the slow penetration of liquid into the pores of the charcoal. The surface of the charcoal has been approximated from the experimentally determined volume of the empty space of the charcoal and the calculated radii of the capillaries in which condensation occurs. The free surface of the capillaries of radius $r > 6 \times 10^{-8}$ cm. is about 600 sq. metres per gram of charcoal and the total area of all capillary walls > 3000 sq. metres. Trouton's sorption rule is shown to be incorrect and in its place it is shown that the volume taken up, and not the mass, of a given liquid is independent of the temperature and only a function of the pressure.

J. F. S.

More General Theory of the Adsorption of Solutions.

WOLFGANG OSTWALD and RAMON DE IZAGUIRRE (*Kolloid Z.*, 1922, **30**, 279—306).—A theoretical paper in which a large number of types of adsorption curves and formulæ have been collected and criticised. The view is expressed that every adsorption is at first a process of "unmixing," whereby a most concentrated solution, the absorbed solution, forms on the surface of the adsorbent whilst the equilibrium solution remains behind. Solutions of substances are adsorbed and not the "dry" dissolved substances. In opposition to the previously held views, the author postulates that the adsorption of the solvent, along with the dissolved substance, is an integral and equally important process in every adsorption from solutions. The assumption is made that the adsorption of the dissolved substances, without reference to the simultaneously adsorbed solvent, increases asymptotically up to the highest concentration in accordance with Boedecker's logarithmic formula. It is shown that this formula is not in keeping with the difference in concentration before and after adsorption, except in the case of very dilute solutions. Since the actual amount of adsorbed substance continuously increases, the difference in concentration ($c_0 - c$) must show a maximum and at the highest concentrations approach the zero value. It is shown that the whole of the adsorption curves may be constructed on the basis of the three assumptions made above and the simultaneous adsorption of the solvent. A number of formulæ are developed which give a quantitative relationship between adsorption and concentration on the basis of the above assumptions. The most important of these are: (1) $N/m(c_0 - c) = kc^n(100 - c)$ for the case where the adsorption of the solvent may be neglected; (2) $N/m(c_0 - c) = kc^n(100 - c) - l(100 - c)^a \cdot c$ for cases where the solvent is adsorbed directly by the adsorbent; (3) $N/m(c_0 - c) = kc^n[100 - c(1 + s(100 - c)^{\beta})]$ for cases in which the solvent of the adsorbed solution is brought into the surface layer by the solvation of the dissolved substance; (4) $N/m(c_0 - c) = kc^n[100 - c(1 + s(100 - c)^{\beta})] - l(100 - c)^a \cdot c$ for cases in which the adsorption of the solvent takes place by both methods

provided for in equations 2 and 3. In these equations N is the weight of solution in grams at the commencement, m the weight of adsorbent, c_0 the initial percentage composition of the solution, c the equilibrium percentage concentration of the solution, $k, l, s, n, \alpha, \beta$ are constants. A graphic method for evaluation of the constants is described. The second equation has been tested by means of the measurements of Schmidt-Walter for the adsorption of acetic acid and water by charcoal (A., 1914, ii, 542) and Gustafson's measurements of the adsorption of phenol and alcohol by charcoal (A., 1915, ii, 824) and a remarkably good agreement between the calculated and experimental values found.

J. F. S.

Relationship of Dolezalek's Theory of Solutions to that of Planck. H. CASSEL (*Z. physikal. Chem.*, 1922, **101**, 235—237).—In earlier papers, Wagner (A., 1920, ii, 596) has shown that Dolezalek's theory of solutions is a special case of Planck's theory of concentrated liquid mixtures, which is of no special importance. The present author shows mathematically that Wagner's conclusions are based on an error.

J. F. S.

Solubility. IV. Principle of the Specific Interaction of Ions. J. N. BRÖNSTED (*J. Amer. Chem. Soc.*, 1922, **44**, 877—898; cf. A., 1920, ii, 536; this vol., ii, 199).—It is shown that the activity coefficient of an ion may be determined by two factors, one of which is due to the salting-out effect of the salt solution serving as solvent and the other to electrical interaction between this ion and the ions of the solvent. Ions are uniformly influenced by ions of their own sign; their activity coefficients depend, therefore, only on the action of ions of the opposite sign and the salting-out effect of the solvent. The salting-out effect of a salt solution can be represented as a product of the salting-out effects of the separate ions. A number of relationships are derived for the solubility of salts at constant concentration of solvent solution and methods for determining the ratios of salting-out coefficients, coefficients of interaction, and activity coefficients. Thermodynamic relationships between activity coefficients and osmotic coefficients in solutions of constant total concentration and a relationship between solubility and freezing point are derived. The above theoretical conclusions and relationships are experimentally verified by solubility determinations in solutions of highly complex salts. A method of determining liquid junction potentials, on the basis of the present considerations, is put forward. In the case $0.1M\text{KNO}_3|0.1M\text{NaNO}_3$, a small concentration of silver nitrate is added and the *E.M.F.* of the cell $\text{Ag}|\text{KNO}_3(0.1M)\text{AgNO}_3(0.001M)||\text{AgNO}_3(0.001M)\text{NaNO}_3(0.1M)|\text{Ag}$ measured. The *E.M.F.* is given by $\pi_1 = RT \log_e f_{\text{Ag}(\text{NaNO}_3)} / f_{\text{Ag}(\text{HNO}_2)} + \pi_d$, where π_d is the junction potential and f is the activity coefficient of the Ag in the solution named. Also $\pi_1 = RT \log_e r_{(\text{Na/K})} + \pi_d$ where $r_{(\text{Na/K})}$ is the ratio of the salting-out coefficients of the sodium and potassium ions. This ratio can be determined from solubility measurements and consequently π_d may be calculated.

J. F. S.

Hydration of Electrolytes. S. ASCHKENASI (*Z. Elektrochem.*, 1922, 28, 106—110).—A theoretical paper in which the deviations of osmotic quantities of moderately and very dilute solutions have been collected together with the inflexion points of the experimental series. The Born-Fajans's polarisation-hydration hypothesis is discussed, and it is shown that the forces assumed in this hypothesis would produce a greater effect on the vapour pressure than is observed experimentally. In Fajans's method of calculating the heat of hydration, the influence of the dielectric constant on the work of dissociation is not taken into account. The author presents a chemical mechanism for hydration in salt solutions on the assumption that the associated liquid molecules of water are modified in the process. On the basis of this view, the author attempts to overcome the objections which have been offered to a step-wise hydration. J. F. S.

Calculation of the Osmotic and Activity Functions in Solutions of Uni-univalent Salts. J. N. BRÖNSTED (*J. Amer. Chem. Soc.*, 1922, 44, 938—948).—A theoretical paper in which from the point of view that the individualities of salt solutions have an origin similar to that of the individual salting out effect in the case of non-electrolytes, equations are deduced to govern the osmotic and activity functions of uni-univalent salts in pure and mixed solutions. These equations have been tested by means of the most accurate experimental results, which include measurements of depression of the freezing point, solubility, and electromotive force. Ratios of activity coefficients have been calculated on the basis of these equations in conjunction with the principle of the specific interaction of ions. J. F. S.

The Mutual Solubility of Liquids at High Pressures. JEAN TIMMERMANS (*Arch. Néerland*, 1922, [iii], 6, 147—151).—This work completes the previous researches of Kohnstamm and Timmermans (*A.*, 1913, ii, 481). The apparatus employed is described in the previous communication.

A.—System water-*sec.*-butyl alcohol. The curve obtained for this system under high pressures is analogous to that of methyl ethyl ketone. With increasing pressure, the lower critical solution temperature (normally below the freezing point, -8.45°) is raised and the higher critical temperature, 113.8° , is lowered. Under a pressure of 830 kilos. they meet at about 65° , so that at these high pressures the liquids are miscible in all proportions. The values of dt/dp for both critical values are given. As demanded by theory, dt/dp for the freezing point of water was found to be less than for alcoholic solutions. The alcohol employed had a boiling point $99.50^{\circ} \pm 0.01$. $d_4 = 0.82263 \pm 0.00002$.

B.—System water-*isobutyric* acid (b. p. 154.35° , f. p. -47.0° , $d_4 = 0.96819$). The three-phase system crystallises at -3.0° at ordinary pressures. The critical solution temperature decreases more rapidly than the temperature of crystallisation as the pressure is increased so that the three-phase region soon disappears below the curve of solidification. By extrapolation, this was found to occur

at -8.2° under a pressure of 625 kilos. dt/dp was found to have a fairly constant value of 0.054.

C.—System water-phenol. dt/dp was found to be very small, but increases with the pressure 0.0036 to 0.0055.

D.—System *cyclohexane*-methyl alcohol. dt/dp has a fairly large value, but decreases with increasing pressure 0.0314 to 0.0191.

W. T.

A New Method of using X-Rays in Crystal Analysis.

GEORGE L. CLARK and WILLIAM DUANE (*Proc. Nat. Acad. Sci.*, 1922, 8, 90—96).—Certain alterations in the procedure of X-ray analysis is described. X-Rays belonging to the continuous spectrum are used instead of the line spectrum usually employed. For this purpose, the ordinary X-ray tube with a tungsten target is very convenient. The method has the advantage of flexibility, for short penetrating X-rays may be utilised, and with these it is possible to investigate crystals of high absorbing power. The method is suitable for both powders and large crystals. The values obtained for the distances between the planes of atoms are independent of the constants of any other crystal. The new methods of measurement are applied to the crystal structure of potassium iodide. One of the "peaks" obtained corresponds with the characteristic line spectrum of iodine.

W. E. G.

Isomorphism and Ionic Structure. HANS GEORG GRIMM (*Z. Elektrochem.*, 1922, 28, 75—81).—A theoretical paper in which author discusses the connexion between ionic structure and isomorphism. It is shown that ions built on the argon type differ considerably in size from those built on the neon type, whilst those of the krypton type are only little larger than those of the argon structure, and those built on the xenon type differ from those of the krypton type by intermediate amounts. Thus the expression $r_A - r_{Ne} > r_X - r_{Kr} > r_{Kr} - r_A$ represents the differences of the ionic radii. The characteristic gradation, of the lattice distances of similarly constructed compounds, in which the variable ions have the same number of exterior electrons, is conditioned by the gradation of the atomic radii. This is shown by the fact that the lattice distances of binary compounds is approximately given by the linear equation $r = \alpha a + \beta k$, in which a and k are the radii of the anion and cation respectively and α and β numerical constants. The relationship between isomorphism and ionic structure is shown by means of a table. It is shown that miscibility between ions with the neon and helium structure is unknown, although aluminium hydroxide and boric acid show a slight tendency. In the case of ions of the neon and argon structure, no crystallochemical relationship exists between O'' and S'' , but F', Cl', Na' and K' exhibit miscibility in the case of large molecules and at high temperature, that is, under conditions where the influence of the difference in the radii is overcome. Complete miscibility is found between the ions of the argon and krypton type on account of the small difference between the atomic radii. Ions of the

krypton and xenon configuration also show close crystallo-chemical relationships, but the somewhat greater difference between the radii is expressed in the limited miscibility of potassium bromide and iodide. The ions of the argon and xenon structures form the end members of the well-known isomorphous series, but here also the difference in the ionic radii is shown in the existence of a large gap in the mixture series of potassium chloride and iodide. In general, the isomorphic relationships are determined by the characteristic gradation of the ionic radii in the case of similarly constituted ions.

J. F. S.

Fundamental Principles of Colloidal Chemistry. I. Electrical Charge of the Particles and New Conceptions of Micellæ. RICHARD ZSIGMONDY (*Z. physikal. Chem.*, 1922, **101**, 292—322; cf. this vol., ii, 129).—A theoretical paper in which it is shown that the conception expressed by the term micella has been entirely adopted in the various branches of colloidal chemistry. After considering a number of widely differing colloidal systems it is shown that the term micella has been applied to a series of different structures, which the author proceeds to characterise more exactly. Whilst the micellæ of Nägeli are crystalline individual particles, the term is employed by others for particles of very different constitution. It is pointed out that in most modern colloidal research the electrical charge has become the important factor, whilst the study of the particles themselves has been neglected. It is known that colloidal particles can be either crystalline primary particles (colloidal gold, vanadium pentoxide), secondary particles partly filled with liquid (stannic acid, purple of Cassius), or aggregates of molecules and ions of little stability combined with condensation nuclei (soap solutions). Both the primary particles and the secondary particles, depending on the electric charge can exhibit a considerable stability, and then they behave as multivalent ions of substances of very large molecular weight.

J. F. S.

Energy Principle of the Coagulation of Colloids, particularly of the Thermo-kinetic Mechanism. ROBERT FRICKE (*Z. physikal. Chem.*, 1922, **101**, 185—192).—A theoretical paper in which the heat change of some ideal coagulation processes of hydrosols and gas-dispersoids has been calculated on the basis of the thermo-kinetic shadow theory (A., 1920, ii, 740; 1921, ii, 387). The small heat changes obtained were compared with those calculated from the osmotic work and the work of lattice separation. All values are found to be of small dimensions. A short discussion of the different interdependent heat effects accompanying coagulation is entered on, and it is shown that the electrostatic discharge work must furnish a large portion of the heat of coagulation. The coagulation of discharged colloids in the case of hydrosols is mainly brought about by intermolecular forces (lattice forces) in the sense applied by Zsigmondy, and to a lesser degree by thermokinetic shadow action. In the case of gas-disperse systems the latter cause assumes an importance which may not be neglected in considering the actual precipitation.

J. F. S.

Physico-chemical Investigation of Colloidal Sulphur. G. ROSSI (*Kolloid Z.*, 1922, **30**, 228—230).—In a previous communication (A., 1912, ii, 1037) it was shown that the electrical conductivity of a solution of colloidal sulphur containing sulphuric acid and sodium sulphate is lower than that of a similar solution containing no colloidal sulphur. It is now shown that the freezing point of a solution of the same kind as the above is lower after the colloidal sulphur has been removed than when the colloid is present. Further, if a colloidal sulphur solution containing sulphuric acid and sodium sulphate is dialysed to remove the electrolytes and the same amount of electrolytes added to the dialysed solution, then the electrical conductivity has the same higher value of the solution from which the colloid has been removed. It is thus shown that the action of the colloidal sulphur extends to sulphuric acid and sodium sulphate even when these are present in quantities larger than those required to stabilise the sol, provided that the excess of these substances was present when the colloid was formed. Further quantities of these substances added after the formation of the colloid are not affected by the colloid. It is therefore assumed that crystalloids, in the form of sulphuric acid and sodium sulphate, undergo a change in their physical nature in the presence of colloids, which is shown by a reduction in the electrical conductivity and the osmotic pressure. J. F. S.

Cell for the Observation of Colloidal Solutions for Use with Substage Ultra-Condensers. FRED FAIRBROTHER (*J. Amer. Chem. Soc.*, 1922, **44**, 1071—1072).—A cell is described for use in quantitative work on colloids with substage ultra-condensers. The apparatus eliminates the necessity of readjusting the optical arrangement every time a fresh portion of the colloidal solution has to be examined, as is the case with Burton's method of using a hemacytometer slide ("Physical Properties of Colloidal Solutions," 1921, p. 124). The apparatus consists principally of a circular brass block which has a circular hole in the centre and is bored at two diametrically opposite points to receive two copper tubes 2 mm. diameter. The holes are made so that they pass from the edge of the brass ring to the base. The bottom of the block, which is ground perfectly flat, is carefully cemented to a cover-glass and two holes are bored through the latter to meet the two holes in the base. The arrangement has the advantage of a reinforced cover-glass, and as both surfaces of cover-glass and slide are flat it is not necessary to cement the two together. The apparatus is held in position on the slide while being fixed in position by plasticine. To the copper tubes are fixed a delivery funnel and clip and an exit tube. J. F. S.

Protective Colloids. XII. Gelatin as a Protective Colloid.
I. Colloidal Silver. A. GUTBIER, J. HUBER, and A. ZWEIFLE (*Kolloid Z.*, 1922, **30**, 306—313; cf. A., 1921, ii, 312).—The effect of chloroform, toluene, acetone-chloroform, and ethyl acetate in small quantities on solutions of gelatin has been investigated and it is shown that all four substances act as excellent preservatives

for gelatin solutions. In the case of chloroform (10 c.c. per litre of solution), the solutions are stable, and only after weeks does a small quantity of a white precipitate separate; with toluene, a slight turbidity appears in a 5% gelatin solution after two weeks, but with more dilute solutions no turbidity is observed. The addition of 1% acetone-chloroform increases the stability of gelatin solutions, whilst with 0.5% of ethyl acetate a turbidity appears in two days; this turbidity speedily redissolves and the solution then remains unchanged for forty-two days. The efficiency of gelatin as a protective colloid for colloidal silver has been investigated, and it is shown that colloidal silver obtained by reduction with hydrazine may be protected with a small concentration of gelatin and the stability increased, but an excess of gelatin exerts a disturbing influence on the stability. The most stable and at the same time the most concentrated silver sol is prepared by reducing 10 parts of 0.1*N*-silver nitrate in 30 parts of 0.42% gelatin with hydrazine and immediately dialysing for six hours. This sol is reddish-brown by transmitted light and olive by reflected light; after dialysing for ten days a preparation was obtained which contained 40-45% of silver and was stable for three-quarters of a year. When the colloidal silver was produced by means of sodium hyposulphite, sols were obtained which were much less stable than those reduced by hydrazine. The effect of electrolytes on protected silver sols was investigated and it is shown that chlorides (hydrogen, sodium, magnesium, and barium) effect a rapid precipitation of the colloid; *N*-sulphuric acid produces a precipitation which is not complete in five days, sodium thiosulphate brings about a slow sedimentation, whilst sodium hydroxide and sodium carbonate in *N*-solutions are without coagulating action.

J. F. S.

Dependence of the Base Equilibrium in Permutite on the Concentration of the Surrounding Solution. A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1922, 28, 85-89).—The author has investigated the equilibrium in solutions of two salts of varying concentrations when shaken with permutite containing the same kations as the solution, with the object of ascertaining the concentration of the solution which is in equilibrium with the permutite. The experiments were carried out at 22° with 50% silver and 50% ammonium, 33.33% copper and 66.67% ammonium, and 4% lanthanum and 96% ammonium permutites, and the solutions contained the respective salts as nitrates. The results show that in a certain measure the demands of the law of mass action are fulfilled, but until the ionic concentration can be definitely determined it cannot be proved that the equilibrium is always set up in keeping with this law.

J. F. S.

The System *iso*Butyl Alcohol-Water. A. MICHELS (*Arch. Néerland.*, 1922, [iii], 6, 127-146).—The *isobutyl* alcohol was specially purified, b. p. = 107.47°, d_4^{20} = 0.8197. The higher critical solution temperature was found to be 132.8° and the pressure 332.5 cm. of mercury, the critical concentration being 37% alcohol. Crystal-

lisation of the mixture prevented the realisation of the lower critical temperature. dt/dp for the critical temperature was found to be less than 0.01. The solubility of the alcohol in water was found to have a minimum value at 58° with a composition corresponding with 7% alcohol. The influence of impurities on the temperature of separation into two layers was very marked; 1% of ethyl alcohol lowered it by 50° , other impurities raised the temperature. Measurements were also carried out of the vapour pressure of the system; these are given in tables for $t-x$ and $p-x$; the latter shows a maximum but the composition corresponding with it could not be definitely fixed; it lies in the three-phase region. Further experiments are being carried out.

W. T.

Influence of the Time Factor on the Interpenetration of Solids by Chemical Reaction. H. WEISS and P. HENRY (*Compt. rend.*, 1922, **174**, 1421—1423; cf. this vol., ii, 207).—The time necessary for a given increase in the zone of interpenetration may be divided into two parts, namely, that required for the chemical reaction once the molecules of the two metals, in this case silver and antimony or copper and antimony, are in contact, and the time necessary for the molecules to traverse the layer already formed. The experiments tend to show that the duration of the chemical reaction is negligible as compared with the time required for the molecules to traverse the layer formed. The experimental points at each temperature fall on two distinct curves which are closely connected with the intensity of the blows of the hammer used to establish contact between the two metals.

W. G.

The Rate of Evolution of Carbon Dioxide from Solution in Presence of Colloids. ALEXANDER FINDLAY and OWEN RHYS HOWELL (T., 1921, **121**, 1046—1052).

The Influence of Solvents on the Velocity of Formation of Quaternary Ammonium Salts. JAMES ALEXANDER HAWKINS (T., 1922, **121**, 1170—1176).

The Velocity of Absorption of Carbon Dioxide by Alkaline Solutions. PAUL RIOU (*Compt. rend.*, 1922, **174**, 1463—1466).—Velocity curves have been plotted for the absorption of carbon dioxide by solutions of potassium carbonate under different conditions of concentration and temperature and with or without the presence of potassium hydrogen carbonate or potassium chloride. With potassium carbonate alone the velocity of absorption at first increases with the concentration very rapidly to a maximum and then slowly diminishes. The presence of potassium hydrogen carbonate causes a very marked diminution in the velocity of absorption, but the effect of potassium chloride is less marked. In every case, rise in temperature is accompanied by an increase in the velocity of absorption. Other factors being equal, the velocity of absorption is practically proportional to the concentration of the carbon dioxide in the air mixture.

W. G.

Acceleration of the Solubility of Metals in Acids by Reducible Compounds. H. J. PRINS (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **23**, 1449—1454).—The velocity of solution of a metal in an acid is enhanced by the presence of a reducible substance (cf. A., 1918, ii, 13). Nitrobenzene and benzaldehyde accelerate the rate of solution of iron, zinc, lead, tin, copper, nickel, aluminium, and silver in a large number of acids. In the presence of nitrobenzene, the rate of solution is increased up to 1000 times. The increase in the attack on the metal is accompanied frequently by an increased evolution of hydrogen. Benzaldehyde is selective in its action. Benzophenone retards the rate of solution of the metal and the rate of generation of hydrogen from zinc and an acid. Co-action has been realised in a system of four components—a metal, a salt of hydrochloric acid, a feeble acid (acetic acid), and nitrobenzene. W. E. G.

Landolt's Reaction. ANTON SKRABAL (*Z. Elektrochem.*, 1922, **28**, 224—244).—The Landolt reaction which takes place in solutions of sulphurous acid and excess of iodic acid has been investigated. This reaction takes place according to the equations (1) $\text{IO}_3' + 3\text{SO}_3'' = \text{I}' + 3\text{SO}_4''$, (2) $\text{IO}_3' + 6\text{H}' + 5\text{I}' = 3\text{I}_2 + 3\text{H}_2\text{O}$, (3) $3\text{I}_2 + 3\text{SO}_3'' + 3\text{H}_2\text{O} = 6\text{I}' + 6\text{H}' + 3\text{SO}_4''$. Of the three partial reactions, 1 and 2 take place slowly with respect to 3 and determine the time of the reaction. Because the rapid reaction 3 follows the slow reaction 2 the sum of the equations of these reactions give equation 1 and consequently until the change of colour occurs equation 1 represents the total reaction. If reaction 2 is made more rapid than 1 by adding iodide to the mixture, then the whole of the sulphite will be oxidised according to 2 and 3 and reaction 2 alone will determine the time of the reaction. According to the measurements of Dushman (A., 1921, ii, 315), the expression $-d[\text{IO}_3']/dt = K_2[\text{IO}_3'][\text{I}']^2[\text{H}']^2$ represents this reaction. At the point of change, the whole of the sulphite has been oxidised, and therefore the initial concentration of this substance is a measure of the time required by reaction 2 to occur. If all the variable concentrations are chosen large with respect to the sulphite concentration, then reaction 2 takes place with constant velocity and the time of the reaction must be proportional to $[\text{SO}_3'']/[\text{IO}_3'] \cdot [\text{I}']^2 \cdot [\text{H}']^2$. This simple relationship has been experimentally verified. In this form, the Landolt reaction is particularly suited as a lecture experiment for demonstration of reaction velocity. The time law $-d[\text{IO}_3']/dt = K_1[\text{IO}_3'] \cdot [\text{SO}_3''] \cdot [\text{H}']$ is deduced for both reactions 1 and 2 individually. The constants K_1 and K_2 have been evaluated and tested over a wide range of concentration and shown to be in keeping with Dushman's experimental results (*loc. cit.*). In connexion with the foregoing experimental investigation, chemical kinetics are discussed generally. It is shown that chemical reactions only follow a definite time law over a limited range of concentrations and velocities. They are subject to a change of time law, so the constant K_2 of the iodate-iodide reaction becomes markedly smaller with increasing velocity, as is shown by

the present experiments and those of Dushman. The temperature quotients, $Q_{10}=K_{t+10}/K_t$, holds only for a definite total reaction. In the case of the total reactions, $\text{IO}_3'+6\text{H}'+8\text{I}'=3\text{I}_3'+3\text{H}_2\text{O}$ and $\text{IO}_3'+6\text{HSO}_4+8\text{I}'=3\text{I}_3'+6\text{SO}_4''+3\text{H}_2\text{O}$, the value Q_{10} is 1.3 for the first and 0.85 for the second. These two temperature quotients are connected through the time law of the total reaction with the heat change of reaction $\text{H}'+\text{SO}_4''=\text{HSO}_4'$. Both total reactions have their own heat changes, and the relationship between this and Q_{10} rules the adiabatic course of the reaction. J. F. S.

Kinetics of Reactions in which Halogen Atoms pass from the Inner Sphere of Activity to the Outer. H. FREUNDLICH and R. BARTELS (*Z. physikal. Chem.*, 1922, **101**, 177—184).—The velocity of reaction of the following reactions has been determined quantitatively in some cases and semi-quantitatively in others at 0° and 25° . (1) $[\text{Cr}(\text{NH}_3)_5\text{Br}]^{++}+\text{H}_2\text{O}=[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{+++}+\text{Br}'$; (2) $[\text{Cr}(\text{NH}_3)_5\text{I}]^{++}+\text{H}_2\text{O}=[\text{Cr}(\text{NH}_3)_5\text{H}_2\text{O}]^{+++}+\text{I}'$;

(3) $\text{CH}_2\text{Br}\cdot[\text{CH}_2]_3\cdot\text{CH}_2\cdot\text{NH}_2=\text{CH}_2<\frac{\text{CH}_2\cdot\text{CH}_2}{\text{CH}_2\cdot\text{CH}_2}>\text{NH}_2\cdot+\text{Br}'$; and

(4) $\text{CH}_2\text{I}\cdot[\text{CH}_2]_3\cdot\text{CH}_2\cdot\text{NH}_2=\text{CH}_2<\frac{\text{CH}_2\cdot\text{CH}_2}{\text{CH}_2\cdot\text{CH}_2}>\text{NH}_2\cdot+\text{I}'$. The velocity has been compared with the reactions previously studied (A., 1914, ii, 448). The whole of the reactions are shown to conform with an equation of the first order. The velocity constants are dependent on the nature of the halogen and also on the nuclear atom; they increase very strongly, up to 100 times, in the order $\text{Cl}<\text{Br}<\text{I}$, and in the chlorine series they increase 50 times in the order $\text{Co}<\text{Cr}<\text{C}$. As far as the temperature coefficients were determined, they were found to be large; the constant A of the Arrhenius equation was about 10,000. This corresponds with the rule propounded by Halban, that apparent as well as true unimolecular reactions are characterised by their marked dependence on temperature. J. F. S.

Course of Simultaneous Reactions. RUDOLF WEGSCHEIDER (*Z. Elektrochem.*, 1922, **28**, 99—100).—In connexion with the statement of Martin and Fuchs (*ibid.*, 1921, **27**, 155) that in the chlorination of methane the concentration of methane and its chlorinated product are dependent on the concentration of one of these substances and quite independent of the time and the chlorine concentration, it is shown that this is not a special case, but is generally true for simultaneous reactions, which with regard to one of the reacting substances, H , are of the same order (n^{th}). If the reaction equation for two such actions are: $A_1+nH\rightleftharpoons B_1$ and $A_2+nH\rightleftharpoons B_2$ where A and B are complex molecules which do not contain H , the equilibrium constants are $K_1=[B_1]/[A_1][H]^n=k_1/k'_1$ and $K_2=[B_2]/[A_2][H]^n=k_2/k'_2$. On subtracting the second equation from the first, the equation $A_1+B_2\rightleftharpoons A_2+B_1$ is obtained which must represent a possible equation of reaction. If the equilibrium constant of this is K , then $K=K_1/K_2=k_1\cdot k'_2/k_2\cdot k'_1=n_{12}/n_{12}'$, where n_{12} is the relationship between the equilibrium constants of the two reactions in the direction left to right and

n_{12}' in the opposite direction. This shows that the concentrations of all molecular types of A and B at equilibrium are determined by equations which do not contain the absolute values of the velocities.

J. F. S.

Mode of Action of Platinum in Oxygen-Hydrogen Catalysis and the Application of Titanium Sulphuric Acid for the Control of the Course of the Change. K. A. HOFMANN (*Ber.*, 1922, 55, [B], 1265—1274; cf. A., 1920, ii, 240; this vol., ii, 276).—Sensible quantities of hydrogen peroxide are only produced in the surrounding acid during the catalysis of dissolved molecular oxygen and activated hydrogen at platinum surfaces when the reducing power of the hydrogen-platinum electrode is abnormally reduced, when the liquid surrounding the pole contains large amounts of dissolved oxygen, and when the pole is as free as possible from oxides of platinum. It is highly probable that the hydrogen-oxygen catalysis proceeds normally in two stages (1) $O_2 + 2H = H_2O_2$ and (2) $H_2O_2 + 2H = 2H_2O$. The velocity of the second action at an active platinum surface is, however, so great that hydrogen peroxide does not escape into the surrounding liquid. A specific reducing action towards a third substance of hydrogen peroxide which is liberated at the best only in minute traces is not to be expected in any circumstances. Further, the reduction potential of hydrogen peroxide is much less than the potential of hydrogen activated at a platinum surface.

In preparative or other work in which reductions are to be effected with activated hydrogen, the author recommends the use of the acid titanium sulphate solution for indicating the conditions favourable to maximum reduction or for controlling the course of the change, since the activity of the system is readily shown by the formation of the characteristic violet-brown solutions of tervalent titanium sulphate. In addition, it is to be expected that the reduced titanium will both accelerate and regulate the reducing action since reduced titanium solutions have been successfully utilised on many previous occasions as reducing agents. H. W.

A Graphical Study of the Stability Relations of Atom Nuclei. WILLIAM D. HARKINS and S. L. MADORSKY (*Physical Rev.*, 1922, 19, 135—156; cf. A., 1921, ii, 445, 582, 690).—The following properties are considered graphically: P , the number of positive electrons in the nucleus, which is taken to be numerically equal to the atomic weight; M , the net positive charge, which is equal to the atomic number; N , the number of negative electrons, which is equal to $(P - M)$; $[(N/P) - 0.5]$, the excess of the relative negativeness N/P over the minimum 0.5; n , the isotopic number, which is equal to $(P - 2M)$ and also to $(N - M)$. Except in the case of hydrogen and of the helium isotope $P = 3$, N/P is never less than 0.5, and M/P is never greater than 0.5. For 85% of the atoms composing the earth's crust, both these ratios are 0.5 and $n = 0$. As the atomic number increases, the relative negativeness necessary to stability increases above 0.5; that is, as α -particles are added, extra cementing electrons are required to overcome

the increasing mutual repulsion of the positive units of the nucleus. An α -ray transformation does not change n , but increases N/P , whilst a β -ray change decreases n by two units and also decreases N/P ; thus in each group of isotopes, those with larger values of N/P exhibit greater β -ray and less α -ray instability. Stability considerations require that the number of isotopes is on the whole smaller for the lighter atoms. Further, the number of isotopes is larger for even than for odd numbered elements, especially where M is greater than 29. For most atoms, M , n , and P are either all even or all odd, but N is usually even. The curve for the frequency of occurrence of atoms as a function of n shows periodic maxima four units apart, whilst as a function of M or N the periodic maxima are two units apart. It thus becomes possible to predict the existence of the more abundant isotopes of elements of which the mean atomic weights are accurately known.

A. A. E.

Spectra of X-Rays and the Theory of Atomic Structure.

D. COSTER (*Phil. Mag.*, 1922, [vi], **43**, 1070—1107).—The X-ray spectra of the heavier elements are arranged in a scheme which involves the existence of one K -level, three L -levels, five M -levels, and seven N -levels in the electronic structure of the atom. These levels are associated with the presence of various sub-groups or shells of electrons in the atom. The rules governing the transference of electrons between the various levels are discussed, and further experimental work is adduced in support of these conclusions. New measurements are made of the L -series of X-ray spectra of the elements from rubidium to barium. Fourteen lines are recorded and the wave-lengths offer strong arguments in support of Bohr's theory (this vol., ii, 363). Diagrams, based on these lines, are given of the various transitions which have been found to occur between any two levels. Niton, xenon, and krypton are chosen as typical elements. The lines which disappear with decreasing atomic number fall out at the places in the periodic table predicted by Bohr. Certain faint lines in the L -series which are connected with the M -levels cannot be classified. These and other single lines suggest the existence of new levels associated with only one line. They are attributed, in part, to a more complicated excitation of the atom, due to the removal of two electrons at the same time.

W. E. G.

Structure of Atoms and Molecules in the Light of the Dispersion Theory. JARL A. WASASTJERNA (*Z. physikal. Chem.*, 1922, **101**, 193—217).—A theoretical paper in which it is shown that the atomic volume is the volume of a sphere constructed round the middle point of the nucleus of an atom and on the surface of which the outside electron system is situated. At a collision of two atoms the minimum distance between the nuclei is equal to the sum of the radii of the orbits of the outside electrons of both atoms. An electrolyte molecule can exist in two modifications, of which the one consists of uncharged and the other of charged atoms or atomic groups. When a molecule is present in

the latter form, it may split into ions if it is present in a medium of sufficiently high dielectric constant. An equilibrium exists between the two modifications, which lies strongly on the one side for weak electrolytes and strongly on the other side for strong electrolytes. Amphoteric electrolytes may exist in three modifications. Typical strong electrolytes consist almost entirely of polarised molecules. The above makes possible the calculation of the true ionic refractions, and thereby the Kossel hypothesis of the structure of the atom can be confirmed in some of its important points. From the results of the above-named calculations it follows that the outside sheath of the atoms of the alkali metals contains only a single electron, which in salt formation passes over to the acid radicle. In the case of the alkaline-earth metals, the outside sheath has two electrons, which in the same way pass over to the acid radicle. The next sheath of electrons of both the alkali and alkaline-earth atoms is identical with the outside system of the elements in the preceding horizontal row, which in consequence of the increased attractive force was nearer the centre of the nucleus. The structure of the ions undergoes no great change during the formation of polarised molecules, and the electron orbit of the ions can in most respects be regarded as unchanged. The above can be extended, in all probability, to non-polarised molecules and electro-neutral atoms, except in cases where double and treble linkings or rings in the sense adopted by Baeyer are present.

J. F. S.

Separation of Isotopes by Thermal and Pressure Diffusion.

ROBERT S. MULLIKEN (*J. Amer. Chem. Soc.*, 1922, **44**, 1033—1051).—The theory of the separation of isotopes by thermal diffusion and by centrifuging is discussed. Equations are developed giving the difference in atomic weight obtainable in any operation, similar to the equations for diffusion and evaporation processes obtained in a previous paper (this vol., ii, 295). For thermal diffusion, the difference in atomic weight between portions of an isotopic gas at temperatures T_1 and T_2 respectively is $\Delta_r M = K \times B \log_e T_1/T_2$ approximately, the atomic weight being greater at the colder end; B is the ordinary separation coefficient, previously defined, and K is an approximate constant for each element, having a value which is probably about 0.25 and depending on the behaviour of the molecule during impacts. The term KB may be named the thermal separation coefficient. The method of thermal diffusion is shown to be much less effective as a means of separating isotopes than ordinary diffusion or evaporation. A somewhat more advantageous modification of the method is described under the name evaporative thermal diffusion. For the centrifuging of a gas, the difference in atomic weight between the central and peripheral regions is $\Delta_r M = P(v^2 - v_0^2)$, where P , the centrifugal separation coefficient, is a characteristic constant for each element and v and v_0 are the velocities at the peripheral and central regions of the material under treatment. The values of P for several elements have been calculated and the following are recorded for 20°:

lithium, 1.16×10^{-12} ; boron, 1.85×10^{-12} ; neon, 7.38×10^{-12} ; magnesium, 8.97×10^{-12} ; chlorine, 14.5×10^{-12} ; nickel, 18.4×10^{-12} ; zinc, 53×10^{-12} ; bromine, 20.4×10^{-12} , and mercury, 47×10^{-12} . For ordinary air, the coefficient would be 62×10^{-12} . The value of P is unaffected by the state of combination of the element, even if the compound contains other isotopic elements. Thus the separation is equally great for all compounds of a given element. This is in contrast to the situation with all the other diffusion methods, for which the degree of separation of a given element in one operation is inversely proportional to the molecular weight of the compound. Further, the value of P for any element is independent of the atomic weight, whilst the ordinary separation coefficient B is inversely proportional to the latter. Hence, the theory is on this basis relatively increasingly more favourable to the centrifugal method as the atomic weight increases. $P = (M_2 - M_1)^2 x_1 x_2 / 2RT$ for a mixture of two isotopes and for a mixture of several isotopes it has the value $\sum_a \sum_b x_a x_b (M_a - M_b)^2 / 2RT$. P , unlike B , is inversely proportional to T , but depends on the atomic or molecular weight intervals $(M_a - M_b)$ and the molecular fractions, x , in the same way as B . Although for the heavy elements the theory predicts, for a peripheral velocity of 10^5 cm./sec., a separation many times that obtainable in a single diffusion or evaporation, it is shown that compression and condensation of the gas or vapour into the peripheral region make such large separations impracticable if carried out in the ordinary way. The pressure ratio between the two regions is given by $\log_e p/p_0 = M\Delta_r M / 2RT$. P , and so increases with atomic and molecular weight. A special method, named evaporative centrifuging, is proposed whereby gas condensed in the periphery of the centrifuge at high speed would be allowed to evaporate very slowly, the light fraction being drawn off very gradually at lower pressure from the centre of the apparatus. The process would be in effect precisely analogous to an evaporation in which the separation coefficient was increased from B to Pv^2 . This method, applicable at the ordinary temperature to hydrogen chloride, bromide, selenide, telluride, and silicide, might be expected, with peripheral velocities up to 10^5 , to yield a separation ten or fifteen times as great in a single operation as would ordinary diffusion or evaporation. The method may be the most rapid method of separating the isotopes of some of the elements of medium atomic weight, but for the lighter or heavier elements the method is less promising. The theory of the separation of isotopes by centrifuging liquids is discussed, and it is shown that the degree of separation for a given apparatus is identical for liquids, gases, and intermediate states of matter. An attempt has been made to test the theory in the case of mercury, but negative results were obtained which are attributable to a slight vibration of the centrifuge. This effect is likely to prove a limiting factor in any attempt to use the method of liquid centrifuging. A statement made in a previous paper in connexion with the diffusion of an isotopic gas through a thin layer of another gas enclosed in the pores of a membrane (*loc. cit.*) is corrected. This method

is now found to be always less favourable than molecular diffusion, instead of more favourable as previously stated. This is due to the effect of the increased mean free path of the heavier molecules which results from persistence of velocity. This factor was expressly neglected previously. Further, it is shown that mass motion, either positive or negative, should have practically no effect on the rate of separation, except indirectly as it may affect back pressure.

J. F. S.

The Hydrogen Molecule. III. ALBERT C. CREHORE (*Phil. Mag.*, 1922, [vi], **43**, 1025—1038; cf. A., 1921, ii, 632; this vol., ii, 438).—A theoretical investigation into the stability of the author's model of the hydrogen molecule. On this view, the forces between the electrons and nuclei cause slight deformations of the shape of the electrons. Two of the electrons in the molecule are flattened and two are expanded in the direction of the minor axis, and these processes may be accompanied by energy changes which may be either positive or negative in sign. These energy changes, which are slight compared with the total energy of the electron, correspond with the heat of dissociation or heat of reaction. The change in mass which occurs on dissociation is so small that it must escape experimental detection.

W. E. G.

The Abnormally Long Free Paths of Electrons in Argon. J. S. TOWNSEND and V. A. BAILEY (*Phil. Mag.*, 1922, [vi], **43**, 1127—1128).—A continuation of an investigation into the mean free path of the electron in various gases (cf. this vol., ii, 277). From experiments on mixtures of hydrogen and argon, it is deduced that the mean free path in argon at 1 mm. pressure is about 15 mm., or fifty times the mean free path calculated from the atomic radius of argon.

W. E. G.

Some Linear Relationships in the Periodic System. WILHELM BILTZ (*Z. Elektrochem.*, 1922, **28**, 65—70).—A theoretical paper in which a number of linear relationships between the properties of the elements are described. The relationships described are in every case between the inactive gases and the other elements. In the case of atomic volume, it is shown that this quantity for a halogen is proportional to the value for the inactive gas which precedes it in the periodic system. The expression: $\text{at. vol. (halogen)} = a \times \text{at. vol. (inactive gas)} + b$, where a and b are constants and have in this case the values 0.8015 and zero respectively. Taking the atomic volumes of the inactive gases as known, the corresponding values for the halogen are given with an error of $\pm 0.2\%$. Similar straight line relationships are found for the atomic volumes of potassium, rubidium, and caesium; titanium, zirconium, and cerium; and silicon, germanium, and tin; but for no other cases. In the same way, the boiling points of the halogens are connected with those of the inactive gases by the equation $\text{b. p. (halogen)} = 2.753 \times \text{b. p. (inactive gas)} - 1.8$. Here the accuracy is the same as before. If hydrogen is included with the halogens, the relationship $\text{b. p. (halogen)} = 2.705 \times \text{b. p. (inactive gas)} + 8.5$ is

accurate to $\pm 2.5\%$. In the case of the critical temperature, the expression $T_c(\text{halogen}) = 2.648 T_c(\text{inactive gas}) + 18.1$ is true absolutely both for the halogens or hydrogen. The atomic refraction of the halogens and hydrogen are connected with the similar value of the inactive gases by the expression $R_D(\text{halogen}) = R_D(\text{inactive gas}) + 0.41$. In this case, the divergence between the calculated and experimental values nowhere exceeds the experimental error. For the elements of the sulphur group $R_D(\text{element}) = 1.713 R_D(\text{inactive gas}) + 1.15$ is true to $\pm 1.8\%$, whilst for hydrogen and the alkali metals $R_D(\text{alkali metal}) = 1.13 R_D(\text{inactive gas}) + 0.51$ with an error of $\pm 1.5\%$. The atomic radii of the halogens, elements of the sulphur group, and the alkali metals are connected to within $\pm 1.0\%$ with the corresponding values for the inactive gases by the expressions $r(\text{halogen}) = 0.78 r(\text{inactive gas}) + 0.26$, $r(\text{S element}) = 0.645$, $r(\text{inactive gas}) + 0.53$, and $r(\text{alkali metal}) = 1.18 r(\text{inactive gas}) - 0.23$. From a consideration of the foregoing, the author deduces periodic constants.

J. F. S.

The Determination of the State of Valency of Lower Compounds by means of Ammoniacal Silver Solutions. OSCAR OLSSON COLLENBERG (*Z. anorg. Chem.*, 1922, **121**, 281—297).—The author has investigated this method of determining valency (introduced by Philipp and Schwehel, *Ber.*, 1897, **12**, 2234) with respect to suitable conditions of experiment and accuracy of results. If the reaction takes place on the water-bath, the best results are obtained with concentrated ammonia and not too great an excess of silver nitrate in a comparatively small volume. The results obtained are low, but suitable for valency determinations, wholly unsuitable, however, for accurate work, such as determination of purity. If the reaction has to be carried out at a high temperature and under pressure, then a large excess of silver salt in concentrated ammonia is necessary; the temperature should be kept as low as possible and not maintained longer than necessary. The best results were obtained by using silver chloride or sulphate, in the presence of cyanides; silver nitrate should not be used. Ammonia generally contains reducing impurities (organic bases) and a blank experiment should be carried out.

W. T.

Observations on the Construction and Use of the Steele-Grant Microbalance. E. J. HARTUNG (*Phil. Mag.*, 1922, [vi], **43**, 1056—1064).—A description of the Steele-Grant microbalance used in the study of the action of light on the silver haloids (T., 1922, **121**, 682). A balance with a double knife-edge and giving a sensitivity of 1 in 10^6 was sufficiently accurate for the proposed work. For this type the simple double triangle type of beam is recommended; a single knife-edge balance constructed in this manner gave a sensitivity of 1 in 10^7 . Details are given of the grinding of the knife-edges and the drawing of the suspension fibres. Damage to the fibre suspension is avoided by the attachment of a double hook to the end of the quartz weights; this facilitates the removal of the objects from the balance. The author discusses the various sources of error in manipulation,

affecting the sensitivity of the balance, and producing apparent changes in weight.

W. E. G.

Extraction of Small Quantities of Liquids by the Soxhlet Apparatus. HEINRICH HANDORF [*Z. angew. Chem.*, 1922, **35**, 257—258 (D.R.-P., 807757 and 809512)].—A glass vessel is inserted in the Soxhlet apparatus. In cases where the liquid is to be extracted by a solvent lighter than itself, this vessel has above it a funnel, the stem of which extends to the bottom of the vessel and ends in a rose. The liquid to be extracted is placed in the vessel and is covered by a layer of the solvent. Condensed solvent drops into the funnel, emerges in drops from the rose, and rises through the liquid. In the case of a liquid being extracted by a solvent heavier than itself, a short funnel ending in a capillary rests on the top of the vessel, and a tube opening near the bottom of the vessel passes through its wall at a suitable height. The condensed solvent falls through the liquid and passes through the tube to the outside of the vessel. The apparatus is suited for the extraction of colloidal liquids. Quantitative extraction is attained.

H. M.

Rhythmic Deposition of Precipitated Vapours. ENOCH KARRER (*J. Amer. Chem. Soc.*, 1922, **44**, 951—954).—When two narrow cylinders containing respectively small quantities of aqueous solutions of ammonia and hydrochloric acid are placed under a large glass container and so placed that there is a lateral temperature gradient in the container, a series of rings of ammonium chloride forms on the inside of the cylinder which contains the hydrochloric acid. The number of rings varies with the conditions from 1 per cm. to a very large number. These rings mark the edges of disks, so that the vapour space above the hydrochloric acid may be regarded as divided into a number of compartments by disks of ammonium chloride. Within the cylinder each compartment marks the boundaries of a system of vertical and horizontal convection currents, the necessary elements for the formation of which are a lateral temperature gradient and a vertical density gradient.

J. F. S.

Inorganic Chemistry.

Some Properties of Hydrogen Desorbed from Platinum and Palladium. PAUL ANDERSON (T., 1922, **121**, 1153—1161).

The Radius of Hydrogen Atoms in Crystals. G. AMINOFF (*Geol. Förr. Förh.*, 1921, **43**, 389—396).—It is calculated that the radius of the hydrogen atom in magnesium hydroxide and manganese hydroxide, the elementary parallelepipeds of which are hexagonal, is, respectively, 1.15 and 1.01 Å.U., whilst in ice the radius is 1.12 Å.U. It is shown that the structure $R^H(OH)_2$ may be regarded as ice, H_2OOH_2 , of which one H_2 group has been

replaced by a bivalent metal ion, R^{II} . This explains why the group $\begin{smallmatrix} HO \\ OH \end{smallmatrix}$ of ice has practically the same dimensions in these hydroxides. The relatively high value calculated for the radius of the hydrogen atom is considered to be in keeping with the relation of hydrogen to the alkali metals. CHEMICAL ABSTRACTS.

An Attempt to Separate the Isotopes of Chlorine. E. B. LUDLAM (*Proc. Camb. Phil. Soc.*, 1922, **21**, 45—51).—(Sir) J. J. Thomson has suggested (*Proc. Roy. Soc.*, 1921, [A], **99**, 87) a method of separation of isotopes based on the number of impacts per second of the molecules of a gas on a liquid surface. The number of impacts will be in inverse ratio to the square root of the mass. If on striking the surface the molecules are removed by solution or chemical action, the composition of the residual gas should steadily alter. Hydrochloric acid at a pressure of a few centimetres of mercury was passed over (a) a water surface, and (b) ammonia gas, and a small fraction allowed to remain uncombined. No change in the molecular weight was observed after either process. The failure to obtain a separation indicates that the determining factor in the recombination of ammonia with hydrochloric acid is not mere collision. W. E. G.

Fractional Diffusion of Iodine Vapour. EMIL KOHLWEILER (*Z. physikal. Chem.*, 1922, **101**, 218—234).—Iodine has been subjected to a careful fractional diffusion, and the combining weight of the original material as well as that of the various fractions has been determined by conversion of the iodine into iodide and precipitation as silver iodide. Seventeen determinations with ordinary pure iodine gave a mean value of 126.93, the extreme values being $126.92 + 0.073\%$ and $126.92 - 0.079\%$. Seven determinations with the first fraction of the diffusion gave the value 126.07, which differs by 0.67% from the accepted value for iodine, whilst fourteen determinations with the end fraction gave 127.18, with a divergence of 0.21% from the usual value. These results indicate that, in addition to the isotope of combining weight 127 indicated by Aston, there are at least two others, one lighter and the other heavier than Aston's isotope. It is shown that Aston's results and the present results are not necessarily opposed to one another, for the sensitiveness of Aston's measurement is of the order 5%, whilst that of the present work is much sharper. J. F. S.

Revision of the Density of Oxygen Gas. E. MOLES and F. GONZÁLEZ (*Anal. Fis. Quím.*, 1922, **20**, 72—80; cf. A., 1921, ii, 546).—Measurements were made on oxygen prepared in different ways as described in the former paper. The arithmetical mean of forty-five determinations gave the value 1.4892 ± 0.00007 as the weight of a litre of oxygen at 0° and 760 mm. This value is identical with the mean of two hundred and thirteen previous determinations by other workers. The corresponding value calculated for latitude 45° is 1.42897. G. W. R.

Researches on Sulphuryl Chloride. II. A New Chlorinating Agent : Preparation of Polychloro-derivatives of Benzene. OSWALD SILBERRAD (T., 1922, **121**, 1015—1022).

The "Dynamic" Allotropy of Tellurium. A. DAMIENS (*Compt. rend.*, 1922, **174**, 1344—1346).—Density determinations made on tellurium carefully purified by distillation in hydrogen and then in a vacuum, the material being subsequently crystallised either by vaporisation or by slow cooling of the molten material, do not confirm the views of Cohen and Kröner (A., 1913, ii, 315) as to the dynamic allotropy of tellurium. Tellurium obtained by vaporisation has d 6.310, and is not changed by long heating at various temperatures. Specimens prepared in other ways show a slightly lower density, as, owing to the manner of preparation, they are slightly porous. Amorphous tellurium has d 5.85—5.87; on heating, it is transformed into crystalline tellurium with development of heat and its density rises. W. G.

The Reactivity of Ammonia. EDWARD CHARLES CYRIL BALLY and HERBERT MAXWELL DUNCAN (T., 1922, **121**, 1008—1014).

Polymorphism of Arsenic. PORPHYRY NICOLAEVITCH LASCHTSCHENKO (T., 1922, **121**, 972—978).

Flocculation of Colloidal Arsenic Sulphide. Influence of the Concentration of the Colloid, Shaking, and Temperature. A. BOUTARIC and M. VUILLAUME (*Compt. rend.*, 1922, **174**, 1351—1353).—The influence of different factors varies with the nature of the electrolyte used to cause flocculation. With chlorides of potassium, barium, magnesium, or manganese, the velocity of flocculation increases with the concentration of the colloid, but with aluminium or cadmium chlorides the velocity diminishes as the concentration increases. In comparing once shaking to mix the colloidal solution and the electrolyte, and continuous stirring, the opacity curves for the two conditions superpose one another. With potassium chloride, flocculation of the continuously stirred solution only occurs after the opacity limit has been reached, but with barium or aluminium chlorides flocculation occurs before the opacity limit is reached. The velocity of flocculation varies inversely as the temperature where potassium, sodium, ammonium, or lithium chloride is the electrolyte, directly as the temperature with barium, calcium, strontium, magnesium, or cadmium chloride, and is independent of the temperature with aluminium chloride. W. G.

The Isotope Ratio of New Zealand Boron. ALEXANDER DONALD MONRO (T., 1922, **121**, 986—988).

The Potassium Salt of Hexahydrodioxidyboron. RAMES CHANDRA RAY (T., 1922, **121**, 1088—1094).

The System Potassium Sulphate-Aluminium Sulphate-Water at 25°. HUBERT THOMAS STANLEY BRITTON (T., 1922, **121**, 982—986).

Use of Röntgen Rays in Determining the Structure of the Crystals of Lithium and of some of its Compounds with Light Elements. I. J. M. BLIJVOET and A. KARSSSEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **23**, 1365—1370).—The lithium atoms in lithium metal are arranged in a centred cubic lattice with a lattice parameter $a=3.50 \times 10^{-8}$ cm. The relative intensities of the lines are explained by either (i) a simple centred cubic lattice or (ii) a centred cubic lattice with electrons revolving in circles normal to the trigonal axes. There is no evidence for the presence of a lattice of stationary valence electrons. The atomic diameter is 3.04×10^{-8} , in agreement with the value given by Bragg (3.00×10^{-8}).
W. E. G.

Crystal Structures of Alkali Haloids. EUGEN POSNJAK and RALPH W. G. WYCKOFF (*J. Washington Acad. Sci.*, 1922, **12**, 248—251).—Further X-ray determinations (this vol., ii, 214) are given for lithium chloride, bromide, and iodide, and for sodium, potassium, rubidium, and caesium fluorides. The X-ray constants for the whole series of twenty salts RX are tabulated. The structures of caesium chloride, bromide, and iodide are of the body-centred type, whilst all the others are of the rock-salt type of the simple cubic lattice.
L. J. S.

The Preparation of Ammonium Nitrate. (Mlle) WURMSER (*Compt. rend.*, 1922, **174**, 1466—1468).—Le Chatelier has previously given a square diagram showing the states of equilibrium between the solution of the four salts ammonium chloride, sodium nitrate, sodium chloride, and ammonium nitrate and the solid salts at 16° . A similar diagram showing the states of equilibrium at 100° is now given. The curves at 16° and 100° are essentially of the same shape, and from them it is possible to determine the best experimental conditions for obtaining the maximum yield of ammonium nitrate from a solution of the four salts.
W. G.

The Properties of Ammonium Nitrate. II. Ammonium Nitrate and Water. IDA L. MILLICAN, ALFRED FRANCIS JOSEPH, and THOMAS MARTIN LOWRY (T., 1922, **121**, 959—963).

The Properties of Ammonium Nitrate. III. Ammonium Nitrate and Sodium Nitrate. REGINALD GEORGE EARLY and THOMAS MARTIN LOWRY (T., 1922, **121**, 963—969).

The Transformation of Ammonium Carbamate. C. MATIGNON and M. FRÉJAQUES (*Bull. Soc. chim.*, 1922, [iv], **31**, 394—412).—A résumé of work already published (A., 1920, ii, 250; 1921, ii, 33; this vol., ii, 272).
W. G.

Crystal Structure of Ammonium Fluosilicate. RICHARD M. BOZORTH (*J. Amer. Chem. Soc.*, 1922, **44**, 1066—1070).—The crystal structure of ammonium fluosilicate has been shown to be like that of ammonium chloroplatinate, ammonium chlorostannate, and potassium chlorostannate, namely, the structure is that of fluor spar in which each fluorine atom is replaced by an ammonium

group, and each calcium atom by a fluosilicate group with the six fluorine atoms equidistant from the silicon atom in the directions of the axes of the crystals (cf. this vol., i, 441). The length of the cube constituting the unit of structure containing four molecules was found to be 8.38 Å.U.; the corresponding lengths for the three complex salts mentioned above being respectively 9.84, 10.05, and 9.96 Å.U. The shortest distance between the centres of the atoms of fluorine and silicon is 1.72 Å.U., whilst the sum of the Bragg radii for these atoms is 1.84 Å.U. The corresponding distances between the platinum or tin and the chlorine atoms in the other three salts are 2.3, 2.46, and 2.44 Å.U., respectively.

J. F. S.

The Preparation of a Silver Amalgam of the Composition Hg_3Ag_2 by Precipitation from a Solution of Silver Nitrate in Pyridine. ROBERT MÜLLER and REINHOLD HÖNIG (*Z. anorg. Chem.*, 1922, **121**, 344—346).—Metallic needles were formed by keeping a drop of mercury in contact with a solution of silver nitrate and cuprous iodide in anhydrous pyridine. With silver nitrate solution alone, crystals of mercurous nitrate were deposited and a liquid amalgam was formed. The *E.M.F.* of the cell $\text{Ag}|0.1\text{NAgNO}_3$ in pyridine| Hg is 0.038 volt, the silver being negative. For the formation of the metallic crystals, the addition of an approximately equal amount of cuprous iodide is necessary (1 : 1); the addition of a much smaller amount (1 : 10) causes the precipitation of finely divided black silver, too large amounts (5 : 1) change the drop of mercury into a granular powder. The concentration of the silver ion in pyridine is not increased by the addition of cuprous iodide, the concentration cell $\text{Ag}|0.1\text{NAgNO}_3$ in pyr. sat. with $\text{Cu}_2\text{I}_2|0.1\text{NAgNO}_3|\text{Ag}$ having an *E.M.F.* of 0.37 volt, the silver in the mixed solution being negative. The formation of a blue precipitate of cupric iodide indicates that the silver salt is reduced to metallic silver, whilst the cuprous salt is oxidised to the cupric salt. The cuprous-cupric potential is +0.18 volt, being greater than that of mercury. Cuprous iodide can be replaced by cerous chloride, the separation of crystals being, however, much slower. Ferrous bromide gave a negative result; in water, the ferrous ferric potential is +0.75 volt, but in pyridine it is evidently less than the mercury potential. The amalgam which crystallises in needles corresponds in composition with the formula Hg_3Ag_2 . The potential of the cell $\text{Hg}_3\text{Ag}_2|\text{AgNO}_3.\text{Cu}_2\text{I}_2|\text{Ag}$ equals 0.37—0.38 volt, the silver being negative against the amalgam.

W. T.

Attempts at a Synthetic Manufacture of Mother-of-Pearl by Production of Chemical Tracery. CLÉMENT and RIVIÈRE (*Compt. rend.*, 1922, **174**, 1353—1356).—By precipitating calcium carbonate in the presence of colloidal protein material, such as gelatin in thin layers, a deposit has been obtained having a nacreous structure. The deposit becomes opaque on prolonged drying at 50°, just as mother-of-pearl or pearl itself “dies” when dried for a long period. These experiments support the accepted views as

to the physical and chemical composition of mother-of-pearl and fine pearl.
W. G.

Action of Various Analytical Reagents on Chemical Glassware. W. E. S. TURNER and T. E. WILSON (*J. Soc. Glass Technology*, 1922, **6**, 17—20).—The tests were made on three types (two English, one French) of chemical glassware; in most cases the solution was kept in contact with the glass for three hours at 100°. Nitric acid (*d* 1.2), and 2*N*-ammonium sulphide solution had but little action on the glasses, but the latter were attacked to an appreciable extent by $N/2$ - and $N/4$ -sodium phosphate solutions. The French glass was attacked to a greater extent than were the English glasses by the sodium phosphate solutions, whilst there was but little difference between the three types as regards their resistance to alkali hydroxide solutions, showing that the corrosive action of the alkali salt solutions was not due entirely to their alkalinity.
W. P. S.

Solubility of Crystallised Strontium Hydroxide. D. SIDERSKY (*Bull. Assoc. Chim. Sucr.*, 1921, **39**, 167—177).—Tables and graphs are given showing the solubility of crystallised strontium hydroxide in water at temperatures varying from 0° to 101.2° (*b. p.* of the solution); at 0°, 100 grams of the solution contain 0.90 gram of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$; at 15°, 1.46 grams, and at 101.2°, 49.75 grams. Other tables give the solubility of the hydroxide in sucrose solutions at different concentrations and temperatures. At 15°, 100 grams of 10% sucrose solution dissolve 3.79 grams of $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, whilst 100 grams of a 25% solution dissolve 7.31 grams of the hydroxide.
W. P. S.

The Reaction of Magnesium Salts with Acid Potassium Pyrantimonate. MILIVOJ OBAJIDIN (*Rad. Acad. Sci. Zagreb*, 1922, **226**, 220—233).—The preparation of *magnesium dihydrogen orthantimonate* by addition of a magnesium salt to a solution of dipotassium dihydrogen pyrantimonate is described; according to the concentration, it is obtained either as hexagonal or monoclinic crystals or in the amorphous form. From a solution containing 1% of the pyrantimonate, both hexagonal and monoclinic crystals and a large quantity of the amorphous precipitate are deposited. From a solution containing 0.35% of the pyrantimonate, monoclinic crystals are alone deposited, whilst a solution containing 0.07% of the potassium pyrantimonate yields hexagonal crystals only. The composition of both hexagonal and monoclinic crystals corresponds with the formula $\text{Mg}(\text{H}_2\text{SbO}_4)_2 \cdot 10\text{H}_2\text{O}$. The crystals lose $10[\text{?}8]\text{H}_2\text{O}$ if heated at 176°. When heated further, they lose $2\text{H}_2\text{O}$ and change their colour successively from colourless to pink, orange-yellow, yellowish-green, greyish-green, greyish-blue, and violet, a fact which is probably due to the formation of various polymerides. Finally, the crystals spontaneously incandesce and turn white. The composition corresponds now with magnesium metantimonate, $\text{Mg}(\text{SbO}_3)_2$. The magnesium dihydrogen orthantimonate, *d* 2.57, is insoluble in alcohol; the solubility in water at 16° is 0.7075 gram in 1000 grams of solution.
S. S. M.

Phosphorescent Zinc Sulphide. A. A. GUNTZ (*Compt. rend.*, 1922, **174**, 1356—1358).—The wurtzite and sphalerite forms of zinc sulphide prepared by heating the precipitated sulphide are both phosphorescent. They may be distinguished under the microscope by their crystalline structures, but show no difference in density. Phosphorescence only develops in the presence of a trace of a heavy metal. The phosphorescence of wurtzite is more persistent than that of blende, but in both cases the decrease of luminous intensity is extremely rapid. Under the influence of heat and shock, the two varieties are extremely thermoluminescent and triboluminescent.

W. G.

The Substance between the Crystallites of Metallic Substances. G. TAMMANN (*Z. anorg. Chem.*, 1922, **121**, 275—280).—A piece of metal formed from a regulus consists of crystallites surrounded by a film of impurities which form the residue when the metal is dissolved in a solvent. To study the structure of these thin layers of impurities it is necessary to employ a transparent solvent; the evolution of gas and convection currents should be avoided, as these destroy the structure. A sheet of cadmium was dissolved in ammonium nitrate, and the film was found to have a net-like structure, in the meshes of which were micro-crystals of the metal. When the cadmium was dissolved in hydrochloric acid, the net structure was destroyed by the evolution of gas and the foreign substance was left as suspended particles. The amount of impurity was very much decreased by distilling the cadmium in a vacuum. The author points out the desirability of methods to render these non-metallic impurities visible, to estimate them quantitatively, and to find their influence on the properties of the metal.

W. T.

Monoclinic Double Selenates of the Cadmium Group. A. E. H. TUTTON (*Proc. Roy. Soc.*, 1922, [A], **101**, 245—264).—As in the manganese group (this vol., ii, 505), only three salts, those of rubidium, caesium, and ammonium, could be obtained in the cadmium group of hexahydrated double selenates (cf. preceding abstract). The rubidium and caesium salts were only obtained with great difficulty at a low temperature. No optical investigation was possible of these two salts, and a few optical determinations on the ammonium salt were only just possible, as the crystals rapidly become opaque. The salts crystallise in the holohedral-prismatic class of the monoclinic system.

Rubidium cadmium selenate, $\text{Rb}_2\text{Cd}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, $a : b : c = 0.7402 : 1 : 0.5026$; $\beta = 105^\circ 7'$. The crystals are metastable down to 0° . Caesium cadmium selenate, $\text{Cs}_2\text{Cd}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, $a : b : c = 0.7319 : 1 : 0.5011$; $\beta = 106^\circ 22'$. This salt is less unstable than the rubidium salt. Ammonium cadmium selenate, $a : b : c = 0.7418 : 1 : 0.5026$; $\beta = 106^\circ 1'$; $d_4^{20} 2.450$.

The results of thirty-two years' work on the double sulphates and selenates of the series $\text{R}_2\text{M}(\text{S} \begin{smallmatrix} \text{O} \\ \text{Se} \end{smallmatrix} \text{O}_4)_2 \cdot 6\text{H}_2\text{O}$ are discussed, in the course of which seventy-five salts, comprising nineteen distinct

groups, have been examined. In each group it is shown that there is a regular progression in the minutest details of the structural and physical properties of the crystals as the atomic number of the alkali metal increases in passing from potassium (19) to rubidium (37) and caesium (55). The ammonium salt is always practically isostructural with the rubidium salt of the same group. These results are in agreement with the recently developed theories of atomic and crystalline structure of Langmuir and W. L. Bragg.
E. H. R.

Tellurium Lead and Tellurium Antimony Alloys. MAX DREIFUSS (*Z. Elektrochem.*, 1922, **28**, 100—101, 224).—When lead is added in small quantities of molten tellurium, a portion of the lead forms a slag with the tellurium and a small amount of tellurium passes into solution. Tellurium has a deoxidising action on lead, so that lead containing tellurium may be heated to redness without the free liquid surface losing its brightness. Alloys containing tellurium and lead may be prepared by mixing tellurium with molten antimony; here a continuous series of mixed crystals is formed. To the molten alloy small quantities of antimony-lead alloy are added and eventually pure lead. A stiff, pasty mass is obtained which on heating at 700° becomes liquid and does not readily lose its bright surface. In the same way, small quantities of tin and copper alloy with the antimony tellurium alloy. The addition of 2% tellurium to lead-antimony alloys has no marked effect on the hardness. The addition of 5—6% of tin to antimony-lead alloys produce much more desirable properties than does tellurium.
J. F. S.

The Structure of the Isomorphous Group, $\text{Pb}(\text{NO}_3)_2$, $\text{Ba}(\text{NO}_3)_2$, $\text{Sr}(\text{NO}_3)_2$, $\text{Ca}(\text{NO}_3)_2$. L. VEGARD (*Z. Physik*, 1922, **9**, 395—410).—The space lattice of this isomorphous group of compounds has been determined by the application of the powder method. Little difficulty was experienced with the nitrates of lead, barium, and strontium, but the deliquescent calcium salt gave less satisfactory results. The positions of the maxima of reflection show that the crystals are not built up entirely of face-centred lattices. The metal atoms are arranged, however, in a face-centred lattice, for the intensity of the maxima of this lattice increases with increasing atomic weight of the metal. Three oxygen atoms and one nitrogen atom form a group at four corners of a cube. This group, which possesses a trigonal axis, is surrounded by four atoms of the metal.

The values for the atomic radii of nitrogen and oxygen atoms are appreciably higher than in those substances investigated by W. L. Bragg. The atomic radii vary with the nature of the chemical combination and the geometrical arrangement in space. The X-ray method provides a useful method for the determination of the density of solid substances. The presence of impurities scarcely affects the lattice constants or the atomic radii, from which the density may be calculated. Thus the density of the *pure* substance can be accurately determined from impure material. The values

for the densities of the compounds in the isomorphous group of nitrates, calculated from the atomic radii, are in good agreement with the experimental results. W. E. G.

Thallic-Thallous Sulphate. I. A. BENRATH and H. ESPENSCHIED (*Z. anorg. Chem.*, 1922, **121**, 361—362).—Many double salts of thallic and thallous sulphates are claimed by different authors, but the present authors could obtain only two corresponding in composition with Tl_2SO_4 , $\text{Tl}_2(\text{SO}_4)_3$ and $5\text{Tl}_2\text{SO}_4$, $\text{Tl}_2(\text{SO}_4)_3$; all the other so-called double salts are to be regarded as mixtures of these. The preparations and methods of analysis are given. The double salt, Tl_2SO_4 , $\text{Tl}_2(\text{SO}_4)_3$, has a transition temperature of 48° with a fairly large transition interval. The double salt interval for $5\text{Tl}_2\text{SO}_4$, $\text{Tl}_2(\text{SO}_4)_3$ has its upper limit between 23° and 30° . Between this transition temperature and 48° the whole system is in a transition state, so that at these temperatures mixtures of variable composition will be obtained. W. T.

Determination of the Complex Formation in Aqueous Solutions of Copper Salts by Means of Permutite. A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1922, **28**, 89—99).—The complex formation in solutions of copper chloride, acetate, formate, sulphate, chlorate, nitrate, and bromide has been investigated by shaking known concentrations of the salts with pure potassium permutite. From measurements of the exchange of kations between the permutite and the solution, conclusions may be drawn as to the presence of complexes in the solution. It is shown, by this method, that the simple complex kation CuR^+ is present in practically all the copper salt solutions examined even at the greatest dilutions. The presence of the complex Cu_2R_3^+ has been proved only in the case of copper chloride and bromide, whilst it is probable that the other salts exhibit a higher complex formation, which, however, is not present in such great concentrations. The complexity of copper salt solutions increases at constant concentration with the strength of the acid, and is greater with the salts of halogen acids than with the salts of oxygen acids of equal strength. J. F. S.

Extraction and Purification of Scandium from Thorveitite from Madagascar. PIERRE URBAIN and G. URBAIN (*Compt. rend.*, 1922, **174**, 1310—1313).—The finely ground mineral is fused with sodium hydroxide and the product extracted with water. The insoluble residue is dissolved in the least possible quantity of sulphuric acid, and the rare earth metals are precipitated as fluorides by the addition of an excess of hydrofluoric acid. The fluorides are decomposed by sulphuric acid, and scandium hydrogen sulphate crystallises out on concentrating the solution. The sulphates are converted into nitrates by passage through the hydroxides, and the solution of nitrates is evaporated and heated on a water-bath for a long time to free it from excess of acid. To the concentrated solution an excess of powdered potassium sulphate is added until the solution is saturated with this salt. After three days, the double scandium potassium sulphate is collected and washed as

quickly as possible with a saturated solution of potassium sulphate. Any scandium remaining in the mother-liquors is precipitated as hydroxide and put through the same process. The double sulphate may be dissolved in aqueous ammonium carbonate, and from the solution, on warming, scandium hydroxy-carbonate is precipitated. The residue of the scandium in the mother-liquors may be recovered by conversion into its acetylacetonate, which is soluble in chloroform and sublimes when heated in a vacuum at 200°.

W. G.

The Atomic Numbers of Neo-ytterbium, Lutecium, and Celtium. G. URBAIN (*Compt. rend.*, 1922, **174**, 1349—1351).—An historical paper in which the author points out that Dauvillier's work (this vol., ii, 463) completes the work of Moseley, himself, and others, and definitely establishes celtium as a chemical element with the atomic number 72, and having an atomic weight between that of lutecium, 175, and that of tantalum, 181.5.

W. G.

The Measurements of the Densities of the Haloids of Aluminium with Mercury as Pyknometer Liquid. WILHELM BILTZ and WALTER WEIN (*Z. anorg. Chem.*, 1922, **121**, 257—265).—The author in previous communications (*A.*, 1921, ii, 437; 1922, ii, 487) has discovered an abnormality in the linear relations in the atomic and molecular volumes of the haloids of aluminium. Former workers (Deville and Troost, *Ann. Chim. Phys.*, 1860, [iii], **58**, 279) used "oil of naphtha" as the pyknometer liquid. Inaccuracies due to the solubility of the bromide and iodide of aluminium in this liquid led the author to replace it by mercury. Toluene was employed in the case of the chloride, on which it has no action. Improved methods of preparation of the haloids are given, and density determinations are described. The densities and molecular volumes were found to be: aluminium fluoride (d_4^{25} 3.10), 27.1; aluminium chloride (d_4^{25} 2.44), 54.7; aluminium bromide (d_4^{25} 3.01), 88.7; aluminium iodide (d_4^{25} 3.98), 102.5. These values, however, do not show the linear relationship exhibited by all other haloids. Other abnormalities are found in the physical constants of the haloids of aluminium, for example, the melting point of the bromide does not lie between those of the iodide and chloride. These are ascribed to polymerisation to double molecules, $[\text{Al}_2\text{F}_6]$, $[\text{Al}_2\text{Cl}_6]$, $[\text{Al}_2\text{Br}_6]$, and $[\text{Al}_2\text{I}_6]$. These double molecules correspond with cryolite, $[\text{AlF}_6]\text{Na}_3$, the three univalent sodium atoms being replaced by one trivalent aluminium atom thus: $[\text{AlF}_6]\text{Al}$, $[\text{AlCl}_6]\text{Al}$, $[\text{AlBr}_6]\text{Al}$ and $[\text{AlI}_6]\text{Al}$. An X-ray examination is necessary to test this explanation.

W. T.

Monoclinic Double Selenates of the Manganese Group. A. E. H. TUTTON (*Proc. Roy. Soc.*, 1922, [A], **101**, 225—245).—In the group of the series $\text{R}_2\text{M}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, in which M is manganese, only three salts could be obtained, namely, those in which R is rubidium, caesium, or ammonium. Potassium manganese selenate, like the corresponding sulphate, only exists in the tetrahydrated form, even at 0°. The morphological relationships between the three salts are similar to those observed in every

other group of the series (cf. A., 1920, ii, 690). The salts all crystallise in the holohedral-prismatic class of the monoclinic system. Rubidium manganous selenate, $\text{Rb}_2\text{Mn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, $a:b:c=0.7422:1:0.5008$; $\beta=105^\circ 9'$; d_4^{20} 2.763. Cæsium manganous selenate, $\text{Cs}_2\text{Mn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, $a:b:c=0.7319:1:0.4957$; $\beta=106^\circ 22'$; d_4^{20} 3.008. Ammonium manganous selenate, $(\text{NH}_4)_2\text{Mn}(\text{SeO}_4)_2 \cdot 6\text{H}_2\text{O}$, $a:b:c=0.7427:1:0.4979$; $\beta=106^\circ 16'$; d_4^{20} 2.158. The ammonium salt, besides the cleavage parallel to $\{201\}$ common to the series, exhibits an even more perfect one parallel to $\{010\}$. The optical constants of the crystals of all the salts were measured.

E. H. R.

Equilibria in the Systems Iron-Carbon-Oxygen and Iron-Hydrogen-Oxygen, and the Free Energies of the Oxides of Iron. E. D. EASTMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 975—998).—A theoretical paper in which the data obtained by a number of authors in connexion with the two systems named in the title have been correlated and criticised. A number of calculations have been made from the correlated data, and the following conclusions drawn. Ferric oxide and ferrous-ferric oxide at 1100° and above form a continuous series of solid solutions, although there are indications that at temperatures much below 1000° they may not be soluble in each other in all proportions. Ferroso-ferric oxide and ferrous oxide up to 1100° at least definitely do not form a continuous series of solutions, although they do dissolve in each other to a limited extent. Ferrous oxide appears to be soluble in iron to the extent of 20—25 mol. % (6—8% oxygen), although metallic iron is not appreciably soluble in the oxide. Ferrous oxide is unstable with respect to ferroso-ferric oxide and iron below about 565° , and ferroso-ferric oxide shows an inversion point in the same region. When carbon monoxide reacts with pure iron in a closed tube above 500° , carbon is not ordinarily deposited as a separate phase. At temperatures above 800° , a trivariant equilibrium with iron containing dissolved carbon or carbide as the solid phase may be established, or one in which the solid phase contains dissolved oxygen as well as carbon, and the gas is richer in carbon dioxide than in the former case. It is possible that bivariant equilibria corresponding with these, with a separate dissolved carbon or carbide phase, may also be established on repeated treatment, but this does not appear to be proved. With a stream of carbon monoxide acting on iron in the vicinity of 650° , separate phases consisting of carbon, ferrous oxide, and iron containing dissolved oxygen and carbon (or carbide) are probably formed. At higher temperatures, the oxide and separate carbon phases do not appear, and the amount of dissolved carbon decreases. Carbon dioxide acting on iron in a closed tube probably produces again a trivariant system. At temperatures in the neighbourhood of 600° and lower, carbon is present in the solid phase, decreasing in amount as the temperature is increased. The individual results, of the investigators of univariant and bivariant equilibria involving iron or ferrous oxide, ferrous oxide or ferroso-ferric oxide, carbon

monoxide, carbon dioxide, and carbon under conditions such that the presence of separate and definite solid phases in large amounts was assured, are in sufficient agreement to permit the use of equilibrium constants and free energies based on them. These constants are tabulated for the range 600—1000°. Bivariant equilibria involving iron or ferrous oxide, ferrous oxide or ferroso-ferric oxide, and hydrogen yield such different results that the data cannot be safely used.

J. F. S.

The Penetration of Tempering in Steel. GEORGES CHARPY and LOUIS GRENET (*Compt. rend.*, 1922, **174**, 1273—1276).—A square bar of the steel to be examined is used for the purpose. It is heated in the furnace at the required temperature until its temperature is uniform. The upper part of the bar is then wrapped round with asbestos, and on to the base is directed a regulated stream of cold water. When the cooling is complete, the hardness is determined on one face at different distances from the base. The bar may then, if necessary, be submitted to further thermal treatments and the other three faces used for determining the hardness. The results are in accord with those obtained on a fragment of metal cut out from a thick piece after its tempering. With a nickel-chrome steel, the hardness was found to vary from 387 at 3 mm. from the base to 180 at 90 mm. With an auto-tempering steel, after tempering at 800°, the hardness was practically uniform along the whole length of the bar.

The method may also be used for metals which are not homogeneous, and permits of a study of the influence of cementation on thick plates. In this way, it was found that, in certain cases, the hardness of the part situated behind the cemented region is less than that obtained with a bar of the same composition, tempered under the same conditions, but showing no cemented region.

W. G.

Centrifugal Method for Preparing Colloidal Ferric Hydroxide, Aluminium Hydroxide, and Silicic Acid. RICHARD BRADFIELD (*J. Amer. Chem. Soc.*, 1922, **44**, 965—974).—Colloidal ferric hydroxide, aluminium hydroxide, and silicic acid may be prepared from the freshly formed precipitates of these substances by removing the excess of precipitating agent by a very thorough washing, which is achieved by means of a centrifuge with a rotation of 32,500 per minute. This method has many advantages over the older methods, chief of which are, (a) the removal of the electrolytes formed on precipitation is more complete; (b) the addition of a peptising agent and its consequent incomplete removal by either prolonged boiling or dialysis is unnecessary; (c) sols of a more uniform degree of dispersion can be prepared, since particles of similar size and of similar degrees of hydration are deposited in the same zone of the centrifuge bowl; (d) sols of any desired concentration from a semi-gel to the merest trace can be prepared by the addition of water to the more concentrated form, and all concentrations are very stable. It is shown that aluminium hydroxide

precipitated by ammonium hydroxide in the presence of an excess of sulphate ions is not irreversible. J. F. S.

The Reduction of Oxides by Hydrogen. E. BERGER (*Compt. rend.*, 1922, **174**, 1341—1343; cf. A., 1914, ii, 656; Sabatier and Espil, A., 1914, ii, 276).—From a study of the velocity curves for the reduction, by hydrogen, of specimens of nickel oxide prepared in different ways, the author finds that the discontinuity in the curves occurs at different stages in the reduction varying with the specimen. This discontinuity cannot, therefore, be explained on the basis of the formation of an intermediate oxide, and doubt is therefore cast on the existence of sub-oxides of nickel. W. G.

New Properties of the Green Chromium Sulphate. A. RECOURA (*Compt. rend.*, 1922, **174**, 1460—1463).—It has been shown by Colson (A., 1907, ii, 177, 267, 474) that the green chromium sulphate, immediately after its solution in water, exists in a condensed form, which is slowly depolymerised. In this condensed form, it is found to be capable of masking the sulphate ion in other sulphates to the extent of several hundred molecules for each molecule of the green sulphate present. The number of molecules which can be thus masked depends on the length of time during which the green sulphate has been in solution, the acidity, and the concentration of the solution. W. G.

X-Ray Examination of the Trioxides of Tungsten, Molybdenum, and their Hydrates. H. C. BURGER (*Z. anorg. Chem.*, 1922, **121**, 240—242).—The highest oxide of tungsten, WO_3 , can exist in various forms as large, bright yellow crystals, or long, thin, dark blue, or green needles. All these modifications gave identical angles of reflection which were, however, different from that of the hydrate. This proves that the hydrate is a definite chemical compound with its own characteristic crystal form. It corresponds in composition with $\text{WO}_3 \cdot \text{H}_2\text{O}$, that is, H_2WO_4 ; this, on heating, loses water and gives the above trioxide. A definite chemical compound was also indicated in the case of the other hydrate, $\text{WO}_3 \cdot 2\text{H}_2\text{O}$; that is, H_4WO_5 tungstic acid. In the case of molybdenum, the existence of H_2MoO_4 as a definite chemical compound was proved. This is a much more convenient method for the solution of such problems than that of measuring the vapour pressure as a function of the composition. The phases in the mixture can be found and the whole work carried out in a short time with a few mg. of the substance. W. T.

The Valency of Tungsten and Molybdenum in their Complex Octacyanides. OSCAR OLSSON COLLENBERG (*Z. anorg. Chem.*, 1922, **121**, 298—312).—The author reviews previous work on the subject and shows the sources of error. He determined the valency by means of ammoniacal silver chloride and found that the central atoms were in each case quadrivalent in agreement with their formulæ, $[\text{W}(\text{CN})_8]\text{K}_4$ and $[\text{Mo}(\text{CN})_4]\text{K}_4$. These results were confirmed by another method, using ferric sulphate and potassium

permanganate, this method, due to Friedheim and Hoffmann (A., 1902, ii, 265), being modified and so rendered applicable in the presence of cyanides.

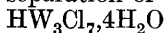
W. T.

The Chlorides of Bivalent Molybdenum, Tungsten, and Tantalum. I. KURT LINDNER [with EMMA HALLER, HERBERT HELWIG, ANTONIE KÖHLER, and HELLMUTH FEIT] (*Ber.*, 1922, 55, [B], 1458—1465).—The formulæ $\text{HMo}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$, $\text{HW}_3\text{Cl}_7 \cdot 4 \cdot 5\text{H}_2\text{O}$, and $\text{Ta}_6\text{Cl}_{14} \cdot 7\text{H}_2\text{O}$ have been ascribed by Rosenheim and Kohn (A., 1910, ii, 300), Hill (A., 1917, ii, 36), and Chapin (A., 1910, ii, 303), respectively, to the dichlorides of molybdenum, tungsten, and tantalum. The preparation of these chlorides has been subjected to exhaustive investigation. It is shown that they are uniformly constituted in accordance with the general formula, $\text{HX}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$, in which the metal is bivalent. The methods used in their preparation are the treatment of the metals with gaseous chlorine under suitable conditions of temperature and pressure and the reduction of the higher chlorides by gases or other reducing agents such as metals.

At all temperatures up to 1200° , molybdenum is converted by chlorine into the pentachloride. The dichloride is obtained conveniently by passing carbonyl chloride over powdered molybdenum at $700\text{--}800^\circ$; a small quantity of the pentachloride sublimes, after which the metal gradually becomes coated with a heavy yellow layer of molybdenum dichloride, which ultimately protects the metal from further action. The dichloride is then extracted with concentrated hydrochloric acid and the residual metal is again treated with carbonyl chloride. The compound, $\text{HMo}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$, separates almost quantitatively from the acid solutions in the form of long, yellow needles. At about 600° , molybdenum trichloride is the main product of the action of carbonyl chloride on molybdenum, whereas below this temperature the pentachloride is produced. Less favourable but useful results are obtained by the reduction of molybdenum pentachloride with finely divided aluminium in the presence of ignited quartz powder (to moderate the violence of the reaction). The product is subsequently extracted with hydrochloric acid. The yield is considerably diminished by the reduction of molybdenum pentachloride to other stages and even to metallic aluminium and the consequent difficulty of working up the residues.

Tungsten dichloride cannot be prepared from the metal and carbonyl chloride, which, over a wide interval of temperature, give carbon and the "red oxychloride," WOCl_2 , in addition to small quantities of tungsten hexachloride and probably of tungsten pentachloride. The reduction of tungsten hexachloride by sodium amalgam (Hill, *loc. cit.*) is uncontrollable, and even if successful only gives minimal quantities of the dichloride; the results with an alloy of sodium and potassium are even less promising. On the other hand, tungsten hexachloride is readily reduced to the dichloride by ignition in a stream of nitrogen with powdered aluminium and quartz; the product is extracted with hydrochloric acid and the

reddish-yellow extract is concentrated and saturated with hydrogen chloride, thus causing the separation of the compound



in slender, yellow needles, which are considerably less stable than the corresponding molybdenum compound and rapidly lose hydrogen chloride when exposed to air.

Tantalum is converted into its pentachloride by carbonyl chloride. Tantalum pentachloride is reduced by powdered metals to the dichloride and, since the reaction proceeds less violently than with the molybdenum and tungsten compounds, the addition of powdered quartz may be omitted. Aluminium, zinc, and lead are efficient. The residues are extracted exhaustively with hydrochloric acid. The isolation of the compound $\text{HTa}_3\text{Cl}_7 \cdot 4\text{H}_2\text{O}$, a blackish-green, unusually stable, crystalline powder, from the extracts is a matter of some difficulty, since it only separates from very concentrated solutions and its crystallisation is greatly impeded by the presence of dissolved aluminium chloride. It is preferable, therefore, to use zinc which can be removed as sulphide after addition of sodium acetate to the solution or lead, the dissolved traces of which can be precipitated directly with hydrogen sulphide. Molten tantalum pentachloride cannot be reduced electrolytically between carbon poles, since the substance is an insulator (cf. Biltz and Voigt, this vol., ii, 302). Electrolysis takes place after addition of alkali chlorides, and the dichloride is formed to some extent; the method has no preparative value. H. W.

Electrolytic Removal of Alkali from Salts. A. LOTTER-MOSER (*Kolloid Z.*, 1922, **30**, 346—348).—The author shows that by the electrolysis of normal sodium tungstate it is possible to prepare paratungstates and other complex tungstates by the removal of sodium hydroxide. In the case of sodium paratungstate, the preparation is carried out as follows. A solution of normal sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$), 51 grams in 200 c.c. of water, is placed in a 250 c.c. porous pot which stands in a beaker containing exactly 750 c.c. of *N*/10-sodium hydroxide. An anode consisting of a coil of platinum wire is placed in the porous cell, and the electrolysis carried out with a current of 2 amperes until the sodium hydroxide has increased in concentration by the calculated amount. When this state is reached, the anode solution is allowed to crystallise; sodium paratungstate separates in large, vitreous crystals. In the same way, sodium ditungstate and metatungstate were also prepared (cf. Kröger, this vol., ii, 212). J. F. S.

The Hydrates of Uranium Tetroxide and Uranium Trioxide. GUSTAV F. HÜTTIG and EDITH VON SCHROEDER (*Z. anorg. Chem.*, 1922, **121**, 243—253).—Details are given of the preparation of the bright yellow, hygroscopic hydrate of uranium tetroxide, which corresponds with the formula $\text{UO}_4 \cdot 3\text{H}_2\text{O}$. This was heated in a vacuum, but the tetroxide, UO_4 , could not be obtained, the final product being the trioxide, UO_3 . The compound loses oxygen before all the water is expelled, and the authors consider the existence of the tetroxide as very doubtful. The changes in composition were

studied in a Hüttig tensi-eudiometer (A., 1921, ii, 195), and the following hydrates were indicated: $\text{UO}_4 \cdot 4.5\text{H}_2\text{O} = \text{UO}_3 \cdot \text{H}_2\text{O}_2 \cdot 3.5\text{H}_2\text{O}$; $\text{UO}_3 \cdot 3\text{H}_2\text{O} = \text{UO}_3 \cdot 0.5\text{H}_2\text{O}_2 \cdot 2.5\text{H}_2\text{O} = \text{H}_2\text{U}_2\text{O}_8 \cdot 5\text{H}_2\text{O}$; $\text{UO}_3 \cdot 5\text{H}_2\text{O} = \text{UO}_3 \cdot 0.5\text{H}_2\text{O}_2 \cdot 1.5\text{H}_2\text{O} = \text{H}_2\text{U}_2\text{O}_8 \cdot 3\text{H}_2\text{O}$ [?]; peruranic acid pentahydrate, $\text{UO}_3 \cdot 0.5\text{H}_2\text{O} = \text{H}_2\text{U}_2\text{O}_7$, pyrouranic acid. It is assumed that these are derivatives of the trioxide and that hydrogen peroxide is contained in the first, second, and third compounds.

In the case of uranium trioxide, indication was given of the following hydrates: $\text{UO}_3 \cdot 2\text{H}_2\text{O} = \text{H}_2\text{UO}_4 \cdot \text{H}_2\text{O}$, $\text{UO}_3 \cdot \text{H}_2\text{O} = \text{H}_2\text{UO}_4$, uranic acid.
W. T.

The Triboluminescence of Uranium Salts and Three New Organic Uranium Compounds. J. A. SIEMSEN (*Chem. Ztg.*, 1922, 46, 450; cf. A., 1919, ii, 346).—A specimen of uranium nitrate which had been kept in a stoppered bottle for forty-one years showed weak triboluminescence compared with other preparations, and its luminosity was very slight. A specimen of sodium uranate which was not triboluminescent was converted into uranium nitrate which showed fairly strong triboluminescence. A preliminary announcement is made of the discovery of three salts, obtained by the action of pyrazolone derivatives on uranium compounds, which possess powerful bactericidal properties. No further chemical particulars are given.
E. H. R.

The Behaviour of the Stannic Acids towards Hydrochloric Acid. GEORGE ERNEST COLLINS and JOHN KERFOOT WOOD (T., 1922, 121, 1122—1133).

The Anodic Corrosion of Bismuth. Bismuth Compounds. E. B. R. PRIDEAUX and H. W. HEWIS (*J. Soc. Chem. Ind.*, 1922, 41, 167—171T).—As a possibly advantageous alternative to attack by nitric acid, the anodic corrosion of bismuth in an anolyte of sodium nitrate was investigated. The bismuth anodes were cast on copper wire, the cathode was a strip of nickel and in order to prevent reduction of the nitrate to ammonia it was placed in a catholyte of dilute alkali in a porous pot.

In the first series of experiments, 10% sodium nitrate solutions were used, with a current density of 12.5 amperes per sq. dm. and an average of 4.6 volts. The current efficiency calculated from the anodic loss was 100%, and 1.76 kilowatt-hours were consumed per kilo. of bismuth dissolved. The product was an oxynitrate containing on the average about 30% of bismuth oxide, and came down partly as a white deposit and partly as a crust on the anode. The amount of bismuth in the solution was negligible. In the second series of experiments, saturated solutions of sodium nitrate were used as the anolyte, and in this case the bismuth oxynitrate came down entirely as a loose precipitate, and one-half to three-quarters of the total bismuth remained in solution, from which it may be obtained as oxynitrate by dilution, or used directly for other bismuth preparations. The fully hydrated white bismuth hydroxide, $\text{Bi}(\text{OH})_3$, can be prepared from this anodic solution by allowing it to run into an equal volume of $N/2$ -sodium hydroxide

diluted about five times. The white precipitate is washed by decantation. An examination of xeroform (bismuth tribromophenoxide) prepared by the usual method of adding bismuth nitrate to a solution of tribromophenol in sodium hydroxide, showed that it contained an appreciable quantity of oxynitrate, and the alcoholic extract contained nitrobromophenols in addition to much tribromophenol. On ignition, moreover, it gave a lemon-yellow residue containing bromine, and it does not therefore yield pure bismuth oxide, as usually stated. Commercial xeroform appears therefore to be very impure, although doubtless quite suitable for the purpose intended. A purer preparation was obtained by using the anodic solution of bismuth nitrate in sodium nitrate. It forms a bulky, pink precipitate, which, although it has a definite bismuth content (15.46%), does not appear to correspond exactly with any of the simpler compounds which might be expected, for example, $(C_6H_2Br_3O)_3Bi$ requires 17.36%. It is possibly a hydrate, and the matter is being further investigated. G. F. M.

Double Haloids of Bismuth and Thallium. G. CANNERI and G. PERINA (*Gazzetta*, 1922, 52, i, 241–246; cf. this vol., ii, 378; Ephraïm and Barteczko, A., 1909, ii, 236).—*Bismuth thallous bromide*, $2TlBr, BiBr_3$, prepared by dissolving bismuth carbonate in nitric acid and adding potassium bromide, crystallises in lustrous, lemon-yellow, hexagonal lamellæ, and in neutral aqueous solution undergoes rapid hydrolysis to thallous bromide, bismuth oxybromide, and bromine. *Bismuth thallous iodide*, $2TlI, BiI_3$, prepared by adding potassium iodide to an acid solution containing thallium and bismuth, forms red, regular hexagonal plates, exhibits physical and chemical properties similar to those of the preceding compound, and is soluble in about 20,000 parts of water.

The formation of this insoluble double iodide may be used as a means of detecting and estimating bismuth after other metals forming insoluble iodides have been removed. A solution containing 0.029 gram of bismuth per litre yields a voluminous red precipitate with a thallous salt and potassium iodide, whereas with hydrogen sulphide only a faint brown coloration is obtained. For the estimation, the solution of the bismuth salt is acidified with hydrochloric acid and then treated with a known volume, in excess, of standard potassium iodide solution. Standard thallous sulphate solution is next run in from a burette until precipitation of the red double iodide ceases and that of yellow thallous iodide is evident. The precipitate is collected on a Gooch crucible and washed thoroughly with absolute alcohol, the residual excess of potassium iodide in the solution being estimated by means of potassium iodate. If a represents the amount in grams of iodine added as iodide to the solution, b that combining with the thallium, and c that remaining in excess, calculated on the basis that 3 atoms of iodine correspond with 1 atom of bismuth, the weight of the latter in grams is given by: $208[a - (b + c)]/380.76$.

Addition to a solution of $K_3Bi(CNS)_6$ (cf. Vanino and Hauser, A., 1902, i, 14) of a proportion of thallium acetate corresponding

with one equivalent of the potassium results in the formation of an orange-yellow *precipitate* of the composition $K_2TiBi(CNS)_6$, whilst with double this proportion of thallium acetate, the *compound*, $KTi_2Bi(CNS)_6$, is obtained as a paler yellow precipitate. All attempts to prepare the trisubstituted salt, $Ti_3Bi(CNS)_6$, have proved unsuccessful, the molecule undergoing demolition with formation of thalious thiocyanate. T. H. P.

The Reduction of Tantalum Pentachloride. OTTO RUFF and FRITZ THOMAS (*Ber.*, 1922, **55**, [B], 1466—1473).—Tantalum pentachloride is reduced by metallic aluminium in the presence of aluminium chloride at 300° to a mixture of various chlorides of tantalum. A larger excess of aluminium remains unchanged even when, as is occasionally the case, metallic tantalum is formed. The temperature is limited by the resistance of the tubes. The dark green product of the reaction evolves aluminium chloride and tantalum pentachloride when heated, the latter being given off in such a manner that the composition of the residue can be regulated by the choice of temperature and pressure. A mixture corresponding approximately with tantalum tetrachloride is obtained at $250^\circ/2-3$ mm.; at $350-400^\circ$ the residue has the composition of a trichloride which is itself decomposed at about 500° , leaving a mixture of di- and tri-chlorides.

The mixtures of chlorides are moderately stable towards air. Treatment with water causes the formation of intensely green solutions of the trichloride, whilst the pentachloride is hydrolysed to hydrochloric and tantalic acids and the dichloride remains undissolved as a blackish-green residue. The green solutions become oxidised slowly on exposure to air, the action being checked by the presence of acids. The di- and tri-chlorides are soluble in cold, sufficiently dilute sodium hydroxide solutions without evolution of hydrogen or alteration in the valency of the element. The alkaline solutions are oxidised with unusual readiness by air and evolve hydrogen when they are warmed; a brown tantalous oxide is thereby produced as an intermediate step in the formation of tantalic acid. The production of this substance is also observed during rapid oxidations (with hydrogen peroxide or nitric acid) in acid solution. When oxidation is effected by hydrogen peroxide in alkaline solution, a brown solution of a pertantalate is obtained which evolves oxygen and becomes colourless when boiled.

The behaviour of aqueous solutions of titanium trichloride towards common reagents is described in detail. H. W.

Gold Sulphides. A. GUTBIER and E. DÜRRWÄCHTER (*Z. anorg. Chem.*, 1922, **121**, 266—274).—Various sulphides of gold are described in the literature. The authors could not obtain the sulphides with the formulæ Au_2S and Au_2S_2 . A rapid stream of hydrogen sulphide passed at the ordinary temperature into a 2% solution of chloroauric acid, $[AuCl_4]H$, in *N*-hydrochloric acid gave a black precipitate of auric sulphide, Au_2S_3 , mixed with small amounts of metallic gold. The relative amounts of sulphide and metal depend on temperature, concentration of the chloro-

auric acid, and the rate of passing in the hydrogen sulphide. At low temperatures -2° , with a low concentration of the chloro-acid and a very rapid stream of gas, the pure sulphide was obtained. The low concentration of the tetrachloro-acid is necessary, because it reacts with the sulphide formed. Auric sulphide reacts more rapidly with auric chloride than with the tetrachloro-auric acid and pure auric sulphide is not obtained as above if the gas is bubbled into a solution of auric chloride.

W. T.

Some Complex Chlorides containing Gold. III. A New Cæsium Auric Chloride. HORACE L. WELLS (*Amer. J. Sci.*, 1922, [v], 3, 414—416).—This salt, $\text{Cs}_5\text{Au}_3\text{Cl}_{14}$, was obtained from a concentrated solution of cæsium chloride containing comparatively little auric chloride. It is best prepared in the presence of concentrated hydrochloric acid, because it is quickly decomposed by water, with the formation of a yellow precipitate of the usual double salt, CsAuCl_4 . The new complex salt was obtained as very minute deep red crystals.

W. T.

Rubidium (Cæsium) Silver Gold Bromides. EUGEN SUSCHNIG (*Monatsh.*, 1921, 42, 399—404).—Triple bromides of rubidium (or cæsium), silver, and gold have been prepared corresponding with the triple chlorides described by Bayer (A., 1920, ii, 688) and discussed by Emich (*ibid.*, 689). The silver and gold are vicarious constituents, and their proportions in the compounds depend on their concentrations in the solutions from which crystallisation takes place. The compounds correspond with the formulæ $\text{Rb}_3\text{Ag}_x\text{Au}_{(2-x/3)}\text{Br}_9$ and $\text{Cs}_3\text{Ag}_x\text{Au}_{(2-x/3)}\text{Br}_9$. In the rubidium compound, the atomic proportion of silver varied from 0.77 to 1.59, and in the cæsium compound from 0.89 to 1.14. The rubidium salt forms almost black needles, deep violet in thin sections, whilst the cæsium salt is similar to Bayer's triple chloride. The salts can only be prepared in strong hydrobromic acid solution; they are decomposed by water. An analogous potassium salt could not be obtained, but microscopical tests showed that an ammonium compound is formed, and also compounds with organic bases such as guanidine, caffeine, pyridine, hexamethylenetetramine, and methyl- and ethyl-amine instead of rubidium or cæsium. The compounds are adapted to the microchemical identification of gold, silver, and rubidium or cæsium in absence of disturbing elements. Microchemical tests indicate that aluminium, chromium, zinc, nickel, cobalt, uranium, mercury, and manganese can replace silver in the triple chlorides and that ferric iron, calcium, strontium, and barium can replace the alkali metal.

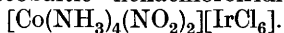
E. H. R.

Determination of the Werner Structure of Inorganic Compounds by means of X-Rays. PAUL SCHERRER and P. STOLL (*Z. anorg. Chem.*, 1922, 121, 319—320).—The space lattices of the following complex salts were determined: $[\text{PdBr}_6]\text{Rb}_2$, $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$, and $[\text{PtCl}_6]\text{K}_2$. The six co-ordinated groups were placed at the six corners of a regular octahedron with the central atom at the centre. The salts resembled calcium fluoride with

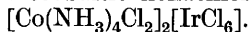
the co-ordinated complex taking the place of the atom calcium. The platinum and chlorine were 1.6×10^{-8} cm. apart and the edge of the octahedron measured 9.7×10^{-8} cm. W. T.

Chloroiridates of Complex Metal Bases. A. BENRATH, W. BÜCHER, and H. ECKSTEIN (*Z. anorg. Chem.*, 1922, **121**, 347—360).—Jørgensen prepared a large number of salts of the amines of cobalt and chromium by combining the complex bases with different acid radicles. The complex acids of the noble metals formed beautifully coloured, crystalline salts. The present authors employed the complex hexachloroiridate as the acid radicle. The salts formed with cobalt as the central atom of the complex base were found to crystallise only with difficulty and to be more unstable than the corresponding platinum compounds. In the hexammine salts the most stable were those in which all the acid radicles were replaced by the complex iridium radicle; the others were very unstable. The hexammine and pentammine salts as well as the aquo-salts with four or five molecules of ammonia are insoluble, stable, yellow to brown in colour, decomposed only by long boiling with an alkali hydroxide, micro-crystalline and decomposed when heated alone at 150° . The tetrammine salts are more soluble, can be precipitated with alcohol, are crystalline and golden-yellow to bronze-red in colour. They decompose in hot water, and when heated alone at 105 — 120° . The preparation and properties of the following are described: Hexamminecobaltic hexachloroiridate, $[\text{Co}(\text{NH}_3)_6]_2[\text{IrCl}_6]_3$. Hexamminecobaltic nitrate hexachloroiridate, $[\text{Co}(\text{NH}_3)_6]_2[\text{NO}_3][\text{IrCl}_6]$. Basic hexamminecobaltic hexachloroiridate, $[\text{Co}(\text{NH}_3)_6]_2[\text{OH}][\text{IrCl}_6]$. Chloropentamminecobaltic hexachloroiridate, $[\text{Co}(\text{NH}_3)_5\text{Cl}][\text{IrCl}_6]$. Aquopentamminecobaltic hexachloroiridate, $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}][\text{IrCl}_6]$. *trans*-Dinitrotetramminecobaltic hexachloroiridate trihydrate, $[\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2][\text{IrCl}_6] \cdot 3\text{H}_2\text{O}$.

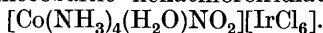
cis-Dinitrotetramminecobaltic hexachloroiridate,



cis-Dichlorotetramminecobaltic hexachloroiridate,



Aquonitrotetramminecobaltic hexachloroiridate,



The salts with chromium in the basic complex resemble the corresponding cobalt compounds. They are dirty yellow in colour. The hexammine and pentammine salts separated as very fine suspensions, the tetrammine salts crystallised much more readily. The following salts are described: Hexamminechromic hexachloroiridate, $[\text{Cr}(\text{NH}_3)_6]_2[\text{IrCl}_6]_3$. Hexamminechromic nitrate hexachloroiridate, $[\text{Cr}(\text{NH}_3)_6]_2[\text{NO}_3][\text{IrCl}_6]$. Basic hexamminechromic hexachloroiridate, $[\text{Cr}(\text{NH}_3)_6]_2[\text{OH}][\text{IrCl}_6]$. Hexamminechromic sulphate hexachloroiridate, $[\text{Cr}(\text{NH}_3)_6]_2(\text{SO}_4)_2[\text{IrCl}_6]$. Chloropentamminechromic hexachloroiridate, $[\text{Cr}(\text{NH}_3)_5\text{Cl}][\text{IrCl}_6]$. Hydroxo-aquotetramminechromic hexachloroiridate, $[\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})\text{OH}][\text{IrCl}_6]$. Dithiocyanatotetramminechromic hexachloroiridate,



Dichloroaquotriamminechromic hexachloroiridiate,
 $[\text{Cr}(\text{NH}_3)_3\text{H}_2\text{OCl}_2]_2[\text{IrCl}_6]3\text{H}_2\text{O}$.

The nitrate iron could not be separated from the chloroiridiate ion by means of nitron as the complex ion also forms an insoluble product, thus resembling the chloro-acids of the other noble metals. The compound, $(\text{C}_{20}\text{H}_{16}\text{N}_4)_2[\text{IrCl}_6]\text{H}_2$, separates as a dark red, crystalline precipitate. Ruthenium can be partly separated from the other noble metals by fractional crystallisation of the nitrous compounds, that of ruthenium being more soluble than the others.

W. T.

Mineralogical Chemistry.

Calcium Uranium Autunites. F. HENRICH (*Ber.*, 1922, 55, [B], 1212—1215; cf. A., 1918, ii, 96).—The detailed analysis is recorded of a calcium uranium autunite from Steinbrüch Fuchsbau, near Leopoldsdorf, in the Fichtelgebirge, the analysis (I) of which agrees closely with the formula $\text{CaO} \cdot (\text{UO}_3)_2 \cdot \text{P}_2\text{O}_5 \cdot 10\text{H}_2\text{O}$. The ratio of radium to uranium is 2.8×10^{-7} , or 87% of the equilibrium value between the two elements. This appears to be the highest value yet recorded for a calcium uranium autunite. A Portuguese calcium uranium autunite from the Beira Alta Province (analysis II) had a ratio of radium to uranium which is only 38% of the theoretical value and was appreciably poorer in radium than the Bavarian specimen.

	UO_3 .	CaO .	P_2O_5 .	Insol.	Ignition.	Total.
I.	59.71	5.92	14.30	1.50	18.17	99.6
II.	60.72	6.04	14.55	0.53	18.27	99.93

H. W.

Ceruleofibrite, a New Mineral. EDW. F. HOLDEN (*Amer. Min.*, 1922, 7, 80—83).—As radiating tufts of bright-blue fibres and as blackish-blue, fibrous masses, this was found on specimens of cuprite from Bisbee, Arizona. The needles are orthorhombic ($a : b : c = 0.78 : 1 : 0.49$) with angles near to those of brochantite, d 3.54, H. 3. The optical characters are stated. The mineral is readily soluble in cold dilute hydrochloric acid. Analysis gives the formula $\text{CuCl}_2 \cdot \frac{1}{3}\text{Cu}_3\text{As}_2\text{O}_8 \cdot 6\text{Cu}(\text{OH})_2$, representing a very basic chloroarsenate.

CuO .	Cl .	As_2O_5 .	H_2O .	Insol.	Total less O for Cl.
73.8	7.5	7.5	11.7	0.3	99.1

L. J. S.

Chemical Investigation of Japanese Minerals containing Rarer Elements. IV. Samarskite and an Unnamed Mineral from Ishikawa, Iwaki Province. YŪJI SHIBATA and KENJIRŌ KIMURA (*J. Chem. Soc. Japan*, 1922, 43, 301—312; cf. this vol., ii, 220).—Samarskite, d 5.50, hardness 5—6, from Ishikawa-machi, Iwaki Province, gave on analysis :

MgO.	CaO.	MnO.	FeO.	Al ₂ O ₃ .	Rare earths.	UO ₂ .	SnO ₂ .	TiO ₂ .	SiO ₂ .	Ch ₂ O ₅ .	Ta ₂ O ₅ .	H ₂ O.	Total.
0.25	1.25	0.84	9.64	0.61	17.34	16.87	0.73	0.10	0.37	41.11	10.00	0.85	99.96

From which is deduced the formula $2[M_2(\text{Cb}, \text{Ta})_2\text{O}_7]_n\text{R}_2(\text{Cb}, \text{Ta})_2\text{O}_8$, where M=Fe, Ca, Mg, Mn, UO, and R rare earth metals.

On spectroscopic examination, lines of lead, barium, strontium, tungsten, yttrium, erbium, dysprosium, gadolinium, samarium, scandium, and terbium were observed.

Imperfect black crystals, with resinous lustre of an unnamed mineral (d 6.2—6.4, hardness 5—6, streak, blackish-brown) from the same locality gave on analysis :

MgO.	CaO.	MnO.	FeO.	Al ₂ O ₃ .	Rare earths.	UO ₂ .	SnO ₂ .	SiO ₂ .	TiO ₂ .	Ch ₂ O ₅ .	Ta ₂ O ₅ .	H ₂ O.	Total.
1.07	0.86	0.40	11.78	0.87	8.40	21.83	1.20	0.30	0.21	36.80	15.00	0.89	99.66

On spectroscopic examination, lines of lead, barium, strontium, zinc, copper, bismuth, beryllium, yttrium, erbium, gadolinium, dysprosium, samarium, lanthanum, and scandium were observed.

K. K.

Composition of Thortveitite from Madagascar. CH. BOULANGER and G. URBAIN (*Compt. rend.*, 1922, **174**, 1442—1443; cf. A., 1920, ii, 627; this vol., ii, 306).—The mean of five analyses is :

SiO ₂ .	Sc ₂ O ₃ .	ZrO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	Gl, Mn, Sn, Sb, Pb.	Total.
44.1	42.4	8.4	3.3	2.0	traces	100.2

The figures for scandia include about 0.5% of yttrium earths (yttrium, neoytterbium, and lutecium). The mineral is only slightly attacked by hydrofluoric acid or by fused bisulphates. Two or three fusions with sodium carbonate are necessary for its decomposition.

L. J. S.

Velardeñite from California. EARL V. SHANNON (*Proc. U.S. Nat. Mus.*, 1922, **60**, Art. 22, 1—4).—A dull olive-green, coarsely-granular mineral with greasy to resinous lustre, from Tulare Co., California, is colourless under the microscope. It is optically uniaxial and negative, $\omega=1.657$, $\epsilon=1.653$. Analysis I corresponds with $14\text{CaO}, 2\text{MgO}, 5\text{Al}_2\text{O}_3, 9\text{SiO}_2$, which is interpreted as a mixture of five parts of velardeñite ($2\text{CaO}, \text{Al}_2\text{O}_3, \text{SiO}_2$) with two of åkermanite ($\text{MgO}, 2\text{CaO}, 2\text{SiO}_2$).

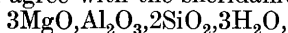
	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	H ₂ O.	Total.
I.	27.88	25.52	1.59	0.43	40.86	4.18	0.34	100.80
II.	32.66	5.95	24.15	—	35.51	2.59	—	100.86

Mixed with it are grains of a yellowish-green garnet which (with some spinel) gave analysis II, indicating andradite.

L. J. S.

White Chlorites. EARL V. SHANNON and EDGAR T. WHERRY (*J. Washington Acad. Sci.*, 1922, **12**, 239—241).—Colerainite (A., 1918, ii, 325) and sheridanite (A., 1912, ii, 1181) are classed as white chlorites. Analysis I is of a white chlorite from Brinton's quarry, Chester Co., Pennsylvania, II from Nottingham, Chester

Co., and III of a greenish-grey schistose rock from Miles City, Montana. I and III agree with the sheridanite formula



but II gives the ratios $9\text{MgO}, \text{Al}_2\text{O}_3, 6\text{SiO}_2, 7\text{H}_2\text{O}$. III agrees also with sheridanite in its optical constants, whilst II is different.

	SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MnO.	CaO.	MgO.	H ₂ O-.	H ₂ O+.	Total.
I.	28.10	26.20	1.66	nil	trace	trace	30.36	0.56	14.00	100.88
II.	36.70	10.38	1.22	trace	trace	0.86	36.44	1.06	13.80	100.46
III.	27.78	24.30	1.43	0.35	nil	trace	32.71	0.06	13.01	99.64

L. J. S.

Crocidolite from Eastern Pennsylvania. EDGAR T. WHERRY and EARL V. SHANNON (*J. Washington Acad. Sci.*, 1922, **12**, 242—244).—Blue pleochroic amphiboles ("glaucamphiboles") occur at many localities in eastern Pennsylvania. Analysis of material from Oley Line shows it to be a semimagnesian crocidolite with the formula $\text{H}_2\text{O}, \text{Na}_2\text{O}, \text{MgO}, \text{FeO}, \text{Fe}_2\text{O}_3, 6\text{SiO}_2$.

SiO ₂ .	Ti ₂ O ₃ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.	Na ₂ O.	K ₂ O.	H ₂ O-.	H ₂ O+.	Total.
51.62	2.27	0.92	18.36	10.93	0.48	5.92	5.62	0.66	1.04	2.57	100.39

Titanium is regarded as replacing aluminium and iron, rather than silicon, and to it the deep blue is ascribed. The low content of alkalis is accounted for by the replacement of sodium by hydrogen.

L. J. S.

Analytical Chemistry.

A New Method of Colorimetry. PAUL DOSNE (*Bull. Soc. Ind. Mulhouse*, 1922, **88**, 73—77).—A beam of light (from a Nernst lamp or other suitable source) is directed upwards through a column of a solution of known strength of the coloured substance under investigation and the height of the column necessary for the complete absorption of the transmitted light, as observed through a spectroscope, is determined. Since under these conditions the colouring power of a substance is directly proportional to the height of the column and to the strength of the solution, the method allows various colouring matters to be compared when dissolved in water, alcohol, or other suitable solvents. A. J. H.

Colorimetry. PAUL FLEURY (*Bull. Soc. Chim. Biol.*, 1922, **4**, 223—232).—A discussion of the conditions under which colorimetric methods yield the most accurate results. E. S.

Colorimetry. (MLLE) Y. GARREAU (*Bull. Soc. Chim. Biol.*, 1922, **4**, 233—234).—The accuracy of the colorimetric method is indicated by the concordant results obtained during a large number of estimations of sugar by the picric acid method. E. S.

Improved Form of Gas-analysis Apparatus. E. W. BLAIR and T. SHERLOCK WHEELER (*J. Soc. Chem. Ind.*, 1922, **41**, 187—188r).—A modification of the usual Bone-Wheeler apparatus is described, in which compressed air and reduced pressure are employed to alter the mercury levels; this saves much of the labour involved in raising and lowering the mercury reservoirs. The pressure of the air supply is about two atmospheres. In other respects, the method of working the apparatus is not altered.

W. P. S.

The Absorption Meter, an Apparatus for Gas Analysis. L. MOSER (*Z. anorg. Chem.*, 1922, **121**, 313—318).—The author describes a simplification of the apparatus he employed for the gravimetric estimation of hydrogen phosphide (A., 1922, ii, 393). The apparatus has been tested and gives good results in the estimation of sulphur dioxide, cyanogen, hydrogen cyanide, silicon fluoride, the hydrides of arsenic and antimony, ozone, and chlorine. It is unsuitable for carbon dioxide or any gases which requires an absorption liquid affected by the air (baryta water).

W. T.

Apparatus for Determining Hydrogen-ion Concentration. Application to the Detection of Mineral Acids in Vinegar. ANDRÉ KLING, A. LASSIEUR, and (MME) A. LASSIEUR (*Ann. Chim. analyt.*, 1922, **4**, 135—137).—A simple apparatus is described for determining hydrogen-ion concentration electrometrically. It is shown that the hydrogen-ion concentration of vinegars containing from 5—7% of acetic acid varies from p_H 2.54 to 2.83 and that the addition of 0.24% of sulphuric acid causes this value to become 1.48 to 2.02.

W. P. S.

The Clark Hydrogen-electrode Vessel and Soil Measurements. DANIEL J. HEALY and PERRY E. KANAKER (*Soil Sci.*, 1922, **13**, 323—328).—Satisfactory measurements of the hydrogen-ion concentration of fresh and air-dried soils can be made with the Clark hydrogen-electrode vessel. Air drying increases the values obtained over those of fresh samples.

A. G. P.

The Estimation of Chlorine in Organic Material. STEFAN VON BOGDÁNDY (*Z. physiol. Chem.*, 1922, **120**, 30—41; cf. A., 1913, ii, 426).—The author shows that if his method is carried out according to his instructions, high results are not obtained as is asserted by Gutmann and Schesinger (A., 1914, ii, 379).

S. S. Z.

Application of Amalgams in Volumetric Analyses. III. Estimation of Iodic, Bromic, and Chloric Acids. SUETARÔ KIKUCHI (*J. Chem. Soc. Japan*, 1922, **43**, 173—177).—Iodic acid reacts at 60° with tervalent titanium obtained by reduction of titanous acid as described previously (A., 1921, ii, 596), the excess of tervalent titanium being then titrated with iron alum. The reaction proceeds as follows: $IO_3' + 6Ti''' + 6H = I' + 6Ti'''' + 3H_2O$. Bromic and chloric acids can be estimated by similar procedure.

K. K.

Sodium Peroxide. JAROSLAV MILBAUER (*Chem. Listy*, **16**, 84—86).—The estimation of the active oxygen of sodium peroxide by means of acid potassium permanganate solution is examined. The author finds that the best results are obtained by the addition of boric acid to the solution, as this fixes the hydrogen peroxide liberated by the acid. This method is very exact and rapid, and does not require the use of ice.

The effects produced by the presence of various metallic salts, and of spongy platinum and palladium are also investigated. It is found that if the salt is added to the water before the sodium peroxide, the results for the estimation of oxygen will be low; if the salt is added after the solution of the sodium peroxide in water, the results are high. This explains the failure of the use of permanganate solution alone, as the manganous sulphate formed acts as a catalyst, which must be neutralised by an anti-catalyst (in this case boric acid).

The iodometric method of Kingzett (T., 1880, **37**, 792) is also examined and found satisfactory.

The influence of catalysts on the method whereby the peroxide is analysed by estimation of the oxygen liberated by its decomposition in acid or alkaline solution is also studied. From the results obtained for this, the author formulates, as a method for the estimation of the active oxygen of sodium peroxide, its decomposition in alkaline solution, in the presence of cupric sulphate, and the measurement of the gaseous oxygen so liberated. The advantage of this method over that of Archbutt (A., 1895, ii, 185) is that the decomposition is complete in two minutes, and that the evolved oxygen is free from carbon dioxide.

By means of these new methods of estimation the author shows that the action of the atmosphere on sodium peroxide is principally due to the presence of moisture.

R. T.

Estimation of Sulphur Dioxide. G. BASIL BARHAM (*Chem. News*, 1922, **124**, 279—281).—Titration with permanganate solution under definite conditions is recommended for the estimation of sulphur dioxide. Dilute sulphuric acid solution is treated with a definite volume of standard permanganate solution, and the mixture then divided into two equal portions; the sulphur dioxide solution under examination is added to one portion and the permanganate solution is added until the coloration is again equal in intensity to that of the other portion, which has been reserved for comparison. To ensure the colorations being of the same tint, the acid solution should be reduced and oxidised once or twice (with sulphite and permanganate solutions, respectively) before it is used for the actual estimation.

W. P. S.

Examination of Foods for the Presence of Sulphites. A. CHASTON CHAPMAN (*Analyst*, 1922, **47**, 204—205).—When foods containing onions or mustard are acidified with phosphoric acid and distilled in a current of carbon dioxide, the distillate on oxidation with bromine will yield a distinct quantity of sulphuric acid; if the oxidation is made with hydrogen peroxide in place of bromine,

these foods will not yield any sulphuric acid unless they actually contain sulphites. W. P. S.

Factors Influencing the Estimation of Sulphates in Soil.

C. T. HIRST and J. E. GREAVES (*Soil Sci.*, 1922, **13**, 231—249).—A comparison was made between the gravimetric method of estimating sulphates as barium sulphate and the volumetric chromate method. By the latter method an average of 97% of the sulphate in soil extracts could be recovered. Sodium and potassium chlorides had little effect on the results obtained; but in the presence of iron and aluminium salts the volumetric method tended to give low results. The presence of nitrates caused high figures by the gravimetric method and low ones by the volumetric method. A 1 : 5 water extract of the soils used, was found to be sufficient to remove all sulphates after forty minutes' shaking. Soils particularly rich in gypsum needed shaking with water for a longer period. Extracts should be clarified by a Pasteur-Chamberland filter.

Very small quantities of sulphates can be detected more easily by the chromate than by the gravimetric method. A. G. P.

The Analysis of Polythionates. ALBIN KURTENACKER and

ALBERT FRITSCH (*Z. anorg. Chem.*, 1922, **121**, 335—343).—The authors have already found that tetrathionates react quantitatively with a cyanide to form thiosulphates (A., 1921, ii, 502). Trithionates were found by Raschig (A., 1920, ii, 756) to react quantitatively with cyanides in hot alkaline solutions to form sulphites. The latter reaction is incomplete in neutral solutions, whereas tetrathionates in alkaline solutions give sulphites as well as thiosulphates. This reaction is therefore unsuitable for the estimation of a mixture of these two polythionates. The estimation of a mixture of polythionates by means of a sulphite as recommended by Raschig was found to be unsatisfactory. The method of Riesenfeld and Feld (this vol., ii, 45) was tested. In the absence of other polythionates, the trithionate reacts quantitatively with copper sulphate, but the estimation is not applicable to mixtures. A tetrathionate boiled for half an hour with copper sulphate gave a precipitate of copper sulphide and sulphur in proportions corresponding with the decomposition of the tetrathionate as follows: $S_4O_6^{2-} = S_3O_6^{2-} + S$. The authors found, contrary to the results of Riesenfeld and Feld, that tetrathionates were quite stable; a solution showed no decomposition after keeping for fourteen days, the instability reported being due to impurities. W. T.

Pregl's Microanalysis. FRIEDRICH HOLTZ (*Ber.*, 1922, **55**, [B], 1496—1497).—The use of a bomb furnace in the estimation of halogen and sulphur is avoided by placing the tubes in brass tubes which are closed at one end and stoppered at the other and are heated in the vapour of boiling diphenylmethylamine, b. p. 295°.

The estimation of nitrogen in difficultly-combustible substances is effected in silica tubes which are filled in the following order: asbestos plug, oxidised copper wire (7 cm.), reduced copper wire

(11 cm.), asbestos plug, copper oxide powder mixed with the substance and a little potassium chlorate (4 cm.), oxidised copper wire (5 cm.). The tube is supported at either end on gutters lined with asbestos in such a manner that the portion of the tube containing the reduced copper is left exposed to the direct heat of the burner. This portion of the tube is doubly protected on its upper side. After displacement of the air by carbon dioxide, the reduced copper is raised to a white heat and after a second passage of carbon dioxide the heating of the remainder of the tube is effected very gradually in the direction towards the reduced copper. In this manner, the decomposition of the oxides of nitrogen is effected with certainty.

Substances may be conveniently dried in a hollow copper cube the walls of which are 1 cm. thick and 6.5 cm. long internally.

H. W.

A "Micro-Kjeldahl" Method of Estimating Nitrogen.

ARTHUR R. LING and WILLIAM JOHN PRICE (*J. Soc. Chem. Ind.*, 1922, **41**, 149—151t).—A weighed portion of the substance containing 1.0—0.1 mg. of nitrogen is boiled until colourless with 8 c.c. of concentrated sulphuric acid, 1 gram of dry potassium sulphate, 0.02 gram of anhydrous copper sulphate, and 2 drops of 2.5% platinic chloride solution. After cooling and diluting with 15 c.c. of water, the liquid is distilled from a 300 c.c. flask with sufficient 40% sodium hydroxide solution to render it alkaline, and the ammoniacal distillate is collected in 50 c.c. of water in a graduated 250 c.c. flask. All the ammonia will have been expelled when 100 c.c. of liquid has distilled. The distillate is then "nesslerised," made up to 250 c.c., and the tint compared with a standard ammonium sulphate solution containing 1 mg. of nitrogen per c.c. The comparison will give the apparent nitrogen content which must be corrected by a factor (obtained from a curve given in the original paper) in order to arrive at the actual nitrogen content. This is due to the fact that intensity of colour and ammonia concentration are not directly proportional. G. F. M.

Kjeldahlisation of Mononitrophenols, Mononitrobenzoic Acids, and Mononitrocinnamic Acids. R. M. MARGOSCHES and ERWIN VOGEL (*Ber.*, 1922, **55**, [B], 1380—1389).—A continuation of previous work (A., 1920, ii, 50), in which it was shown that the Kjeldahl-Gunning method gives accurate results only for the ortho-derivatives when applied to the mononitrophenols and mononitrobenzoic acids.

The Kjeldahlisation of mononitro-phenols and -benzoic acids by sulphuric acid without addition of potassium sulphate gives correct values for the ortho-, and low values for the meta- and para-compounds; it is remarkable that the latter are considerably higher than those given by the Kjeldahl-Gunning method.

Stepwise Kjeldahlisation according to Kjeldahl-Gunning shows that in the case of o-nitrophenol and o-nitrobenzoic acid, the major part of the nitrogen value is attained during the stage of the initial discoloration which occurs at the commencement of the heating

and the theoretical nitrogen value is almost attained at the period of most violent action. With *p*-nitrobenzoic acid, on the other hand, practically no nitrogen value is attained at the stage of initial darkening and the nitrogen is almost entirely present in such a form that the calculated nitrogen value is observed after addition of phenol; at the period of most violent action, the "converted" nitrogen increases somewhat, whereas that "convertible" by subsequent addition of phenol declines, ultimately becoming reduced to zero when the solution is colourless.

In the case of *p*-nitrobenzoic acid, the replacement of potassium sulphate in the Kjeldahl process by copper oxide or mercuric oxide leads to analytical results which are in harmony with the calculated values. The activity of copper oxide is not affected by the presence of potassium sulphate, whereas that of mercuric oxide is greatly depressed. The activity of sodium sulphate is inferior to that of potassium sulphate and approximately equal to that of lithium sulphate.

A further series of experiments is described in which the Kjeldahlisation of *p*- and *m*-nitrobenzoic acid and of *p*-nitrophenol is effected by the presence of potassium sulphate; the volatile products are collected and heated with concentrated sulphuric acid, phenol, and copper oxide. *p*-Nitrobenzoic acid and *p*-nitrophenol are found to behave in an entirely different manner; the former yields a volatile nitrogenous compound in which the nitrogen can be converted into ammonia by sulphuric acid, phenol, and copper oxide, whereas the latter undergoes a far more complex decomposition with the formation of products which do not yield ammonia under the described conditions.

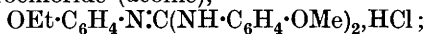
In striking contrast to the nitrobenzoic acids, the three nitrocinnamic acids yield almost the whole of their nitrogen as ammonia when heated with sulphuric acid and potassium sulphate. Satisfactory results are also obtained with sulphuric acid alone or mixed with copper oxide.

H. W.

A Micro-method for the Estimation of Ammonia in Blood and in Organic Fluids. K. L. GAD-ANDRESEN (*J. Biol. Chem.*, 1922, **51**, 367—372).—One c.c. of blood is used for the estimation. After addition of borate, it is evaporated to dryness by heating at 25° in a current of dry air. The ammonia thus removed is absorbed in sulphuric acid, decomposed by hypobromite, and the nitrogen measured in Krogh's microrespirometer as in the author's urea method (*A.*, 1920, ii, 646). The method is also applicable to secretions, but not to tissues.

E. S.

New Insoluble Organic Nitrates. JOSÉ GIRAL PEREIRA (*Anal. Fís. Quím.*, 1922, **20**, 84—92).—In a study of organic compounds giving precipitates or turbidities with nitrates, the following compounds are mentioned as new precipitants: *p*-dianisylphenetylguanidine hydrochloride (acoine),



dicyanodiamide, $\text{NH}:\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}_2$, produced by the hydrolysis of dicyanodiamidine, $\text{NH}:\text{C}(\text{NH}_2)\cdot\text{NH}\cdot\text{CN}$; the hydrochloride

of hydrocupreine ethyl ether (optoquine), hydrastine hydrochloride. The common features in the constitution of nitrate precipitants is discussed.

G. W. R.

So-called Di-9 : 10-monohydroxyphenanthrylamine suggested as a Reagent for Nitric Acid and Phenanthroxazine. B. FORESTI (*Gazzetta*, 1922, 52, i, 278—285).—The author has investigated Bamberger and Grob's phenanthroxazine (A., 1901, i, 280) and finds that the melting point 350—355° given by these authors is that of a mixture of the compound with its decomposition products. The value obtained for the melting point depends on the initial temperature of the heating bath. With a bath at 422° (non-corrected), fusion occurs after the lapse of six seconds from the time of immersion, and since this is the length of time required for the tube and substance to assume the temperature of the bath, the melting point is taken as 422°.

It is found, further, that the substance obtained by Schmidt and Lumpp (A., 1910, i, 312; ii, 450) by the action of aqueous ammonia on dihydroxyphenanthrene, and described by these authors as di-9(10)-monohydroxyphenanthrylamine, consists of a mixture of phenanthroxazine with impure phenanthrazine and that the characteristic behaviour of the substance towards nitrates is due to the presence of the phenanthroxazine. In testing for nitrate, use is made of a solution of 0.01 gram of phenanthroxazine in 100 c.c. of concentrated sulphuric acid, and as dilution of this blue solution with water may give rise to a violet coloration similar to that obtained with nitrates, the substance to be tested must not be in aqueous solution. The dry residue left in a porcelain dish by a drop of the liquid to be examined is treated with a drop of the reagent; in presence of a nitrate, a reddish-violet coloration is formed, but if the amount of nitrate is very small, only a violet ring appears after some time. In this way 1×10^{-7} gram of nitric acid is detectable. This reaction is not disturbed by moderately high proportions of chlorate or chromate, and although slightly less sensitive than that of brucine with nitric acid, is not given by nitrous acid. The coloration is not destroyed by sulphur dioxide, but is changed to pale yellow by stannous chloride. T. H. P.

Estimation of the Nitro-group in Aromatic Organic Compounds. II. T. CALLAN and J. A. RUSSELL HENDERSON (*J. Soc. Chem. Ind.*, 1922, 41, 157—161r).—The low results obtained with certain compounds by the Knecht-Hibbert reduction method with titanous chloride for the estimation of nitro-groups is due in the case of readily chlorinated substances such as *o*-nitroanisole, α -nitronaphthalene, etc., to chlorination by the titanous chloride and the reducing action of the thereby liberated hydrogen, whereby a lesser amount of titanous salt is oxidised than would otherwise be the case. This source of error can be entirely obviated by using titanous sulphate solutions instead of the chloride, or may be very largely avoided even by using sulphuric acid instead of hydrochloric acid to acidify the titanous chloride solution. In general, the greater the excess of hydrochloric acid used the greater will be

the error due to chlorination. Another source of error, due to the volatility in steam of the simpler nitro-compounds, may be obviated by sulphonating, but much more simply by reducing under a ground-in reflux condenser about 9 inches long. By adopting these modifications and precautions, it is shown that, contrary to statements by English (A., 1920, ii, 776), nearly all types of nitro-compounds can be accurately estimated, including mononitro-hydrocarbons, chloronitro-compounds, and other negatively substituted nitrohydrocarbons. Recrystallised *p*-nitroaniline is recommended as the ultimate standard for the titanous solutions.

G. F. M.

Separation of Phosphoric Acid in Qualitative Analysis.

D. BALAREFF (*Z. anorg. Chem.*, 1922, **121**, 254—256).—The precipitates of the ammonium sulphide group (Groups III and IV taken together) are dissolved in hydrochloric acid (solution is thus free from cobalt and nickel) and the solution neutralised with ammonia. A large excess of lead nitrate is added and then sodium acetate until the solution is neutral to methyl-orange. The phosphoric acid is precipitated as lead phosphate, mixed with lead chloride and phosphates of ferric iron, chromium, and aluminium. The large excess of lead-ion, however, ensures that some ferric, chromium, and aluminium-ions remain in solution. The excess of lead is then removed by hydrochloric acid. The author claims that this method possesses advantages in speed and completeness of separation over the older methods.

W. T.

Effect of Adsorption by Stannic Sulphide on the Estimation of Phosphates. SÜETARÔ KIKUCHI (*J. Chem. Soc. Japan*, 1922, **43**, 329—333).—When phosphate is determined by the usual method, it is found after the tin in solution is removed as sulphide, that there is a deficiency of phosphate. This is due to adsorption of the phosphate by stannic sulphide; stannous sulphide, on the contrary, does not adsorb phosphate; therefore the quadrivalent tin in the solution is reduced to the stannous state by zinc in the presence of carbon dioxide and removed as sulphide. Estimation of the phosphate in the filtrate then gives correct values. K. K.

The Citric Solubility of Mineral Phosphates. J. F. TOCHER (*J. Agric. Sci.*, 1922, **12**, 125—143).—The proportion of phosphoric acid extractable by citric acid from basic slags and mineral phosphates is closely dependent on the conditions of experiment. The three variables being the amount of citric acid used, the amount of mineral phosphate used, and the volume of liquid used, the author has investigated the influence on the amount of phosphoric acid extracted of varying one of these factors whilst keeping the other factors in a constant ratio. With constant weights of mineral phosphate and citric acid, the amount of phosphoric acid dissolved increases with the volume. With constant weight of mineral phosphate and constant volume, the amount of phosphoric acid dissolved increases with increase of the amount of citric acid used. With constant weight of citric acid and constant volume, the

amount of phosphoric acid extracted decreases with increase in the amount of mineral phosphate used. The quantitative relationships are connected with considerations of mass action and it is shown that the solubility curves obtained can be made to fit an empirical formula. It is held that citric solubility is influenced by so many factors that it is an untrustworthy test of the agricultural value of mineral phosphates and slags. The only standard tests to be accepted are total phosphate content, fineness of grinding, and freedom from injurious substances.

G. W. R.

Invisible "Mirrors" of Arsenic, Antimony, and Bismuth.

HERMANN SCHEUCHER (*Monatsh.*, 1921, **42**, 411—420).—Bettendorff's test for arsenic, consisting in reducing an oxide of arsenic with stannous chloride and hydrochloric acid, when arsenic is thrown down as a voluminous, brown precipitate, has been developed into an extremely sensitive microchemical test. The reactants are introduced into a capillary tube which is then sealed to a point at one end and heated for a short time in a bath of boiling amyl alcohol (130°). The tube is then centrifuged and the arsenic appears as a brown precipitate in the point of the capillary. In this way, 0.01γ of arsenic ($\gamma=0.001$ mg.) can be detected at a dilution of 1 in 250,000. By contrast, the magnesium ammonium arsenate test is uncertain with 0.1γ of arsenic. The test is not interfered with by antimony, tin, lead, copper, or cadmium. The Marsh test, using Lockemann's method (A., 1905, ii, 353), is sensitive to 0.1γ , whilst with less arsenic the mirror becomes scarcely visible, and invisible with 0.04γ . If, however, the glass capillary containing the mirror, or supposed mirror, is treated with bromine vapour to oxidise the arsenic, and the Bettendorff test is then applied as above, as little as 0.01γ of arsenic can be detected.

The Marsh test applied to antimony is sensitive to 0.2γ , but the presence of antimony in invisible mirrors can be demonstrated by the luminescence test described by Paneth (A., 1919, ii, 68). Bismuth can be detected in a similar way when the hydride is prepared by Paneth's method. The mirror is dissolved in a drop of nitric acid, which is then transferred to a piece of ignited calcium carbonate held in a platinum loop and the flame test applied. For antimony, the limit of sensitiveness is 0.001γ . An invisible mirror can also be "developed" with a solution of ferrous sulphate in acetic acid containing silver nitrate. After a short time, silver is deposited in the place where the mirror should be. The reaction is extraordinarily sensitive, but, unfortunately, a glass tube which has merely been ignited with only a current of air passing through may give the reaction, although a quartz tube will not do so.

E. H. R.

Colorimetric Estimation of Arsenic by means of Quinine Molybdate. D. CHOUGHAK (*Ann. Chim. analyt.*, 1922, **4**, 138—142).—A solution containing a trace of arsenic is oxidised with nitric acid, evaporated to dryness, and the residue treated with 0.5 c.c. of 17.5% nitric acid, 4.5 c.c. of water, and 20 c.c. of quinine molybdate reagent; the turbidity produced is compared with that

given by a known amount of arsenic under similar conditions. As little as 0.00002 mg. of arsenic gives a visible turbidity. The reagent is prepared by dissolving 0.5 gram of quinine hydrochloride in 10 c.c. of water, adding 5 c.c. of arsenic acid solution (containing 0.01 mg. of arsenic per c.c.), 10 c.c. of 17.5% nitric acid, and 1 c.c. of sodium molybdate solution (3.5 grams of sodium carbonate and 9.5 grams of molybdic acid per 100 c.c.); after a few minutes, the mixture is diluted with water to 120 c.c., and filtered through a filter-paper moistened previously with nitric acid and washed. If heavy metals are present in the solution under examination, the arsenic must be separated by distillation with hydrochloric acid, potassium bromide, and hydrazine sulphate, the distillate oxidised with nitric acid, evaporated to dryness, and the dry residue used for the estimation. W. P. S.

Inadequacy of the "A.R." test for Alkalis in Calcium Carbonate. W. SINGLETON and H. WILLIAMS (*Analyst*, 1922, 47, 252—254).—Only about 50% of the total extractable sodium carbonate is washed out on boiling 5 grams of calcium carbonate with 50 c.c. of water for ten minutes. The alkalis present in 5 grams of "A.R." calcium carbonate were therefore determined by the Lawrence Smith method (this Journal, 1871, 442) and the amount of sodium carbonate obtained was more than ten times that given by the "A.R." method. The result was checked by decomposing 5 grams of the calcium carbonate with hydrochloric acid and precipitating the calcium twice with ammonium carbonate and ammonium oxalate. Substantially the same result was obtained. It therefore appears that only about 10% of the alkali carbonates present in the calcium carbonate are removed by one extraction with water. H. C. R.

A Comparison of the Calcium Content of some Virgin and Cultivated Soils of Kentucky by an Improved Method for the Estimation of this Element. O. M. SHEDD (*Kentucky Agr. Exp. Sta. Bull.*, 236 (October 1921)).—In estimating the total calcium in the soils, 1 gram of soil (passing through a 100-mesh sieve) is fused with 5 grams of a mixture of sodium and potassium carbonates (10 : 13) for ten minutes. The fused mass is dissolved in hydrochloric acid, evaporated to dryness, and the silica dehydrated. The residue is extracted with dilute hydrochloric acid and the silica filtered off. Filtrate and washings should not exceed 100 c.c. The solution is made just alkaline to litmus with strong ammonia and then just acid with hydrochloric acid. The solution, which is not always perfectly clear at this stage, is heated to boiling and the calcium precipitated by adding 1—2 grams of solid ammonium oxalate. Further addition of hydrochloric acid may now be necessary to maintain the solution acid to litmus. After two to three minutes' boiling, the solution is placed on the steam-bath for a few hours and allowed to remain over-night. The precipitate is filtered, washed twice with water, and ignited to convert it into oxide or carbonate. This is redissolved in acid and manganese precipitated by the addition of bromine

and excess of ammonia. After heating until only a little ammonia remains, the solution is made faintly acid with oxalic acid and filtered. The calcium is then precipitated from the filtrate as before and finally weighed as oxide.

A. G. P.

Flame Reactions of Thallium. JACOB PAPISH (*Proc. Indiana Acad. Sci.*, 1918, 166—169).—Thallous chloride dissociates in a Bunsen flame to the free metal which colours the flame and may be precipitated on a cold surface as a brown mirror. In a hydrogen flame in air, thallous chloride produces five zones of luminescence. Metallic thallium will condense from the innermost cone on a cold surface but not from the outer cone where the luminescence is probably due to oxidation of the thallium.

CHEMICAL ABSTRACTS.

Tervalent Titanium. II. Estimation of Copper and Iron in the Presence of each other. WILLIAM M. THORNTON, jun. (*J. Amer. Chem. Soc.*, 1922, 44, 998—1001; cf. A., 1921, ii, 279).—A method is described for the estimation of iron and copper in the presence of one another by means of a standard solution of titanium trisulphate. The method is as follows. The mixture of cupric and ferric sulphates is dissolved in less than 100 c.c. of water, acidified with 10 c.c. of 1:1-sulphuric acid, and cooled to 15°. A quantity of 10% ammonium thiocyanate solution from 2.5 to 5 c.c., depending on the amount of copper anticipated, is added and the solution titrated with a standard solution of titanium trisulphate until the pink colour just vanishes. The titre gives the sum of the copper and iron present. The whole is then heated to incipient ebullition, to coagulate the cuprous thiocyanate, cooled, and filtered. The precipitate is thoroughly washed with cold water and the filtrate and washings are cooled to 15°. The solution has by this time probably become pink again, due to oxidation by air. If so, the colour is bleached by the careful addition of titanium trisulphate, and sufficient silver nitrate (2.5—5 c.c. of 25% solution) is added to precipitate the whole of the thiocyanate. The ferrous iron is then titrated with a standard solution of potassium permanganate. The method is shown to be accurate and trustworthy, but the precaution of previously testing the titanium solution for iron must be taken, and if such is found the permanganate value corrected for this amount.

J. F. S.

Quantitative Analysis of Aluminium Alloys, especially of Duralumin. E. MENDES DA COSTA-VET (*Chem. Weekblad*, 1922, 19, 249—251).—The alloy of aluminium introduced for airships by the Dürerer Metallwerke contains Cu 3.5—4.5%, Mn 0.5—1.0%, Mg 0.5%. The methods of Collit and Regan (A., 1918, ii, 175) and of Withey (A., 1916, ii, 538) for analysis of this alloy are unsatisfactory, since in the first the magnesium is almost completely carried down in the ammonia precipitation of iron, manganese, and aluminium, whilst in the second it is impossible to precipitate the magnesium from the tartaric acid solution by means of pyrophosphate.

It was found that magnesium can best be estimated after removal of copper by means of hydrogen sulphide, and of iron, aluminium, and part of the manganese by means of ammonium chloride and ammonia, the latter separation being performed twice, by precipitation with phosphate. Some of the manganese remains from the ammonia precipitation, and is weighed with the magnesium as pyrophosphate; this is estimated by redissolving the precipitate and titrating with permanganate.

The ammonia precipitation must be carefully carried out, and the liquid filtered immediately to avoid separation of magnesium at this stage.

S. I. L.

The Quantitative Estimation and Separation of Aluminium.

GERHART JANDER and ERWIN WENDEHORST (*Z. angew. Chem.*, 1922, **35**, 244—247).—Precipitation of large amounts of aluminium hydroxide from solutions containing other metals such as magnesium and manganese leads to such high results that the direct estimation of aluminium in alloys consisting chiefly of aluminium is not possible by the usual methods. In such cases, the authors recommend heating the alloy in a current of well-dried hydrogen chloride at 200°, whereby all the aluminium sublimes as chloride together with small amounts of silicon, magnesium, and manganese chlorides, whilst iron, copper, and zinc remain in the boat. The sublimate is dissolved in dilute nitric acid and the solution evaporated repeatedly with further quantities of the same acid until all chlorine is expelled. The silica that separates is removed by filtration and the solution is evaporated to dryness. The residue is ignited, gently at first, then strongly, and weighed as aluminium oxide containing some manganese and magnesium oxides, which are determined separately, the former colorimetrically and the latter as pyrophosphate, and deducted. [Cf. *J. Soc. Chem. Ind.*, 1922, July.]

A. R. P.

A Proposed Estimation of Chromium and Nickel in Steel.

FRITZ SIMON (*Chem. Ztg.*, 1922, **46**, 504).—The sample is dissolved in aqua regia, the solution neutralised and poured into an excess of a solution of sodium hydroxide containing hydrogen or sodium peroxide. After boiling to expel oxygen, the precipitate is collected on a Nutsche filter, well washed, then returned to the beaker and digested with ammonia and ammonium carbonate to extract the nickel. The chromate in the filtrate is estimated by any suitable method. [Cf. *J. Soc. Chem. Ind.*, 1922, July.]

A. R. P.

Applications of Amalgams in Volumetric Analyses. IV.

The Uses of Cadmium Amalgam. NAOTSUNA KANÔ (*J. Chem. Soc. Japan*, 1922, **43**, 333—340).—In earlier papers (A., 1921, ii, 596, 714), the volumetric estimation of molybdenum, titanium, etc., after reduction by means of liquid zinc amalgam was described. To extend the method, the zinc is now replaced by cadmium. The method of preparation of the amalgam and the reducing operation are practically the same as in the former case. In the cases of molybdenum and iron, the cadmium amalgam acts

as well as the zinc amalgam, but in the cases of vanadium and titanium, the reduction is not complete. With uranium, it is necessary to carry out the reduction in an atmosphere of carbon dioxide.

K. K.

The Estimation of Uranium in Presence of Phosphoric Acid. A. SCHOEP and W. STEINKUHLER (*Bull. Soc. chim. Belg.*, 1922, **31**, 156—159).—The analysis of dewindtite (this vol., ii, 305) and of stasite (this vol., ii, 386), phosphates of uranium, and lead, necessitated more satisfactory methods than those hitherto used. The following procedure has given trustworthy results for both phosphate and uranium in a series of control experiments. Silica and elements which are precipitated by hydrogen sulphide in acid solution are first eliminated, the uranium is oxidised by means of nitric acid, and the phosphoric acid then precipitated with molybdate solution. Addition of ammonia transforms the uranium into ammonium uranate; from this the metal is precipitated as uranium sulphide on the addition of ammonium sulphide, the precipitate being washed until the washings are free from molybdenum. No solution and reprecipitation is necessary.

H. J. E.

Iodometric Studies. II. BOHDAN KÖHLER (*Chem. Listy*, **16**, 87—91; cf. A., 1921, ii, 410).—The best results in the iodometric titration of tin are obtained by dissolving the tin in 6*N*-hydrochloric acid, adding to this a known amount of iodine dissolved in potassium thiocyanate, and determining the excess of iodine with a standardised sodium thiosulphate solution.

Contrary to the observation of Zulkowski and Bruhns (*J. pr. Chem.*, 1859, **103**, 351), the velocity of the reaction $\text{Cr}_2\text{O}_7^{''} + 14\text{H}^+ + 6\text{I}^- \rightarrow 2\text{Cr}^{+++} + 7\text{H}_2\text{O} + 6\text{I}$ is quite considerable.

The titration of tin by means of potassium dichromate solution gives exact results if atmospheric oxygen is excluded from the solutions. Since it is, in practice, difficult to have air-free solutions of potassium dichromate, a correction of +0.068 mg. of tin per c.c. of aqueous aerated potassium dichromate solution is advocated. This correction is based on the assumption that the solubility of oxygen in decinormal potassium dichromate solution is little different to that in pure water.

R. T.

Reduction of Vanadic Acid Solutions with Mercury. LE ROY W. MCCAY and WILLIAM T. ANDERSON, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 1018—1021; cf. this vol., ii, 217).—When vanadic acid in the presence of sulphuric or hydrochloric acid is vigorously shaken with mercury the vanadium is reduced to the quadrivalent state according to the equation $2\text{HVO}_3 + 2\text{Hg} + 3\text{H}_2\text{SO}_4 = 2\text{VOSO}_4 + \text{Hg}_2\text{SO}_4 + 4\text{H}_2\text{O}$. If the solution before shaking is mixed with a little more sodium chloride than is equivalent to the mercurous sulphate formed, the whole of the mercury is precipitated as mercurous chloride and a pure blue solution left which may be quantitatively titrated with potassium permanganate when the reaction,

represented by the equation $10\text{VOSO}_4 + 2\text{KMnO}_4 + 12\text{H}_2\text{O} = 10\text{HVO}_3 + \text{K}_2\text{SO}_4 + 2\text{MnSO}_4 + 7\text{H}_2\text{SO}_4$ takes place. A method of estimating vanadic acid by means of the above reactions is described. The solution of vanadic acid containing sulphuric acid and the requisite amount of sodium chloride (0.3 gram for each 50 c.c. of *N*/10-permanganate required) is diluted to 100 c.c., placed in a stoppered bottle, and vigorously shaken with 20 c.c. of mercury for five minutes. The liquid above the grey mercury mixture is decanted into a small beaker and poured through a suction filter. The residue in the bottle is washed four times by decantation, 20 c.c. of water being used for each washing, and the washings are severally decanted into the beaker and then through the filter. The total filtrate is diluted to 250 c.c., heated at $80-90^\circ$, and titrated with permanganate to the faintest pink. The whole process may be completed in thirty minutes; it gives results which are identical with those obtained by the sulphur dioxide method, and since uranic acid and arsenic acid are not reduced by mercury, the method may be employed in the presence of these acids.

J. F. S.

Detection of Antimony in Analysis. TH. SABALITSCHKA and H. SCHMIDT (*Ber. deut. Pharm. Ges.*, 1922, **32**, 132—135).—To obviate the necessity of using platinum foil, antimony may be detected in the solution of the sulphides of antimony and tin in concentrated hydrochloric acid as ordinarily obtained in the course of analysis, by diluting a portion of this solution with an equal volume of water, adding a piece of arsenic-free zinc to the cooled liquid in a test-tube, and allowing the issuing gases to impinge on a piece of filter-paper freshly moistened with a 10% solution of silver nitrate. In presence of antimony the paper will become quite black on the under side within two minutes, or immediately if considerable quantities are present. A slight brown coloration is to be disregarded, and it is important that the silver solution is not too concentrated, otherwise small amounts of hydrogen antimonide may cause only a brownish-yellow coloration instead of black, as is always obtained with dilute silver solutions.

G. F. M.

Detection of Benzene in Light Petroleum. P. SCHWARZ (*Chem. Ztg.*, 1922, **46**, 401).—If 5 c.c. of pure light petroleum are added to 2 c.c. of a mixture consisting of equal volumes of aniline and 95% alcohol, the aniline separates as a layer; should as little as 5% of benzene be present in the light petroleum, the aniline does not separate from the mixture and a clear solution is obtained. If desired, the light petroleum may be fractionated previously, and the test applied to the fraction having b. p. 80° to 110° .

W. P. S.

The Detection and Estimation of Acidity and Alkalinity in Cotton Fabrics. HUBERT FRANK COWARD and GLADYS MARY WIGLEY (*Trans. Text. Inst.*, 1922, **13**, 121—126).—The testing of cotton fabrics for traces of strong acids, such as might

give rise to "tendering," is complicated on the one hand by the fact that cotton exhibits a preferential attraction for the basic constituent of neutral salts and thus produces an acid reaction in their aqueous solutions, and, on the other, by the fact that cotton retains absorbed mineral acids so tenaciously that they can only be completely removed by repeated extractions with boiling water. It is now shown that the first factor is of far less moment in the titration of acid in the presence of the fabric than the second factor would be in a titration of the extract. Acidimetry of bleached cloth, correct to 0.01% of hydrochloric or sulphuric acid, and alkali-metry, correct to 0.02% of soda, calculated as sodium hydroxide, can be carried out by titrations with 0.02*N*-solutions, at the boil, in the presence of the fabric, using phenolphthalein as indicator. A fabric which contains up to 0.1% of sulphuric acid might, however, retain up to 0.05% after two extractions with boiling water.

The use of organic indicators, and a mixture of potassium iodide, iodate, and starch, for "spot" tests on the fabric is also described, and the sensitivity limits are indicated. Methyl-red is responsive to about 0.005% of strong acid or alkali. Difficulties arising from the presence of weak acids, soap, "finishing" compositions, and dyes are briefly discussed, but methods for testing raw cotton fabrics have still to be investigated.

J. C. W.

Estimation of Volatile Fatty Acids. G. WIEGNER and J. MAGASANIK (*Mitt. Geb. Lebensmitt. Hyg.*, 1919, **10**, 156—174; from *Bied. Zentr.*, 1922, **51**, 140—145).—In the distillation of aqueous solutions of volatile fatty acids the following relationship is established, $(\log y_1 - \log y_2)/(\log x_1 - \log x_2) = \text{constant}$, where y_1, y_2 , are the amounts of acid in terms of c.c. of standard alkali required for neutralisation of the residue at the beginning and end of a distillation interval and x_1, x_2 , the corresponding amounts of water. Values of the constant are given for the volatile fatty acids. The formula is applied to the estimation of volatile acids in silage. An example is given in which an aqueous extract containing acetic and butyric acids is made up to a known volume and distilled to half volume, the operation being repeated three times. From the titre of the distillates the acid value of each successive residue is obtained, whence by calculation the amounts of acetic and butyric acids respectively in the original extract are obtained. The method may be applied to the estimation of volatile acids in wines. Analytical figures are given for the amounts of acetic, butyric, and lactic acids in different kinds of silage.

G. W. R.

Analysis of Acetic Anhydride. A. RECLAIRE (*Perf. Essent. Oil Rec.*, 1922, **13**, 148—149).—Ten grams of acetic anhydride are weighed out into a 250 c.c. flask, diluted with 75 c.c. of water free from carbon dioxide, and heated on a water-bath for fifteen minutes under a reflux condenser. The product is diluted to 500 c.c. with a further quantity of carbon dioxide-free water, and 50 c.c. are titrated with *N*/2-potassium hydroxide solution free from carbonate. The percentage of acetic anhydride present is then $(\text{c.c. } N/2 \text{ KOH used} \times 17.144) - 570.45$. The necessity for using

water and alkali free from carbon dioxide is emphasised. The latter is readily obtained by mixing 1000 c.c. of ordinary potassium hydroxide solution with 50 c.c. of milk of lime, and after keeping one or more days the clear liquid is syphoned off and standardised.

G. F. M.

Detection and Estimation of Free Sulphuric Acid and Sulphoacetates in Cellulose Acetates. M. ENTAT and E. VULQUIN (*Ann. Chim. analyt.*, 1922, 4, 131—135).—To estimate free sulphuric acid, 10 grams of the cellulose acetate are digested for thirty minutes with 200 c.c. of water at 15°, the mixture is then filtered, and the filtrate is titrated with standardised barium hydroxide solution, the end-point being determined electrometrically. There is a sharp break in the titration curve when all the free sulphuric acid has been neutralised. None of the samples examined by the authors contained free sulphuric acid, and it is suggested that this acid is not present in normal cellulose acetates, the quantities found by other observers being actually due to the presence of alkali or alkaline-earth sulphates, acetic acid giving the acid reaction. Cellulose acetate prepared by methods involving the use of sulphuric acid as catalyst invariably contains sulphoacetic acid combined with the cellulose ester. The sulphoacetate is estimated by heating 10 grams of the cellulose acetate with 50 c.c. of water in an autoclave at 125° for five hours; the sulphuric acid resulting from this hydrolysis is then titrated electrometrically. The amount of sulphuric acid present as sulphoacetate in well-prepared cellulose acetate is always less than 0.03%. W. P. S.

Determination of the Iodine Value of Aliphatic and Aromatic Unsaturated Compounds. D. HOLDE, P. WERNER, IDA TACKE, and C. WILKE (*Chem. Umschau*, 1922, 29, 185—188).—The determination of the iodine value is a valuable criterion of the purity of higher unsaturated fatty acids and their derivatives when other methods, such as molecular weight and melting point determinations, fail, and has been used by Holde and Wilke in the case of erucic acid (this vol., i, 317). For this purpose, the Hanus reagent (10 grams of iodine monobromide in 500 c.c. of glacial acetic acid) is preferred, as it gives results in close agreement with those obtained with Hübl's reagent, and is more easily prepared, more stable, and more rapid in action, fifteen minutes being sufficient, with about 50% excess of the reagent, for the completion of the reaction. Accurate results are also obtained with aromatic unsaturated compounds, for example, safrole, under similar conditions. Nevertheless, as is well known, anomalous results are given by the Hübl-Waller reagent, and by Wijs's reagent for cholesterol and phytosterol, the former giving abnormally low, and the latter abnormally high results. With the original Hübl solution, however, consistent, although slightly high results (73—77 compared with 65.7 theoretical) were obtained with cholesterol, but with phytosterol values varying from 41 to 76 were obtained, according to the duration of the reaction and the excess of Hübl solution employed. With both alcohols, Wijs's solution gave values of

about 135, that is, approximately double the theoretical. A similar difference in the results obtained with the Hübl-Waller and with Wijs's reagents has been observed with mineral lubricating oils and with naphthenic acids, which may indicate the presence of cholesterol derivatives in these products. G. F. M.

Estimation of the Various Acids of Wine. TH. VON FELLENBURG (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 217—255).—The author has developed a scheme of analysis by means of which the separate proportions of weak organic acids (tannic acids) and of tartaric, malic, succinic, and lactic acids may be estimated. [Cf. *J. Soc. Chem. Ind.*, 1922, 514A.] T. H. P.

A Colorimetric Method for the Estimation of Homogentisic Acid in Urine. A. P. BRIGGS (*J. Biol. Chem.*, 1922, **51**, 453—454).—The method depends on the reduction of phosphomolybdic acid by homogentisic acid (cf. Bell and Doisy, *A.*, 1920, ii, 769). The diluted urine is treated first with a solution containing 5% of ammonium molybdate in 5*N*-sulphuric acid and then with a 1% solution of potassium dihydrogen phosphate. The colour produced is compared with a quinol standard, experiments having shown that 1 mg. of quinol is equivalent to 0.79 mg. of homogentisic acid. Albumin and sulphides interfere with the reaction, but these may be removed, if present, by means of trichloroacetic acid and silver sulphate. E. S.

Estimation of the Iodine-Bromine Number without using Potassium Iodide. L. W. WINKLER (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 201—204).—The use of potassium iodide in this estimation can be avoided by treating the oil or fat with excess of bromine, adding a solution of arsenious oxide, and titrating the excess of the latter with potassium bromate solution. A blank estimation is carried out, using the same quantities of the reagents as for the actual estimation and allowing them to react for the same length of time. The results are almost identical with those obtained from using potassium iodide solution according to the original method (*ibid.*, 1916, **32**, 358). H. C. R.

Use of Semi-microchemical and Microchemical Methods in Place of Macrochemical Methods in the Analysis of Foods. H. LÜHRIG (*Pharm. Zentr.-h.*, 1922, **63**, 218—221, 227—232).—The Reichert-Meissl, Polenske, saponification, and iodine numbers of fats and oils may be estimated on quantities of substance varying from 0.02 to 0.2 gram. The procedure employed is similar to that used in the methods in their usual form and is described in detail; in the case of the Reichert-Meissl number, the distillation requires about five minutes, 10 c.c. of distillate are collected (when 0.1 gram of fat is taken), and the result obtained must be multiplied by 0.9 to obtain the true Reichert-Meissl number. W. P. S.

The Constants of Indian Beeswax. O. D. ROBERTS and H. T. ISLIP (*Analyst*, 1922, **47**, 246—251).—Tables are given of the constants of twenty-three samples of honeycomb and wax

collected under the supervision of District Officers in Bengal, Eastern Bengal, and Assam. The low acid values obtained are remarkable, being in many cases lower than 6, the figure hitherto accepted as the lowest representing unadulterated Indian beeswax. Both Weinwurm's test and Salamon and Seaber's test are shown to be untrustworthy. H. C. R.

The Estimation of Aldehydes and Ketones by means of Hydroxylamine. A. H. BENNETT and F. K. DONOVAN (*Analyst*, 1922, 47, 146).—The method originally proposed for the estimation of citral in lemon oil (A., 1909, ii, 192) can be applied to other aldehydes and ketones. With formaldehyde, acetone, and benzaldehyde, very close results are obtained. Carvone requires rather more carefully standardised conditions. The analyses of citronellal and citral are slightly less accurate. No satisfactory results could be obtained for camphor. The hydroxylamine hydrochloride used for this process should be recrystallised from water, and not from alcohol. A. G. P.

The System Camphor-Alcohol-Water in Relation to the Titration of Camphor-spirit. K. SCHERINGA (*Pharm. Weekblad*, 1922, 59, 389—395).—The proportions of camphor, alcohol, and water which can remain in equilibrium in a single-phase system at various temperatures have been determined, and the results expressed graphically on the ordinary equilateral triangle presentation. Known solutions of alcohol and camphor were treated with water until a permanent separation occurred, and the increase in weight was then determined.

It is shown that many mixtures can be prepared to satisfy the requirements laid down in the Pharmacopœia, and that in analysing the preparation as recommended by titration with water the temperature must be kept between 20° and 25°, and also that the amount of camphor which can be added and held in solution at 15° should be specified. S. I. L.

The Detection of Vernin. H. STEUDEL and R. FREISE (*Z. physiol. Chem.*, 1922, 120, 126—129).—Vernin when boiled with acetic anhydride containing a small particle of sodium acetate and then cooled yields lustrous, pale rose needles, which after twice recrystallising from absolute alcohol give colourless prismatic needles of triacetylvernin, m. p. 226°, $[\alpha]_D^{25} + 2.306^\circ$. S. S. Z.

The "Cotton Wool Plug" Test for Indole. S. N. GORE (*Indian J. Med. Research*, 1921, 8, 505—507).—The under-surface of the plug is evenly moistened, first with a few drops of a solution of 1 gram of *p*-dimethylaminobenzaldehyde in 95 c.c. of absolute ethyl alcohol and 20 c.c. of hydrochloric acid, and then with a few drops of a solution of 1 gram of potassium persulphate in 100 c.c. of distilled water. The tube containing the plug, pushed down to about an inch above the surface of the broth culture, is placed upright in a gently boiling water-bath and heated for about fifteen minutes. Indole, when present to so small an extent as

0.0005 mg. per c.c. of the broth culture, volatilises and develops on the plug a rose colour which is viewed through the tube.

CHEMICAL ABSTRACTS.

The Detection and Estimation of Monoamino-acids. R. ENGELAND (*Z. physiol. Chem.*, 1922, **120**, 130—140).—The author estimated proline by means of his betaine method in glutin and elastin. The former protein showed a content of 10.9% and the latter of 4.3% of proline. The same method was applied in the case of ascitic fluid. Six and a half litres of fluid yielded 0.06 gram. of the chloroaurate of the betaine of leucine and 0.025 gram. of the chloroaurate of the betaine of lysine by this method. S. S. Z.

Colorimetric Estimation of the Amino-acid Nitrogen in Normal Urine. OTTO FOLIN (*J. Biol. Chem.*, 1922, **51**, 393—394).—Ammonia is removed by shaking with permittite and the estimation is then carried out as for blood (cf. this vol., ii, 540). E. S.

The Manipulations Preparatory to the Estimation of Amino-acids in Blood. FERNAND PETITJEAN (*Bull. Soc. Chim. Biol.*, 1922, **4**, 108—114).—For the preparation of blood for the estimation of its amino-acid content by Van Slyke's method, the author recommends, from the numerous methods which have been proposed, decomposition of urea by means of the soja bean, followed by precipitation of proteins by the addition of trichloroacetic acid. Details of the technique used are given in the original. E. S.

Estimation of Urea from the Carbon Dioxide Produced by Urease. ZOLTÁN ASZÓDI (*Biochem. Z.*, 1922, **128**, 391—395; cf. A., 1920, ii, 519).—An improvement in Partos's apparatus is described and examples given of its use. H. K.

A Micro-urease Method for the Estimation of Urea in Blood, Secretions, and Tissues. K. L. GAD-ANDRESEN (*J. Biol. Chem.*, 1922, **51**, 373—376).—The urea is first decomposed by means of urease and the ammonia then estimated by the method described for ammonia (this vol., ii, 523). A correction is made for the ammonia originally present. E. S.

The Estimation of Guanidine. A. H. DODD (*J. Soc. Chem. Ind.*, 1922, **41**, 145—147T).—The presence of guanylecarbamide, which is likely when guanidine has been prepared from dicyanodiamide and dilute acids, interferes with the estimation of guanidine as picrate, as this substance also gives an insoluble picrate with picric acid or ammonium picrate. It is found, however, that guanylecarbamide picrate is much more soluble in sodium hydroxide solution than the guanidine compound, and by choosing suitable concentrations it is possible to precipitate the latter whilst the former is retained in solution. The guanidine solution, of less than 1% strength, is added to 50 c.c. of the precipitant consisting of a solution of 20 grams of picric acid in 100 c.c. of N/1-sodium hydroxide solution. The precipitation is carried out in hot solutions

(90°), and the mixture kept for at least six hours before filtering through a Gooch crucible. The correction which would have to be applied to the weight of picrate obtained on account of its slight solubility in water can only be determined for each individual case, but empirically it was found that under the conditions above mentioned washing the precipitate with only 50 c.c. of water left just about sufficient sodium picrate behind to compensate for the solubility of guanidine picrate. It was found incidentally that precipitation of guanidylcarbamide by neutral sodium picrate was a distinct improvement on the use of picric acid. G. F. M.

The Method of Estimating Allylthiocarbimide in Mustard Flour. E. LUCE and A. DOUCET (*J. Pharm. Chim.*, 1922, 25, 458—464).—In estimating allylthiocarbimide by Dieterich's method, using ammoniacal silver nitrate, exact results may be obtained either volumetrically or gravimetrically, providing certain precautions are observed. In the case of mustard flour, the reaction is complete after six hours' contact even in the cold. Rise in temperature and extension of the time of maceration are both followed by a secondary reaction which destroys some of the essence formed at first, and hence a low figure is obtained. During the first hour of maceration, this secondary reaction is negligible whatever the temperature may be. Hence to obtain accurate results the duration of the maceration should be reduced to one hour and the essence left in contact with the ammoniacal silver nitrate in the cold for six hours or at 80—85° for one hour, using a flask with a reflux condenser. W. G.

Characteristics of Identity of a Water Distilled from the Cherry Laurel HENRI PECKER (*J. Pharm. Chim.*, 1922, [vii], 25, 424—429).—The distillate from the cherry laurel as officially prepared and containing 1 gram of hydrocyanic acid per litre should also contain a marked amount of benzaldehyde, usually above 3 grams per litre. Under such conditions, the amount of free hydrocyanic acid does not exceed 0.25 gram per litre. The distillate should give an almost immediate precipitate, in the cold, with Denner's phenylhydrazine reagent, and with a solution of ammonium molybdate in sulphuric acid should give a deep blue colour. W. G.

Potentiometric Titrations of and by means of Potassium Ferrocyanide. I. The Titration of Potassium Ferrocyanide by means of Potassium Permanganate. I. M. KOLTHOFF. (*Rec. trav. chim.*, 1922, 41, 343—352; cf. Kelley and Bohn, A., 1920, ii, 134).—In the potentiometric titration of ferrocyanides by means of potassium permanganate, the former solution should contain sufficient acid to prevent the precipitation of potassium manganese ferrocyanide, $K_2MnFeCy_6$. The acid may be either hydrochloric or sulphuric, the change of potential denoting the end-point being smaller with the former, but constant potential is more rapidly attained than with sulphuric acid. The author's experiments fail to confirm the objection that an error is intro-

duced owing to the liberation of chlorine by the action of hydrochloric acid on the permanganate. The method is accurate with ferrocyanide solutions of very small concentration. It is advantageous to add a definite quantity of potassium ferricyanide before titration, as, by this means, atmospheric oxidation of the ferrocyanide is avoided. The necessary stirring is effected by passing a current of carbon dioxide through the mixture. Details of experimental results with ferrocyanide solutions of different concentrations and in the presence of different amounts of both acids are given.

H. J. E.

The Estimation of Uric Acid in Tissue Extracts. H. STEUDEL and K. SUZUKI (*Z. physiol. Chem.*, 1922, **119**, 166—171).—The fresh spleen from cattle contains substances other than uric acid which reduce phosphotungstic acid to blue compounds. It is therefore pointed out that in order to obtain trustworthy results with Folin's method for the estimation of uric acid in tissues it is necessary to isolate the uric acid quantitatively previously to estimating it colorimetrically.

S. S. Z.

Methods for the Estimation of the Alkaloids. PAUL HERZIG (*Arch. Pharm.*, 1922, **259**, 249—308).—A comprehensive and critical survey of all the known methods, gravimetric, volumetric, colorimetric, refractometric, and polarimetric, for the estimation of alkaloids. Direct weighing, although possessing many obvious advantages, has the great disadvantage that it is difficult without loss to isolate the alkaloid in a sufficiently pure condition. Of all the methods suggested for weighing as insoluble salts or double salts only precipitation by picric acid, phospho- or silico-tungstic acid, or picrolonic acid (dinitrophenylmethylpyrazolone) have any practical value, and of these only the latter is considered really useful for practical purposes, and even here comparative estimations made on nux vomica seeds and extracts showed that the results obtained were always 2.5—5% low. Of the volumetric methods titration with standard acid is the most generally employed, iodometric estimations are not to be recommended, but iodometric estimation with iodide-iodate of the excess of acid unneutralised by the alkaloid gives good results except in the case of feebly basic alkaloids the sulphates of which are much dissociated, for example, narcotine, pilocarpine, and purine derivatives, and is particularly useful if much colouring matter is present. Volumetric precipitation methods using Meyer's reagent, phosphomolybdic acid, potassium ferrocyanide, or picric acid are regarded as inexact except in special cases such as ferrocyanide for the estimation of strychnine in presence of brucine, and picric acid for the cinchona alkaloids. Quantitative colorimetric and optical methods all demand the isolation of the alkaloid in a colourless condition, and they are often cumbersome as well, and consequently are very little used.

G. F. M.

The Titration of the Cinchona Alkaloids and their Salts. N. SCHOORL (*Rec. trav. chim.*, 1922, **41**, 228—235; *Pharm. Weekblad*, 1922, **59**, 369—374).—The neutralisation curves of quinine

and hydrochloric acid have been determined, using methyl-orange, methyl-red, neutral-red and phenolphthalein as indicators, both in aqueous solution and in 50% alcohol. The addition of alcohol to the aqueous solution diminishes the dissociation constant of quinine, thus rendering the base less alkaline and increasing the hydrolysis of the salts; but as the dissociation constant of the indicators is diminished at the same time, the experimental results obtained in alcoholic solution may appear to contradict this statement. Methyl-orange and methyl-yellow are unsuitable owing to indefinite end-points. Titration of quinine as a monacid base can be carried out very accurately with the use of methyl-red. The monohydrochloride is alkaline to methyl-red and acid to neutral-red; this property may be made use of, not only for quinine, but also in the case of the other cinchona alkaloids. Cinchonine gives similar results. Experimental details of the titrations are given. H. J. E.

[Detection of] Quinotoxine in Quinine Salts. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1922, **61**, 193—199).—The presence of quinotoxine in a salt of quinine may be detected as follows: The salt is dissolved in water, if necessary with addition of sulphuric acid, and the solution rendered alkaline by means of sodium hydroxide and extracted with ether or chloroform. After separation of the solution and evaporation of the solvent, part of the residue is carefully evaporated to dryness with a few drops of concentrated nitric acid. If quinotoxine is present, the residue thus obtained is deep yellow and is turned intense brownish-yellow by ammonia solution. The remainder of the residue from the solvent is dissolved in a little warm water acidified with acetic acid and the solution filtered if necessary. One portion is shaken with a little sodium nitrite, the nitrous acid liberated converting the quinotoxine into its nitroso- and nitroso-oximino-derivatives, which form a yellow precipitate; on quinine, nitrous acid has no action. Another portion is shaken with a drop of phenylhydrazine, the quinotoxine phenylhydrazone formed being gradually deposited as a precipitate which ultimately becomes deep orange-yellow; here also quinine remains unaffected. Bromophenylhydrazine gives a deep red coloration with quinotoxine. Solutions of quinine salts which turn yellow when sterilised probably contain quinotoxine and should not be employed for medicinal purposes. T. H. P.

Colorimetric Methods for the Separate Estimation of Tyrosine, Tryptophan, and Cystine in Proteins. OTTO FOLIN and JOSEPH M. LOONEY (*J. Biol. Chem.*, 1922, **51**, 421—434).—Certain defects in the method of Folin and Denis (*A.*, 1912, ii, 1012) for the estimation of tyrosine are remedied, and an extension is made to include the separate estimation of tryptophan and cystine. When tryptophan is to be estimated, the protein is hydrolysed by means of barium hydroxide to avoid loss due to humin formation. In the case of cystine, which is decomposed by boiling alkali hydroxides, acid-hydrolysis is used. For the estimation of tyrosine and tryptophan, the hydrolysate, which must contain between 3.5% and

7.5% of sulphuric acid, is filtered from barium sulphate, and tryptophan is precipitated from an aliquot part of the filtrate by the addition of Hopkins and Cole's mercuric sulphate reagent. After separation by centrifuging, tyrosine is estimated colorimetrically in the supernatant liquid by means of Folin and Denis's phenol reagent in the presence of sodium carbonate and sodium cyanide. The estimation of tryptophan is made similarly in the solution obtained by dissolving the mercuric sulphate precipitate in sodium cyanide. In the case of cystine, sodium carbonate is added to the hydrolysate and the cystine is reduced by means of sodium sulphite. The colour produced on addition of the uric acid reagent is then compared with a standard. Results of the application of the method to a number of proteins are given. E. S.

A System of Blood Analysis. Suppl. III. A New Colorimetric Method for the Estimation of the Amino-acid Nitrogen in Blood. OTTO FOLIN [with HSIEN WU] (*J. Biol. Chem.*, 1922, 51, 377—391; cf. A., 1919, ii, 308; A., 1920, ii, 337).—The method described is applicable to the tungstic acid filtrate and depends on the red coloration which is produced when amino-acids react with β -naphthaquinonesulphonic acid in alkaline solution. Five or 10 c.c. of the filtrate are used. One per cent. sodium carbonate and a 0.5% solution of the sodium salt of the sulphonic acid are added under specified conditions and the mixture is left for thirty hours in the dark. The colour is then intensified by the addition of an acetic acid-sodium acetate solution, after which the surplus quinone is decolorised by means of a 4% solution of sodium thiosulphate. A glycine solution is used as a standard. In the cases of histidine and tryptophan only one nitrogen atom reacts. Proline, tryptophan, arginine, and, to a lesser extent, alanine give unsatisfactory results. Ammonia also gives the coloration with the reagent, but this may be neglected in blood analysis. The blue colour which indole gives with β -naphthaquinonesulphonic acid is not produced under the conditions of alkalinity used in the estimation. E. S.

Use of the Conventional Carbon Factor in Estimating Soil Organic Matter. J. W. READ and R. H. RIDGELL (*Soil Sci.*, 1922, 13, 1—6).—In soil analysis it is usually assumed that 58% of carbon represents 100% of organic substance, this ratio being based on the results obtained by various observers. Estimations of the carbon content of thirty-seven surface soils from different parts of the United States showed that the percentage varied from 30.20 to 56.27, the average being 49.26, which is about 9% below the accepted value. The authors consider that the trustworthiness of any carbon factor is doubtful; if one is employed, more accurate results will be obtained if it is based on 50 to 52% of carbon.

W. P. S.

General and Physical Chemistry.

Optical Properties of certain Substances important in Microchemistry. LUIGI RAITERI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 112—116).—The following refractive indices have been measured: sodium uranylacetate, 1.5082 ($\lambda=535$), 1.5044 (589), 1.5003 (671); sodium silicofluoride, 1.3112 (677), 1.3125 (589), 1.3132 (535), 1.3146 (458); potassium silicofluoride, 1.339; potassium platinichloride, 1.8103 (677), 1.8209 (606), 1.8353 (535), 1.856 (458).
T. H. P.

Aspects of the Neon Spectrum. LAURENCE ST. C. BROUGH-HALL (*Phil. Mag.*, 1922, [vi], **44**, 204—214; cf. this vol., ii, 213).—An attempt to explain the spectrum of neon by the application of the principles of Bohr and by the employment of the Langmuir hypothesis of the cubic atom. After making certain assumptions with regard to the axes of revolution of the outer electrons and taking the value $2c=1.30 \times 10^{-9}$ cm. for the radius of the neon atom (W. L. Bragg, A., 1920, ii, 537), it is shown that the radius of the orbit of the two inner electrons in the normal atom is $r=6.19 \times 10^{-9}$ cm. This figure does not apply to the atom in the gaseous state. From these two values of c and r the wave-lengths of the spectral lines have been calculated. The discussion of the ionised atom is very complex, the general mathematical treatment being impossible without further experimental evidence. Ionisation may occur by an electron penetrating the nucleus of the neon atom. The result of the alteration in the charge on the nucleus is to increase the number of lines in the part of the spectrum of greater wave-length.
W. E. G.

The Structure of the Line $\lambda=6708 \text{ \AA}$. of the Isotopes of Lithium. J. C. MCLENNAN and D. S. AINSLIE (*Proc. Roy. Soc.*, 1922, [A], **101**, 342—348).—When strong arcs are maintained in the vapour of metallic lithium the wave-length $\lambda=6708 \text{ \AA}$. consisted of a close quartet with separations of 0.128 \AA ., 0.173 \AA ., and 0.165 \AA .. It is possible that these lines are two doublets of Li^6 and Li^7 . The doublet of Li^7 should be about sixteen times as intense as that of the Li^6 form. If a and c of the four components is ascribed to Li^6 and the components b and d to Li^7 , then the relative intensities would fit the relative amounts of isotopes present. On this basis, the doublet separation of Li^6 would be 0.301 \AA . and for Li^7 0.338 \AA ., instead of 0.55 \AA . calculated on the basis of the law known to hold for the other alkali elements. The isotope separation on this view would be 0.128 \AA . to 0.165 \AA .. If a and b and c and d are the two doublets, the average isotope separation would be 0.32 \AA .. Line $\lambda=6103.77 \text{ \AA}$. consisted of at least three well-defined components and $\lambda=4602.37 \text{ \AA}$., although difficult to resolve, had as a minimum two components.

W. E. G.

The Absorption Spectrum of Sulphur for X-Rays. AXEL LINDH (*Compt. rend.*, 1922, 175, 25—27).—A study of the absorption spectra of sulphur in its different combinations shows that, as in the case of chlorine (A., 1921, ii, 344), the limits of absorption K for sulphur are displaced towards the shorter wave-lengths for the higher valencies. The differences between bivalent and quadrivalent and sexavalent sulphur respectively corresponds with 7 and 11 volts. The absorption spectra of the thiosulphates offer a special interest in that they show two different limits of absorption, one corresponding with bivalent sulphur and the other with sexavalent sulphur. W. G.

The Precise Measure of the Layers of Energy of the Barium Atom and the Appearance of the L -Spectrum of Ionisation. A. DAUVILLIER (*Compt. rend.*, 1922, 174, 1543—1546).—Using the method previously described (A., 1921, ii, 421, 475 ; this vol., ii, 463), the author has studied the high frequency spectrum of barium. The photographs show two white rays, L_1 and L_2 , the positions of which coincide with those of the limits of absorption. These two rays are immediately followed by two weak black lines of slightly greater wave-length. From these rays the energy of the layers of low frequency has been measured, and for the layer P the value found is 7.0 ± 0.3 volts, although the ionisation potential of barium vapour has been found to be 5.2 volts. The doublet $\gamma_2 \gamma_7$ has been found for barium, γ_3 being much more intense than γ_7 , and each of these rays has a satellite of greater wave-length. Further, a number of weak rays have been found which are satellites of the principal rays, and certain lines of ionisation have been noted and measured. The wave-lengths of the L -rays for barium are tabulated and their intensities given, and amongst these are certain new lines which cannot at present be attributed with certainty to barium. W. G.

A New Absorption Phenomenon Observed in the Domain of X-Rays.—M. DE BROGLIE and A. DAUVILLIER (*Compt. rend.*, 1922, 174, 1546—1548).—The existence of absorption rays in the neighbourhood of the limits of high frequency has previously been recorded (A., 1920, ii, 655 ; 1921, ii, 475). A study of the L emission spectrum of barium, without the interposition of any screen, has shown such rays to be much more apparent and without any absorption band being visible (preceding abstract). This phenomenon is attributed to the state of intense ionisation in which the barium atoms occupying the focus of the anticathode are found. W. G.

Spectral Study of the Triboluminescence of Sucrose. HENRI LONGCHAMON (*Compt. rend.*, 1922, 174, 1633—1634).—The spectrum of triboluminescence of sucrose shows almost all the constituents of the second positive band spectrum of nitrogen and no others. The triboluminescence of sugar is thus due to a

discharge in the air between two solid particles which have just been suddenly separated and are electrically charged. A triboluminescent effect may be obtained in a tube in which sugar has been finely powdered by shaking, the tube being evacuated by sudden compression or expansion of the residual air. W. G.

The Fluorescence of Mercury Vapour Excited by Röntgen Rays. J. STEPH. VAN DER LINGEN (*Z. Physik*, 1922, **10**, 38—40).—The fluorescence spectrum of mercury vapour at low densities, obtained with soft Röntgen rays, consists of two structureless bands and five emission lines. The bands reach from 4350 to 5500 and from 3100 to 3600 Å., and have their maxima at 4350 and at 3300 Å. The emission lines are 3140 Å., 3660 Å., 4050 Å., 4350 Å., and 5500 Å. The spectrum excited by Röntgen rays is in no way similar to that excited by ultra-violet light between 1860 and 2550 Å., with the possible exception of bands in the visible spectrum. In no case was any trace found of the lines 2536 and 2346 Å. discovered by Steubing (*Physikal. Z.*, 1909, **10**, 797).

W. E. G.

The Characteristic Röntgen Radiation from Carbon and Boron. J. HOLTSMARK (*Physikal. Z.*, 1922, **23**, 252—255).—Measurements are made of the *K* radiation for boron and carbon, and these are compared with the previous values of Richardson and Bazzoni (this vol., ii, 14), Hughes (this vol., ii, 184), and Kurth (*Physical Rev.*, 1921, **18**, 461). The wave-lengths of the *K* radiation of carbon and boron are $\lambda=42.9$ and $\lambda=83.6$, respectively. The boron point is not in line with the *K_α* emission points for other elements. Theoretical reasons are advanced to account for this deviation.

W. E. G.

The Chemical Action of Penetrating Radium Rays.
XIV. The Action on Oxalic Acid, Potassium Tetroxalate, and Potassium Chlorate. ANTON KAILAN (*Monatsh.*, 1922, **43**, 1—12).—When a 0.01 *N*-solution of oxalic acid was exposed for 2136 hours to the action of the rays from about 100 mg. of radium, a considerable loss of acidity occurred and a smaller loss of reducing power when titrated with permanganate. The radiated solution contained also formic acid and an aldehyde. The quantitative determinations showed that the greater part of the oxalic acid which disappears decomposes according to the equation $C_2H_2O_4 = CO_2 + H \cdot CO_2H$. Some hydrogen peroxide is formed according to the equation $C_2H_2O_4 = 2CO + H_2O_2$, and this causes the apparent loss of oxalic acid, as shown by the permanganate titration, to be smaller than the loss estimated by acidity. From previous work on the equilibrium of hydrogen peroxide under the influence of radium rays (this vol., ii, 466) it is concluded that the decomposition of the oxalic acid is not conditioned by hydrogen peroxide formation. In presence of uranium nitrate, oxalic acid disappeared at the same rate under the influence of radium rays as in its absence,

but no formic acid was found in the radiated solution. Experiments showed that the decomposition of formic acid by the rays was not accelerated by uranium nitrate, and it must be concluded that no formic acid is produced from the oxalic acid when the uranium salt is present. On the other hand, more hydrogen peroxide is formed, as shown by the permanganate titre of the radiated solution. The ratio of number of molecules affected by the rays, m , to number of ion pairs, n , is in each case 0.3, whether calculated on oxalic acid or hydrogen peroxide.

* Under the influence of rays from a quartz mercury lamp, in absence of uranium salt decomposition of the oxalic acid occurred without formation of formic acid, whilst in presence of uranium salt much formic acid appeared and the permanganate titre fell more rapidly than the acidity.

When potassium tetroxalate solution was exposed to radium rays, less formic acid and more hydrogen peroxide was produced than when oxalic acid was used. The lower hydrogen-ion concentration might have led to more rapid decomposition of the formic acid. The rays from the quartz mercury lamp resulted in hydrogen peroxide formation but no formic acid; in presence, however, of uranium nitrate 1 mol. of formic acid was found for each mol. of oxalic acid disappearing.

Potassium chlorate in 0.1*N*- to 0.01*N*-solution undergoes very slight reduction to chloride by prolonged action of radium rays at 8—14°. After sixty-four hours' exposure at 45—50° to the rays of a quartz mercury lamp there was only slight reduction, about equal to that produced by 1000 hours' exposure to radium rays.

E. H. R.

The Binding of Electrons by Atoms. J. W. NICHOLSON (*Phil. Mag.*, 1922, [vi], 44, 193—203).—A mathematical paper in which it is shown that the hyperbolic orbits of Epstein which have been used extensively in the interpretation of certain groups of X-rays rest on a mathematical error. A determinate and finite value of W cannot be obtained for an electron moving about any atomic nucleus, if the path involved takes the electron to infinity.

W. E. G.

New Differential Method for the Measurement of the Conductivity of Electrolytes. L. ROLLA and L. MAZZA (*Gazzetta*, 1922, 52, i, 421—428).—The apparatus used in this method consists of an induction coil, I , a resistance box, R , a telephone, T , and three coils, P_1 , P_2 , and S , wound on an iron core. P_1 and P_2 have equal resistances and coefficients of self-induction, and the three coils together form a differential transformer with two primary circuits and one secondary.

The electrolytic resistance, X , to be measured is connected, in series with the induction circuit, P_1 , to the terminals of the induction coil; the resistance box is similarly connected, in series with P_2 , to the same terminals so that the current at any moment flows

through P_1 and P_2 in opposite directions. S is connected directly to the telephone.

Consideration of the two circuits XP_1I and RP_2I shows that P_1 and P_2 produce at any instant two opposite magnetic fluxes, F_1 and F_2 , the resultant flux being $F_1 - F_2$. When $F_1 - F_2 = 0$, the *E.M.F.* induced in S is zero and the telephone is silent; this condition is evidently satisfied when X and R are equal. The arrangement of P_1 , P_2 , and S on a cylindrical iron core gives poor results, but if the core consists of two L-shaped pieces juxtaposed to form a rectangle and P_1 and P_2 be wound together on one long side and S , composed of three separate coils capable of being grouped variously, be wound on the opposite long side of the core, excellent results are obtained. The sensitiveness of the method may be greatly increased by the use of the audion. T. H. P.

The Electromotive Properties of Magnesium and the Potentiometric and Thermal Analysis of the System Magnesium—Mercury. R. PH. BECK (*Rec. trav. chim.*, 1922, **41**, 353—399).—The normal potential of magnesium has not been ascertained with certainty, and as some magnesium amalgams in contact with solutions appear to yield as great a potential difference as the metal itself, the author has extended the work of Cambi and Speroni (A., 1915, ii, 453) on the thermal analysis of magnesium amalgams in an endeavour to complete the fusion diagram, to investigate the potential differences due to amalgam as compared with those due to the pure metal, and to ascertain whether the values obtained for the potential are in accord with the dilution law. The figures given by Cambi and Speroni (*loc. cit.*) for amalgams containing from 70 to 84 atomic % of mercury are confirmed; no measurements were made for higher percentages. The following compounds were found in the system: MgHg_2 , transition temperature 170° , at which it is coexistent with MgHg ; MgHg , m. p. 625° ; Mg_3Hg_2 , m. p. 562° ; Mg_2Hg , m. p. 580° ; and the thermal diagram is given and discussed in detail. The existence of Mg_{10}Hg , stated by Kremann and Muller, is disproved; it is suggested that their mixtures were not sufficiently heated to attain equilibrium. The vapour pressures of two amalgams were measured, but little value is claimed for the results owing to experimental difficulties; similar measurements made by Kremann and Muller are criticised for the same reason.

Determinations of the potential differences between amalgams varying from 0—60 atomic % of mercury in a solution of anhydrous magnesium chloride of 0.1982*N*-concentration in ethyl alcohol against a calomel electrode were made. The results obtained show considerable fluctuations with change of composition of the amalgam, but no conclusion is drawn that these correspond with new phases. It seems, however, that no mixture or compound of the two constituents is more negative than magnesium itself. The author points out that the usual method of preparing amalgams for such

experiments does not exclude the possibility of working with a metastable substance and that measurements made against aqueous solutions may give too low a value but never too high. Further, if the potential difference undergoes the normal change on dilution, this would tend to confirm the accuracy of the figure obtained. But in the case of magnesium, the potential becomes less positive with increasing dilution. In order to compare the potential of magnesium and of magnesium amalgams in contact with neutral acid and alkaline solutions, several series of experiments were carried out in which the measurement was made in open vessels, using a normal calomel electrode. The conclusions drawn are that the potential of magnesium may be measured in acid solution and that the figures obtained differ but little from those for magnesium amalgams, that in neutral solution atmospheric oxygen may cause the metal to be somewhat passive, and that in alkaline solution there is a considerable tendency towards passivity. In the case of magnesium in contact with solutions of magnesium sulphate of various concentrations, the results appear to contradict the hypothesis put forward by Kistiakowsky (A., 1910, ii, 258), that magnesium passing into solution from an electrode is primarily transformed into the hydroxide. In acid solutions of different concentrations, the potential becomes more negative with increasing dilution; the figure finally reached is $E_H = -1.854$. Experiments on cathode polarisation of magnesium showed that measurements of potential made after interruption of the polarisation are never more negative than the highest values obtained for the metal and from its amalgam with no current passing. Thus this last figure should be considered as very close to the equilibrium potential which the author suggests is most probably $E_H = 1.856-1.876$ volts.

H. J. E.

Absorption of Hydrogen by Elements in the Electric Discharge Tube. F. H. NEWMAN (*Phil. Mag.*, 1922, [vi], 44, 215—226).—A further study of the behaviour of hydrogen in the presence of various elements in a discharge tube (cf. A., 1921, ii, 295). Evidence is obtained that the "clean up" of hydrogen in a discharge tube is partly due to chemical changes. On the admission of hydrogen, activated by an electric discharge, to the clean surface of a sodium-potassium alloy a white, crystalline compound was produced which was probably composed of the hydrides of the two metals. The white layer slowly changed to a dark grey deposit. Similarly, the activated gas gave hydrogen sulphide with sulphur. These effects were not due to the ions of the discharge tube, as these were eliminated by charged platinum strips before the gas reached either the alloy or the sulphur. Measurements were made of the rates of disappearance of hydrogen in the presence of sodium-potassium alloy, and of sulphur and other elements. A considerable proportion of this absorbed hydrogen was recovered when the tube was heated at 300°. Nitrogen, on the other hand, cannot be again liberated, even when the tube is heated to the softening point. The

modifications of hydrogen and nitrogen which are absorbed in the discharge tube are probably triatomic.

The absorption is not entirely due to chemical action, for the law of constant proportions does not appear to be followed.

W. E. G.

Rapid Electrolysis without Rotating Electrodes. GRAHAM EDGAR and R. B. PURDUM (*J. Amer. Chem. Soc.*, 1922, **44**, 1267—1270).—Rapid electrolysis may be carried out without the use of rotating electrodes if the solution is stirred by means of a current of air. A piece of apparatus is described for such analyses. The cathode is a platinum gauze cylinder in the centre of which is a spiral platinum electrode. The electrodes are contained in a glass tube 31 mm. diam. to which are sealed three glass "air lifts," connected in a single tube at the bottom and entering symmetrically about half-way up the wide tube, the seals being made tangentially. When air is forced into the apparatus half filled with liquid, both vertical and rotational stirring is effected. Experiments are described which show that the results obtained with this apparatus are equally as good as those obtained with rotating electrodes.

J. F. S.

An Electrochemical Study of the Reversible Reduction of Organic Compounds. J. B. CONANT, H. M. KAHN, L. F. FIESER, and S. S. KURTZ, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 1382—1396).—The authors have developed the general equation $\pi = \pi'_0 + 0.0295 \log \frac{[A]}{[AH_2]} - 0.0295 \log K_1K_2 + 0.059 \log [H^+] + 0.0295 \log \{K_1(K_2 + [H^+]/[H^+]^2) + 1\}$ (in which A represents the oxidised and AH_2 the reduced form) to express the oxidation-reduction potentials of compounds of the type of quinone in both acid and alkaline solutions. The potentials of six anthraquinonesulphonic acids have been measured by a titration method, using titanous chloride and sodium hyposulphite, and the results obtained over a wide range of hydrogen-ion concentration have been found to be in accord with the above equation. The validity of the method is shown by determinations of the potentials of mixtures of the reduced and oxidised compounds.

W. G.

Thermo-regulator. E. B. STARKEY and N. E. GORDON (*J. Ind. Eng. Chem.*, 1922, **14**, 541).—A thermo-regulator is described which is capable of giving a steady temperature to 0.05° . The regulator consists of a U-tube, connected through a short vertical capillary with a toluene container. The U-tube and capillary are filled with mercury, the two ends of which are connected with wires which form one of the leads of the heating lamp. Expansion of the toluene causes the mercury to be pushed away from one wire and so break the circuit, whilst contraction remakes the circuit. Corrosion of the mercury is prevented by filling the space above the mercury with an inert gas.

J. F. S.

Entropy of the Elements and the Periodic System. W. HERZ (*Z. Elektrochem.*, 1922, **28**, 258—259).—A theoretical paper in which the author shows that the entropy of the elements varies regularly in keeping with the arrangement of the elements in the periodic system. Using the entropy values calculated by Lewis and Gibson (*A.*, 1918, ii, 29), it is shown that in any group of the periodic system the value of the entropy increases with increasing atomic weight in the case of the metallic elements, the elements of the fourth group and the inactive gases, whilst the electro-negative elements of the oxygen and halogen groups have decreasing entropies with increasing atomic weights. J. F. S.

Proposal for the Fixing of a Unit of Measurement in Thermochemistry. W. SWIENTOSŁAWSKI (*Roczniki Chemji*, 1921, **1**, 479—487; cf. *A.*, 1921, ii, 679).—The following proposals were put forward at the International Chemical Conference at Brussels in 1921. The heat of combustion of 1 gram of benzoic acid, in cal. at 15°, should be taken as the unit, rather than that of cane-sugar, which is hygroscopic, or of naphthalene, which is liable to sublime. By using one substance only for the standard, many constant calorimetrical corrections would not be needed, and a simpler formula could be used. Certain discrepancies in the values for the heat of combustion of benzoic acid, as obtained by various workers, are pointed out, and also in the ratios for the heats of combustion of benzoic acid, cane-sugar, and naphthalene. It is proposed that the heat of combustion of benzoic acid at constant volume be taken provisionally as 6321 cal., with the proviso that the determination of this value be repeated as soon as possible, with the greatest possible accuracy, using the method of adiabatic measurements. R. T.

Temperatures of Combustion. J. BRONN (*Z. angew. Chem.*, 1922, **35**, 328).—The temperature of combustion of a gas is calculated from the heat of combustion and the specific heat of the products of combustion. An accepted figure for the combustion of hydrogen in pure oxygen is 6670°, which would presume the specific heat of steam to be 0.485. It is shown that the specific heat at 4000° may be taken at 0.85, from which the temperature of combustion may be calculated to be 3900°. The temperatures for carbon monoxide (5000°), methane (4400°), and acetylene (6200°) are given. The temperatures of combustion of gases are greatly influenced by their velocities of flame propagation, except in so far as flameless combustion affects the result. The velocities of flame propagation of ethylene, acetylene, and benzene differ. H. M.

Thermochemical Researches on Oximes. I. Ketoximes not Exhibiting Stereoisomerism. ALICJA DORABIALSKA (*Roczniki Chemji*, 1921, **1**, 424—447).—The heats of certain reactions of some ketoximes are measured. From the results so obtained, and from those obtained previously (W. Swientoslawski, *A.*, 1919, **2**, 336), various generalisations are made. The ketoximes used were

acetoxime, phenylmethylketoxime, and diphenylketoxime. The chief reactions studied are the formation of the hydrochloride of the oxime, its solution in 10% sodium hydroxide solution, and the formation of the sodium salt of the oxime. The results obtained, together with those calculated from these, are given in the following table, where q_{HCl} is the heat of formation of the hydrochloride, in ethereal solution. For aqueous solution this is expressed by q'_{HCl} . The heat of the solution of the hydrochloride in 10% sodium hydroxide solution is Q_{HCl} , in water, S_{HCl} . The heat of solution of the oxime in dilute sodium hydroxide solution is q , in water, S , in ether, S' . The degree of hydrolysis of sodium salts of these oximes is given as $\nu\%$. Results are expressed in calories per millimole.

	q_{HCl}	q'_{HCl}	q	$\nu\%$	Q_{HCl}	S	S_{HCl}	S'
Acetoxime .	10.93	1.19	5.70	39.6	17.16	-1.28	-1.95	-2.89
Phenylmethyl- ketoxime .	8.17	0.51	6.34	40.3	16.52	-2.98	-3.52	—
Diphenyl- ketoxime .	7.71	—	5.80	—	12.51	-4.06	-6.99	—

In the case of phenylmethylketoxime, the hydrochloride, prepared at different temperatures, and from different media, gave the same Q_{HCl} , thus showing that no stereoisomeric modification of this oxime is produced under the conditions in question.

It is concluded that the heat of formation of the hydrochlorides of the ketoximes differs little from that of the aldoximes, and diminishes as the acidity of the ketoxime increases. The heat of solution of these hydrochlorides diminishes with increasing acidity of the ketoxime, owing to a parallel increase in the negative heat of the solution, and decomposition of the former in water. Finally, the negative heat of solution of ketoximes in water appears to be greater than that of aldoximes. R. T.

Pycnometry. R. SAAR (*Chem. Ztg.*, 1922, **46**, 433—435).—Tables and formulæ are given for calculating specific gravities from one temperature to another. W. P. S.

An Experimental Comparison of the Viscous Properties of (a) Carbon Dioxide and Nitrous Oxide; (b) Nitrogen and Carbon Monoxide. C. J. SMITH (*Proc. Physical Soc.*, 1922, **34**, 155—164).—The viscous properties of these gases have been compared directly by observing the time required by a mercury pellet to force a certain volume of the different gases through a capillary tube. Measurements were carried out at different temperatures, absolute viscosities were obtained by comparison with air, and the mean area of collision deduced by using Chapman's formula.

The viscosities expressed in C.G.S. units $\times 10^{-4}$ are: carbon dioxide and nitrous oxide, 0.0° , 1.366; 15.0° , 1.441; 100.0° , 1.845. Carbon monoxide and nitrogen, 0° , 1.665; 15.0° , 1.737; 100.0° , 2.118. The mean collision areas in square centimetres are: carbon dioxide and nitrous oxide, 0.834×10^{-15} . Carbon monoxide and nitrogen, 0.767×10^{-15} .

The fact that carbon dioxide and nitrous oxide (or carbon monoxide and nitrogen) have molecular dimensions which are identical within experimental error is consistent with Langmuir's view that the outer electron arrangements of these molecules are the same; this is also supported by the fact that the viscosities are equal at the three temperatures chosen.

W. T.

Theory of Adsorption Processes. A. EUCKEN (*Z. Elektrochem.*, 1922, **28**, 257—258).—Polemical; an answer to Polanyi's criticism (this vol., ii, 479) of the author's paper on the theory of adsorption processes (this vol., ii, 262).

J. F. S.

Adsorption in Solution and at Interfaces of Sugars, Dextrin, Starch, Gum Arabic, and Egg-albumin, and the Mechanism of their Action as Emulsifying Agents. GEORGE L. CLARK and WILLIAM A. MANN (*J. Biol. Chem.*, 1922, **52**, 157—182).—Measurements were made of the surface tension and viscosity of solutions of the above substances for a large number of concentrations both with and without the addition of electrolytes. The interfacial tension between each solution and benzene was also measured, and the efficiency of the emulsifying agent with respect to both benzene and kerosene estimated. The factors of predominating importance in an emulsifying agent appear to be viscosity and ability to lower interfacial tension. In the case of sugar, viscosity is the more important, whilst with egg-albumin, which gave the best emulsions, film formation is of primary importance. Two types of agglomeration are distinguished, namely, that accompanied by an increase in viscosity, in which coalescence of the particles is accompanied by enclosure of water, and that producing a decrease in viscosity, in which there is a decrease both in surface and amount of bound water. Dextrin and starch, considered separately, provide examples of the former type. When these substances are considered in relation to one another, however, it is found that the viscosity curves run parallel, the curve for dextrin being slightly above that for starch, thus resembling the viscosity curves of sulphur sols of different degrees of dispersion (cf. Odén, A., 1912, ii, 1143). This is considered to be evidence that starch and dextrin differ merely in the degree of agglomeration (second type) of the particles, and thus to furnish experimental proof of the view put forward by Herzfeld and Klinger (A., 1920, i, 713).

E. S.

Carrying Down by Precipitates. PAUL DUTOIT and ED. GROBET (*J. Chim. physique*, 1922, **19**, 328—330).—The carrying down of soluble salts by precipitates is explained by the authors as due to the fact that the adsorption of these substances on the surface of the precipitate causes the soluble substance to attain locally a value which exceeds its solubility product and hence causes its precipitation. With the object of testing this hypothesis, the author has estimated calcium in the presence of magnesium

salts as oxalate, and barium in the presence of calcium both as sulphate and chromate. Two series of experiments were carried out, in the first stirring by hand with a glass rod was employed, and in the second series very rapid mechanical stirring was used. Very different results were obtained in the two series, but the values of the second series are in good agreement with the theoretical values, thus showing that soluble substances are not appreciably carried down by precipitates if the solution is rapidly stirred during the mixing.

J. F. S.

The Sorption of Neutral Soap by Wool, and its Bearing on Scouring and Milling Processes. BRITISH RESEARCH ASSOCIATION FOR THE WOOLLEN AND WORSTED INDUSTRIES (*Trans. Text. Inst.*, 1922, **13**, 127—142).—The sorption of soap from aqueous solution by carefully cleansed wool at 25° has been studied. Analyses of the solution were made after an arbitrarily fixed interval, without waiting for equilibrium to be established, and corrections were applied for the amount of water sorbed by the wool on the assumption that the material contains 15% of moisture under ordinary atmospheric conditions and 33% when immersed. The results indicate preferential sorption of the kation, and it is suggested that the fatty acid is removed from solution both by sorption and by precipitation on the fibre. With mixtures of soaps of oleic and palmitic acids, preferential sorption of oleic acid occurs, but the potassium and sodium oleates are almost identical in behaviour. The effect of the fatty acid is apparently to lower the sorption of alkali.

J. C. W.

Mordants. I. WILDER D. BANCROFT (*J. Physical Chem.*, 1922, **26**, 447—470).—A historical review of the use of mordants in dyeing.

J. S. G. T.

The Dissociation of Barium Platinichloride. G. GIRE (*Compt. rend.*, 1922, **174**, 1700—1703).—The author has measured the dissociation pressures of barium platinichloride over the temperature range 428° to 665°, and has obtained the equation

$$\log P = -3446.316/T + 7.702 \log T - 17.41669.$$

The dissociation of barium platinichloride is an equilibrium of the type, $\text{sol.} + \text{gas} \rightleftharpoons \text{sol.} + Q$, and the value of Q is calculated to be 30.35 cal. for the temperature 948°, which corresponds with a pressure of 760 mm.

W. G.

A Rapid Dialyser. A. GUTBIER, J. HUBER, and W. SCHIEBER (*Ber.*, 1922, **55**, [B], 1518—1523).—The apparatus consists of a wooden disk supporting a framework composed of glass rods in the form of a hollow cylinder. The membrane is passed over the framework and secured in its natural folds to the wooden disk. A stirrer is placed within the vessel, which is mounted in such a manner that the frame and stirrer can be rotated in opposite directions (the apparatus is fully figured in the original). The

apparatus is placed in an inverted, tubulated bell-jar, through the tubulus of which water is admitted, which can be heated or cooled by coils placed in the jar; the level of the water and its discharge are governed by a lever arrangement. Comparative experiments show the dialyser to be much more rapid in its action than those of Graham and Zsigmondy-Heyer. In addition to rapidity of action, the following advantages are claimed for the apparatus: extensive exclusion of external air from the internal liquid, from which, however, samples may readily be taken; small liability to changes in volume, particularly to dilution of the internal liquid; great safety in action, since only a single piece of parchment is used; simple method of securing a continuous change of external water; the possibility of dialysis at raised or lowered temperatures without complicated arrangements. H. W.

Dolezalek's Theory of Solutions. K. HERRMANN (*Z. angew. Chem.*, 1922, **35**, 349—351, 353—355).—A theoretical paper in which liquid mixtures and solutions are differentiated and discussed generally and in connexion with the Dolezalek theory of solutions. J. F. S.

Measurement of Solubility by Floating Equilibrium. Solubility of Lead Acetate. MERLE L. DUNDON and W. E. HENDERSON (*J. Amer. Chem. Soc.*, 1922, **44**, 1196—1203).—A new method for the determination of solubility is described. The method consists in placing a float, which has been calibrated so that it will just sink in a solution of known composition of the substance under investigation, into a weighed quantity of the saturated solution and adding the solvent until the float just sinks. The quantity of solvent added is noted, and from this, the weight of the solution taken, and the calibration constant of the float the solubility is readily calculated. This method has been applied to the determination of the solubility of lead acetate in water at temperatures from 0° to 50°. The following values in grams of lead acetate per 100 grams of water are recorded: 0°, 19.7; 5°, 23.7; 10°, 29.3; 15°, 35.6; 20°, 44.3; 25°, 55.2; 30°, 69.7; 35°, 88.9; 40°, 116.0; 45°, 153.0; 50°, 221.0. The method is capable of considerable speed or great accuracy, and in ordinary circumstances of a considerable amount of both. Some variation is found in duplicate experiments at the higher temperatures, which is shown to be due to the hydrolysis of the acetate followed by subsequent evaporation of acetic acid. J. F. S.

Influence of Electrolytes on the Solubility of Non-electrolytes. ANDREW MCKEOWN (*J. Amer. Chem. Soc.*, 1922, **44**, 1203—1209).—The heats of solution of ether in various solutions of sodium chloride have been calculated from Thorne's solubility data at 15° and 25° (T., 1921, **119**, 262), by means of an expression which connects solubility, heat of solution, and temperature, of the form of the van't Hoff isochore. Statistical

treatment of the phenomena of solution and precipitation leads to an expression for solubility, $S = Ae^{Q/RT}$, which is in agreement with the isochore relation mentioned above. The salting-out effect of salt on ether has been examined so far as the effect depends on the activities of the ions of the salt. It is shown that the relative specific influences of the kation and anion are -21.7 and $+67.1$, that is, the anion is the predominating factor in the process.

J. F. S.

Amorphous Precipitates and Crystalline Sols. F. HABER (*Ber.*, 1922, **55**, [B], 1717—1733).—The method of distinguishing between the crystalline and amorphous condition depends on the ability of crystalline substances to give Röntgen-ray interference fringes. The trustworthiness of the method is dependent on the conditions (i) that the lattice constants are not less than the half wave-length of the Röntgen rays employed, (ii) that they are not much greater, and (iii) that the material under investigation is uniform in its lattice properties.

Crystalline or amorphous, solid masses are obtained by supersaturation processes which may be considered to occur in two distinct phases, the formation of aggregates and the rearrangement of such aggregates, with loss of free energy, into ordered lattice formations. The former process can be studied conveniently in supercooled, molten masses of a uniform chemical material which may be regarded as unarranged molecular aggregates the further fate of which depends on their rate of arrangement. With regard to the process of arrangement, its energy is known (latent heat of liquefaction), and also that it is divisible into two parts, the formation of nuclei and their growth. Tammann's work on this subject has shown that the formation of nuclei frequently only occurs with considerable velocity at temperatures far below the melting point at which the nuclei can only grow very slowly; if, however, the mass is heated to just below its melting point, the nuclei grow rapidly and crystallisation occurs throughout the entire mass. Thermodynamical treatment of the subject shows that the minute aggregates are only stable when the condition is fulfilled that $AT/T = 2S/rqd$, in which AT/T is the fraction of the mass melting point T in absolute values by which cooling must occur if the solid phase, regarded as spheres of radius r , is to be in (labile) equilibrium with the molten mass. S is the specific free energy of the boundary surface, q the latent heat, and d the density of the solid phase.

The processes involved in the formation of precipitates and sols differ from those described above in that the rate of aggregation can be controlled by exceeding the limit of solubility to a greater or less extent. The connexion between the mass solubility H_M (solubility as generally accepted) and the solubility of the smallest aggregates, l , is given by the equation $2S'M/rd = RT \log l/L_M$, in which S' is the specific free surface energy of the particles, T the temperature of the experiment, d the density of the solid phase,

M the molecular weight, and r the radius of the particles regarded as spheres.

The considerations outlined above are applied to the formation of very sparingly soluble substances. If the rate of aggregation is high and as far as possible in excess of that of arrangement, amorphous precipitates are to be expected which gradually, particularly on warming, pass into the crystalline condition. If, however, the rate of aggregation is depressed by only slightly exceeding the solubility limit, the rate of arrangement may be sufficient to cause the orderly formation of crystals before the formation of visible particles has occurred. This, however, involves an alteration in the rate of aggregation due to electrical phenomena at the boundary of the molecules and liquid, the net result of which is that the growth of the aggregates is greatly impeded and sols are produced. These conclusions are illustrated by the cases of the precipitates and sols of aluminium or ferric hydroxides which, however, are to be regarded as the ideal case from which deviations are to be expected in two directions. If the rate of arrangement is greater, it is not to be expected that the precipitate will be obtained in the amorphous condition and be retained as such during the Röntgen exposure. The rate of arrangement may be expected to be at its maximum in binary, heteropolar compounds in which the bipolar character is most marked. (This is illustrated in the cases of the silver haloids and the sulphides of mercury, zinc, and cadmium). On the other hand, with molecules in which the bipolar character is not strongly accentuated, the tendency towards the formation of amorphous sols and precipitates must be more marked; this is illustrated experimentally by the cases of the hydroxides of zirconium and thorium.

H. W.

Molecular Arrangement and Liquid Crystal Formation.

D. VORLÄNDER (*Z. angew. Chem.*, 1922, **35**, 249—250).—A close relationship is shown to exist between the symmetry of the molecule and its capacity to form liquid crystals. This property is shown to the greatest extent by those molecules containing long chains of atoms and possessing a definite axis of symmetry. Thus para-substitution in the benzene ring is especially favourable to the formation of liquid crystals. The introduction of groups which destroy the symmetry of the molecule either reduces the range of stability or else completely destroys the power of formation of liquid crystals.

Benzidine derivatives $(\text{CHR}:\text{N} \langle \text{C}_6\text{H}_4 \rangle - \langle \text{C}_6\text{H}_4 \rangle \text{N}:\text{CHR})$ give liquid crystals with a great range of stability, but the introduction of a CH_2 group between the two benzene nuclei causes the disappearance of this enantiotropic form. On account of the angle between the carbon valencies ($109^\circ 28'$) the molecule will no longer be symmetrical. Similar results are obtained by the introduction

of CO, CS, S, and O groups into the same position. The NH group reduces the range of stability practically to zero, although monotropy is sometimes observed in these compounds. Further lengthening of the chain with the formation of diphenyl ethane derivatives causes a reappearance of the property, although it is not so strongly developed as in the diphenyl derivatives. The diphenylpropanes do not yield liquid crystals, which, however, appear again with the derivatives of diphenylbutane. The author explains these phenomena by the departure of the molecule from the straight line arrangement.

W. E. G.

Electrical Precipitation of Colloids. CLAUDE HAINES HALL, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 1246—1249).—Finely divided suspensions of arsenious sulphide, mercuric sulphide, prussian blue, barium sulphate, aluminium, copper, lead, silver, and iron, in transformer oil of resistance 1.5×10^{16} ohms per c.c., have been subjected to alternating and direct currents of voltages from 10^4 to 2×10^5 with the object of effecting a precipitation. In no case was any precipitation brought about, even although the current was applied for three hours. A theoretical treatment of the subjects shows that the rate of precipitation would be $1/20000$ of that for smoke for the same application of energy.

J. F. S.

A Static Method of Study of Hydration. MARCEL GUICHARD (*Bull. Soc. chim.*, 1922, [iv], **31**, 552—554).—A simple form of apparatus is described in which it is possible to follow the equilibrium between an absorbent substance and water vapour in a vacuum and over a fairly considerable range of temperature. It consists of a glass tube to contain the absorbent substance and having sealed to it at right angles a graduated tube which contains the water. The whole is evacuated and sealed off. The two parts of the apparatus can be maintained at different temperatures as desired.

W. G.

The Geometric Representation of Saline Equilibria. HENRY LE CHATELIER (*Compt. rend.*, 1922, **174**, 1501; cf. A., 1894, ii, 223).—A reaffirmation of priority in the method of representing saline equilibria by square diagrams as opposed to the claim of Jänecke (this vol., ii, 427).

W. G.

Effect of an Electrolyte on Solutions of Pure Soap. Phase-rule Equilibria in the System Sodium Laurate-Sodium Chloride-Water. JAMES WILLIAM MCBAIN and ARTHUR JOHN BURNETT (T., 1922, **121**, 1320—1333).

The System Silver Perchlorate-Water-Benzene. ARTHUR E. HILL (*J. Amer. Chem. Soc.*, 1922, **44**, 1163—1193; cf. A., 1921, ii, 261).—The ternary system silver perchlorate-water-benzene and the binary systems made up of pairs of the components have been investigated. It is shown that the system silver perchlorate-water has a eutectic point at -58.2° , at which temperature the saturated solution contains 73.9 % of the silver salt. This is

the lowest eutectic known for a true salt and water. The solubility of silver perchlorate rises to 88.8 % at 99°. The eutectic of silver perchlorate-benzene is at +5.12° and the solution contains 3.44 % of the silver salt. The solubility curve rises steeply with the temperature, reaching an almost perpendicular form between 50° and 145°; at the latter temperature the saturated solution contains 63.0 % of silver perchlorate. Attention is directed to the similarity between this solubility curve and those which are found where the system gives rise to two liquid phases, either in the stable or metastable region. The hydrate $\text{AgClO}_4 \cdot \text{H}_2\text{O}$ has been isolated and its transition temperature found to be 43.1°; the compound $\text{AgClO}_4 \cdot \text{C}_6\text{H}_6$ has also been isolated and its transition point found to be 145°. The ternary system, silver perchlorate-water-benzene is marked by the possession of six realisable invariant equilibria, and a very large number of univariant equilibria, which furnish at least one example of every type of equilibrium theoretically possible for a ternary system containing volatile components. The ternary eutectic representing three solid phases, solution, and vapour, lies at -58.4°, and the eutectic of highest temperature is at 42.1°. The course of the twenty-four univariant equilibria originating at these two quintuple points and the four intermediate quintuple points has been investigated. Isothermal diagrams have been constructed to show the various equilibria existing at temperatures between -58.4° and +145°. Between 5.24° and 23.4° three coexistent liquid phases can be prepared in stable equilibrium with each other and their vapour. The occurrence of two separate fields of unsaturated solution is explained as due to the intersection of the solubility curve of silver perchlorate with the bi-nodal curve representing the limited solubility of benzene and water. The occurrence of a third field is explained as due to the existence, between -2.7° and +30°, of an additional closed bi-nodal curve which does not extend to any one of the two component axes at any temperature. It appears that this is the first demonstrated case of a closed bi-nodal curve.

J. F. S.

Use of Iron Pyrites in a Friedel-Crafts' Reaction. JOHN ARMSTRONG SMYTHE (T., 1922, 121, 1270—1279).

Combination in Detonating Gas in Presence of Colloidal Palladium Solution. C. SANDONNINI and A. QUAGLIA (*Gazzetta*, 1922, 52, i, 409—416; cf. this vol., ii, 557).—In mixtures containing only hydrogen and oxygen, the reaction in presence of colloidal palladium solution is proportional to the concentration of the detonating mixture. If, however, this concentration is the same in two cases, the velocity of reaction is somewhat the greater when the hydrogen is in excess than when the oxygen is in excess. Since it is also found that the reaction of combination in pure detonating gas may be accompanied by phenomena of reduction or hydrogenation, the conclusion is drawn that in this case the combination is due to the action of active hydrogen.

The hydrogenation of ethylene and the formation of water have velocities of the same order when the ratio between the amounts of hydrogen and oxygen is that normal to detonating gas. When ethylene and oxygen are in concentrations requiring the same quantity of hydrogen and the latter is present in sufficient amount for both reactions, the latter proceed with almost equal velocities; when, however, the amount of hydrogen is insufficient for either reaction, only the formation of water occurs to an appreciable extent. T. H. P.

Limits for the Propagation of Flame in Vapour-Air Mixtures. I. Mixtures of Air and One Vapour at the Ordinary Temperature and Pressure. ALBERT GREVILLE WHITE (T., 1922, 121, 1244—1270).

Limit of Inflammability of the Vapours of the System, Alcohol-Petrol, and of a Triple System with a Basis of Alcohol and Petrol. ROGER G. BOUSSU (*Compt. rend.*, 1922, 175, 30—32).—A study of the variation of the lower limit of inflammability of the binary system petrol-alcohol and of the ternary system petrol-alcohol-ether, using the method of Le Chatelier and Boudouard (A., 1898, ii, 574). The results verify the formula $n/N + n'/N' = 1$, where N and N' are the limits of inflammability of each of the two vapours and n and n' the proportions in which they are present in the mixture under examination. W. G.

A Study of the Rate of Saponification of Oils and Fats by Aqueous Alkali under Various Conditions. MABEL HARRIET NORRIS and JAMES WILLIAM MCBAIN (T., 1922, 121, 1362—1375).

Behaviour of certain Metals as Catalysts. I. C. SANDONNINI (*Gazzetta*, 1922, 52, i, 394—408).—The author has carried out a number of series of experiments with the object of ascertaining the behaviour of a catalyst, highly active in the case of two separate, analogous reactions, when it is introduced into a system in which both these reactions can occur. The catalysts employed were platinum black, reduced nickel, copper, and silver, and the systems were composed of hydrogen and oxygen, mixed with either ethylene, or phenanthrene, or nitrobenzene, or allyl alcohol, these being compounds able to undergo ready oxidation or hydrogenation.

In the system, $C_2H_4 : H_2 : \frac{1}{2}O_2$, the possible reactions are: (1) formation of water from the hydrogen and oxygen, (2) hydrogenation of the ethylene, (3) oxidation of the ethylene, and (4) decomposition of the ethylene. In presence of finely divided nickel, reaction (1) becomes explosive at the ordinary temperature, (2) becomes appreciable at 30° and has its optimum at 130—250°, whilst (3) is not markedly influenced, its products being essentially water and carbon dioxide. The results now obtained show that the velocity of reaction (1) is diminished enormously by the presence of ethylene, although at the ordinary temperature this reaction is the only one

taking place to an appreciable extent; when the temperature is raised, reaction (2) assumes an increased velocity, so that most of the ethylene is hydrogenated to ethane at 225°, and reaction (3) also becomes of measurable velocity. Various possible causes of the alternations in the velocities of reactions (1) and (2) are discussed. The retardation of reaction (1) by ethylene is analogous, up to a certain temperature, to the similar effect observed by Henry (*Phil. Mag.*, 1836, **65**, 329) for carbon monoxide, with which oxygen combines more rapidly than with hydrogen in presence of platinum. The presence of atomic or active hydrogen produced either, as Sabatier supposed, by way of a hypothetical hydride or in some other way, is insufficient to explain the author's results, which may, however, be determined in some degree by the specific adsorption of gases by metallic catalysts studied by Taylor and Burns (*A.*, 1921, ii, 630). The possible formation of an unstable compound of nickel and ethylene, analogous to the formation of nickel tetracarbonyl from nickel and carbon monoxide, is also discussed.

In presence of copper, the velocities of the different reactions are only slightly increased, the greatest velocity at all temperatures being that of the formation of water; the copper undergoes marked oxidation, which favours oxidation phenomena. None of the reactions is appreciably accelerated by the presence of silver. The formation of water under the influence of platinum is retarded by the presence of ethylene, but is the principal reaction taking place. In the system containing nitrobenzene, the reduction of the latter in presence of nickel is more rapid than the formation of water from its elements. The results of Bone and Wheeler (*T.*, 1904, **85**, 1637) are discussed.

T. H. P.

Catalytic De-hydroxidation of Formic Acid. ERICH MÜLLER [with K. SPONSEL] (*Z. Elektrochem.*, 1922, **28**, 307—310).—The catalytic conversion of formic acid into hydrogen and carbon dioxide, by means of rhodium, first studied by Deville and Debray in 1874, is due to the presence of impurities in the catalyst, the catalytic activity decreasing as the purity of the metal increases. Osmium exhibits considerable catalytic activity, and a detailed investigation has been made of the dependence of the activity on the mode of preparation of this catalyst, more especially on the temperature of reduction of the metal, the composition of the catalysed solution as regards the concentration of the acid and the presence or absence of sodium formate, and the mass of catalyst employed. Osmium prepared by reduction of the hydrated dioxide at 150° possesses very considerable activity, 0.3 gram effecting the evolution of 10 litres of gas in three hours. The activity is increased by any conditions favouring the existence of the catalyst in the colloidal state.

J. S. G. T.

The Use of the Oxides of Platinum for the Catalytic Reduction of Organic Compounds. I. V. VOORHEES and ROGER ADAMS (*J. Amer. Chem. Soc.*, 1922, **44**, 1397—1405).—When

chloroplatinic acid is fused with sodium nitrate a brown oxide of platinum is obtained which is an excellent catalyst for the reduction of various types of organic compounds. The speed of reduction with this catalyst is greater than when ordinary platinum black is used. The most satisfactory conditions for preparing this oxide in its most active form have yet to be worked out. W. G.

Effect of a Magnetic Field on Catalysis by Ions in the Presence of a Paramagnetic Salt. WILLIAM EDWARD GARNER and DOUGLAS NORMAN JACKMAN (T., 1922, **121**, 1298—1299).

Analysis of the Electronic Structure of the Elements. A. DAUVILLIER (*J. Phys. Radium*, 1922, [vi] **3**, 154—180).—A further discussion of the theory of atomic structure (cf. A., 1921, ii, 475, and this vol., ii, 43). A new arrangement of the periodic table is proposed which conflicts with the chemist's view as to the positions of the elements of the manganese and iron groups in the periodic table. The spectra and atomic volumes of these elements are in accord with the view that they should be placed, together with oxygen, in the sixth group. They should possess only six electrons in the outer shell of the atom. This would remove certain anomalies present in the modern theory of the periodic table. An arrangement of the electrons in the shells is advanced which differs in some respects from that of Langmuir. The maximum number of the electrons in the successive shells of the atom are respectively 2, 8, 18, 18, 32, 8 instead of 2, 8, 8, 18, 18, 32 according to Langmuir. An apparatus is described by which the author has measured the *K*, *L*, and *M* series of the heavy elements. These results, which will be communicated in a future paper, throw light on the distribution of the electrons in the various shells of the atom. W. E. G.

Complex Compounds. A. MAGNUS (*Physikal. Z.*, 1922, **23**, 241—247).—A theoretical paper in which the theory of Kossel (A., 1916, ii, 243) is applied to the stability relations and the valency forces of complex compounds. On this theory, the most stable complex is one which is formed from its components with the greatest liberation of energy. The case of positively charged central atoms is considered. The stability of a complex is dependent on the number of positive charges (*n*) on the central atom and on the number of groups (*p*) held in combination. It is shown that the stability of complexes with different values of *n* and *p* may be derived from purely electrostatic considerations. Maximum values are found for the stability at values of *p* which are in agreement with experience. For complexes with a small charge on the central atom, high co-ordination numbers are not to be expected unless the groups attached are bipolar in nature. Ions of the form XO_6 , in consequence of the energy conditions, are rarely stable. The stability of hydrates and compounds with ammonia is shown to

be dependent on the bipolar nature of the water and ammonia molecules.

W. E. G.

The Electron Theory of Valency as Applied to Organic Compounds. JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1922, **44**, 1293—1313).—A theoretical paper in which the author discusses the relative merits of the theories of polar and non-polar valencies in organic compounds as applied to various types of compounds. In the molecular rearrangement of *s*-bistriphenylmethylhydrazine the theory of polar valencies gives an evident cause for the rearrangement, revealing a "fault" in the molecule, and expresses the intramolecular oxidation and reduction characteristic of the rearrangement. This theory is also applicable to the analogous molecular rearrangements of chloro- and bromo-amides, of hydroxylamine derivatives, and of peroxides. In the absorption reactions of carbon dioxide and of a large number of organic compounds containing unsaturated groups of the types C:O, C:S, C:N, polar valencies are recognised as the directing forces. The same applies to ethylene hydrocarbons.

The author develops the Crum Brown-Gibson rule of substitution in the benzene series from a polar electronic structure for benzene, which does not require the assumption of negative hydrogen, but is based on the application to benzene of results firmly established in the aliphatic series. The different behaviour of negative halogen, in compounds of the type RX, and of positive halogen, in compounds of the type RNHX, is taken as further evidence in support of polar valencies.

Evidence of the complete polar structure of acids, such as sulphuric, phosphoric, or organic acids is found in (a) Faraday's observation of the deposition of sulphur at the negative electrode in the electrolysis of concentrated sulphuric acid, (b) the work of Bird and Diggs (*A.*, 1914, ii, 614) on the use of yellow phosphorus as the equivalent of a metal for the production of an electric current, (c) the production of currents by the use of organic compounds as the source of escape of electrons in oxidation-reduction cells.

In the oxidation and reduction of organic compounds at the ordinary temperature, exposed valencies on double and triple bonds, in bivalent and trivalent carbon, etc., are the common seat of oxidation and reduction reactions. Although polarity in organic compounds is insisted on as giving an invaluable guide in following organic reactions, it need not be of the extreme character shown by common salts, but may well be of the character proposed by Bohr, Lewis, and Kossel, where the transfer of electrons from atom to atom is not so complete as in the case of common electrolytes.

W. G.

A Discussion of Triple Salts. HORACE L. WELLS (*Amer. J. Sci.*, 1922, [v], **4**, 27—30).—In some cases where analogous triple salts are known, these occur in extensive series, but there are a great many cases where analogy is lacking between salts of analogous

metals, and there appear to be no definite laws, based on the valency or other characters of the constituent salts, according to which they are formed. A number of examples of triple chlorides, thiocyanates, and nitrites are quoted. E. H. R.

New Small Autoclave for Hydrolysis Experiments.

R. EBERHARD GROSS (*Z. physiol. Chem.*, 1922, **120**, 185—188).—A description of a small autoclave which can be heated and cooled quickly. It is therefore suitable for hydrolysis experiments in which samples need to be withdrawn at different times for testing for various reactions. S. S. Z.

Inorganic Chemistry.

The Rectilinear Diameter of Hydrogen. E. MATHIAS, C. A. CROMMELIN, and H. KAMERLINGH ONNES (*Ann. Physique*, 1922, **17**, 463—474).—A résumé of work already published (A., 1921, ii, 256; this vol., ii, 440). W. G.

The Rectilinear Diameter of Oxygen. E. MATHIAS and H. KAMERLINGH ONNES (*Ann. Physique*, 1922, **17**, 416—441).—A résumé of work already published (A., 1910, ii, 771, 829; 1911, ii, 387). W. G.

Equilibrium between Sulphur and Iodine in Solution. M. AMADORI (*Gazzetta*, 1922, **52**, i, 387—394).—In view of the fact that the results of recent investigations indicate that the so-called compounds of sulphur with iodine described by various authors are merely mixtures of the two elements, the author has examined the solubility and cryoscopic relations of sulphur and iodine when present together. It is found that the separate solubilities of each of these elements in carbon disulphide, benzene, and bromoform are less than those which obtain in presence of the other element; in the first of these solvents both solubilities are increased by more than 100% by mixing the sulphur and iodine. The corresponding solubility curves of the mixtures in benzene and in carbon disulphide consist of two branches meeting in a point of double saturation.

Cryoscopic measurements of the mixtures in bromoform solution show that the depression of the freezing point of the solvent is somewhat less than that calculated from the molecular weights of the sulphur and iodine. No evidence is obtained of the existence of a solid compound of the two elements. T. H. P.

The Crystallisation of Amorphous Tellurium. A. DAMIENS (*Compt. rend.*, 1922, 174, 1548—1550).—From a study of the heats of reaction of different forms of tellurium with a mixture of bromine and bromine water, Berthelot and Fabre have found the relationship $Te_{\text{cryst.}} = Te_{\text{amorph.}} + 12.096 \text{ cal. (for 64 grams)}$. Previous work on the allotropy of tellurium did not confirm this equation (cf. this vol., ii, 498), and the author has accordingly repeated the work of Berthelot and Fabre, using, however, a mixture of bromine and concentrated hydrochloric acid diluted with its own volume of water. His results do not confirm those of Berthelot and Fabre, but establish the equation $Te_{\text{amorph.}} = Te_{\text{cryst.}} + 2.63 \text{ cal.}$, which is in accord with his work on the allotropy of tellurium (*loc. cit.*).
W. G.

The Rectilinear Diameter of Nitrogen. E. MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN (*Ann. Physique*, 1922, 17, 455—463). A more detailed account of work already published (A., 1915, ii, 143).
W. G.

Normal Density of [Chemically Pure] Nitrogen. E. MOLES (*J. Chim. physique*, 1922, 19, 283—289).—The results of twenty-nine determinations of the density of pure nitrogen have been systematically discussed, and from calculations, the weight of the litre of nitrogen at 0° , 760 mm., and 45° latitude is found to be $L_N = 1.2507 \pm 0.0001$ grams. The measurements used are those of Rayleigh and Ramsay, Leduc, Gray, and Moles, in which two entirely different methods were used, and the material was drawn from eight different sources. Under the conditions 0° , 760 mm., and $g = 980.665$, the rounded value is $L_N = 1.2507$ grams. The actual value obtained from nitrogen obtained from sodium nitrite is $L_N = 1.2506$ grams, a value which is almost identical with the above-cited mean. This result is remarkable, since it was obtained from volumetric determinations.
J. F. S.

The Synthesis of Ammonia by Collision with Slow-moving Electrons. E. BUCH ANDERSEN (*Z. Physik*, 1922, 10, 54—62).—A study of the action of a stream of electrons on the production of ammonia from mixtures of nitrogen and hydrogen at low pressures. A current was passed between a glowing tungsten wire and two platinum electrodes in an atmosphere of the two gases. The current was kept constant and the effect of variations in the composition of the gas mixture and in the applied *E.M.F.* were investigated. The maximum rate of formation of ammonia did not correspond with the stoichiometric mixture, but with mixtures containing a great excess of nitrogen. This result is in agreement with the view that the first step in the production of ammonia is the ionisation of the nitrogen molecule. Curves are given showing the velocity of formation of ammonia plotted against the applied electromotive force. These curves show a series of maxima at 22, 26, and 33 volts. No appreciable quantities of ammonia were produced below an applied electromotive force of

17.7 volts. This potential is identical with the ionisation potential of nitrogen (17.75 volts). It is, however, difficult to distinguish by direct measurement between the ionisation potentials of hydrogen and nitrogen.
W. E. G.

Oxidation of Nitric Oxide and the Recovery of Nitrogen Oxides from Mixtures with Air. E. BRINER, S. NIEWIAZSKI, and J. WISWALD (*J. Chim. physique*, 1922, **19**, 290—309; *Helv. Chim. Acta.*, 1922, **5**, 432).—The work which has been done on the commercial oxidation of nitric oxide and the recovery of oxides of nitrogen is reviewed and a number of points requiring further investigation are emphasised. Some of these points have been investigated by the authors. It is shown that the formation of nitrite by absorption of a gaseous system $\text{NO}-\text{NO}_2$ by alkali takes place according to the scheme proposed by Leblanc (*Z. Elektrochem.*, 1906, **12**, 541), based on the fact that nitrous anhydride exists in small concentrations, and this is in keeping with Raschig's experiments. Experiments on the oxidation of nitric oxide at low temperatures confirm the results of Lunge, Bodenstein, and Wourtz, and show that the oxidation proceeds directly from nitric oxide to nitrogen tetroxide without the intermediate formation of nitrous anhydride. Comparative experiments made at ordinary temperatures, the temperature of carbon dioxide "snow" (-80°), and the temperature of liquid air (-190°) show that a low temperature is very favourable to the oxidation of oxides of nitrogen and to the recovery of the oxides. It follows from the experiments that cooling to a very low temperature will be the best means of effecting a complete recovery of the oxides of nitrogen from very dilute mixtures of these gases such as are obtained after passage through the electric arc, provided that the technical difficulties can be overcome, whilst without this low temperature very large oxidation chambers will be necessary.

J. F. S.

Economic Realisation of Oxidation Reactions in Factories where Nitric Acid is Synthesised. Applications. CAMILLE MATIGNON (*Bull. Soc. chim.*, 1922, [iv], **31**, 555—561).—The author proposes to use the dilute nitric acid such as is obtained at first in the fixation of atmospheric nitrogen or in the oxidation of ammonia, for chemical preparations in which it can be used as an oxidising agent, providing the reduction of the nitric acid does not proceed beyond the stage of nitric oxide. The oxides of nitrogen can be reconverted into nitric acid by atmospheric oxygen and again absorbed in the towers. In this way there is practically no loss of nitric acid and thus the expense of the oxidation process is very small. Suggested applications are the preparation of copper sulphate from copper by the combined action of sulphuric and nitric acids, and the preparation of oxalic acid from sugar or molasses by oxidation with nitric acid. This latter process was satisfactorily performed on a cargo of sugar damaged by sea water.

W. G.

The Accessory Elements of the Dephosphoration Slags.

A. DEMOLON (*Compt. rend.*, 1922, **174**, 1703—1706).—Estimations have been made on a number of slags of the amounts of calcium soluble in solvents under definite conditions. The solvents used were: distilled water, 5% sugar solution, 2% phenol, a neutral solution of ammonium humate, cold solutions of ammonium chloride of different strengths, a saturated solution of carbon dioxide, and mineral acids. The amount of free calcium oxide in the slags was small, varying from 1% to 3%. In all the solvents the amount of calcium going into solution increased at first very rapidly with the time of shaking and then only very slowly over a long period of time. This is considered to be due to the presence of calcium silicates which react slowly with the solvents. The amounts of magnesium oxide present in the slags varied from 3% to 15% with an average of 8.90%. The amount of manganese found was fairly constant at about 4—5%, which was easily soluble in 2% citric acid.

W. G.

Magnetochemical Investigations of Constitutions in Mineral Chemistry. The Acids of Arsenic.

PAUL PASCAL (*Compt. rend.*, 1922, **174**, 1698—1700).—The results of measurements of the magnetic susceptibilities of a large number of arsenic compounds indicate that combined arsenic has two atomic susceptibilities according to the degree of saturation of its compounds. The results furnish further evidence in support of the rule that the logarithm of the atomic susceptibility of an element is a linear function of the atomic weight in each natural family. It is verified exactly for the group phosphorus, quinquivalent arsenic, and quinquivalent antimony and for the group trivalent arsenic, antimony, and bismuth.

W. G.

Reaction between Boron Nitride and Various Metallic Oxides with Production of Nitric Oxide.

U. SBORGI and A. G. NASINI (*Gazzetta*, 1922, **52**, i, 369—387).—Estimations have been made of the yields of nitric oxide obtained when air is passed over mixtures of boron nitride with various metallic oxides heated at different temperatures. Four samples of the nitride, prepared and stored in different ways, were employed. The yield of nitric oxide obtained varies greatly with these different samples and also with the nature of the admixed oxide. With the oxides Fe_2O_3 , Ni_2O_3 , Co_2O_3 , MnO_2 , Mn_3O_4 and CuO , yields as high as 72% are given, and the residue remaining after the reaction gives an increased yield of nitric oxide with a fresh quantity of boron nitride; this result is repeated four or five times, the yield increasing each time until the residue becomes converted into a compact mass.

T. H. P.

Carbon and its Neighbours in the Periodic System.

ALFRED STOCK (*Z. angew. Chem.*, 1922, **35**, 341—343).—A discussion of the regularities occurring between the compounds of

the elements boron, carbon, nitrogen, and silicon. The greatest resemblances are found between the hydrides and their derivatives containing oxygen, nitrogen, or chlorine. In these compounds, carbon unites the chemical properties of its neighbours. It resembles boron in its tendency to form long chains of atoms, nitrogen in forming volatile compounds, and silicon and boron in giving rise to high-boiling derivatives. The property of combining equally readily with either electro-positive or electro-negative elements is shared to some extent by nitrogen and silicon. W. E. G.

The Preparation of Carbon from Carbon Monoxide by means of a Catalyst. J. P. WIBAUT (*Rec. trav. chim.*, 1922, **41**, 400—401).—An attempt to prepare pure carbon which, from the method of preparation, could not contain hydrogen or hydrocarbons, was unsuccessful. Carbon monoxide was passed over iron oxide at a temperature of about 450° and a good yield of carbon obtained. The resulting gas contained from 80—90% of carbon dioxide. The catalyst, however, was found to be fairly evenly distributed throughout the carbon, and prolonged attempts to extract it yielded a product the ash content of which was above 6%. H. J. E.

The Rectilinear Diameter of Argon. E. MATHIAS, H. KAMERLINGH ONNES, and C. A. CROMMELIN (*Ann. Physique*, 1922, **17**, 442—455).—A résumé of work already published (A., 1913, ii, 112, 478). W. G.

The Analysis by Positive Rays of the Heavier Constituents of the Atmosphere; of the Gases in a Vessel in which Radium Chloride had been stored for Thirteen Years, and of Gases given off by Deflagrated Metals. (Sir) J. J. THOMSON (*Proc. Roy. Soc.*, 1922, [A], **101**, 290—299).—The positive ray method of analysis is applied to the solution of several problems. The residues from a thousand tons of liquid air have been examined for the presence of molecules heavier than krypton and xenon. Two new constituents of the atmosphere were found with molecular weights 163 and 260. The lighter of these is the more abundant, but the quantity in the air is very small compared with xenon. There is evidence that the lighter molecule carries two positive charges. No place in the periodic table can be found for a new element with this atomic weight, and it is possible that the two new lines are due to diatomic molecules of xenon and krypton.

The gases from 70 mg. of radium, stored in an evacuated vessel by (Sir) J. Dewar in 1909, have been analysed by the positive ray method. Helium and hydrogen were both present, but no neon or H_2 was found. In addition, a faint line, for which $m/e = 5$, seems to indicate a compound of helium with one atom of hydrogen. The analysis was also applied to gases which had stood over radium and to gases lit by deflagrating wires. The presence of doubly, triply, and quadruply charged atoms of oxygen and nitrogen, and

of doubly and triply charged atoms of carbon, was detected. A compound $m/e=10$ is believed to exist, consisting of an atom of oxygen and four atoms of hydrogen. This invariably carries a double charge. The deflagration of fine wires of tungsten, gold, or copper by powerful electric currents did not yield any helium, although H_3 was detected.

W. E. G.

Constitution of Metallic Substances. CHARLES A. KRAUS (*J. Amer. Chem. Soc.*, 1922, **44**, 1216—1239).—A theoretical paper in which it is pointed out that the constitution of substances cannot be derived from their properties in a condensed state with any considerable degree of accuracy. In order to determine the constitutions of metallic substances, it is necessary to study their properties at low concentrations. At low concentrations, the elementary metals are salt-like substances, and it is suggested that metallic compounds will exhibit salt-like properties in even a more decided manner. In solutions of metallic compounds in liquid ammonia, the more electro-negative element functions as anion, as follows from the fact that it is precipitated on the anode on electrolysis. All but the strongly electro-positive elements exhibit a negative as well as a positive valency. The normal anions of metallic elements form complex anions in the presence of the element in question. These complex metallic compounds are similar to the complex iodides and sulphides which have been studied in aqueous solution. The property of forming complex anions is one common to many metallic as well as non-metallic elements. It is shown that the complex telluride-ion carries two charges. In solution in ammonia, the complex anions $TeTe^-$ and Te_3Te^{--} exist. It is inferred that the anions of the metals of the fifth group carry three charges, and those of the fourth four charges. Since it has been shown that selenium, tellurium, bismuth, antimony, arsenic, tin, and lead form complex anions in ammonia solution, it may be inferred that other metals not soluble in ammonia form similar complex anions. Metallic compounds of this class are, therefore, virtually salts. The multiplicity of compounds derivable from a given pair of metallic elements is accounted for on the hypothesis that in their compounds the more electro-negative elements form complex anions, and this view brings metallic compounds into line with the present conceptions of atomic structure. The physical properties of metallic compounds are in keeping with the hypothesis that they possess a salt-like structure. It is pointed out that the energy effect accompanying the formation of metallic compounds is of the same order of magnitude as that accompanying the formation of salts, and as in the case of salts, the energy change is the greater the more electro-negative one element is with respect to the other. Electro-positive groups, such as the ammonium group, are virtually metals, although their stability in the free state is not sufficient to permit their isolation in most instances. The most stable groups possess sufficient stability to demonstrate their

metallic properties in the free state. Such groups resemble elements in their properties. The property of metallicity is not an atomic one, it may be imparted to non-metallic elements by combination with other non-metallic elements, and it is due to the presence of uncombined negative electrons. The electrons which impart metallic properties to an element are those to which the chemical reactions of this element with other elements are due. The reaction between strongly electro-positive and strongly electro-negative elements, or groups of elements, consists essentially in a combination of the negative electrons of the electro-positive constituent with the atoms of the electro-negative constituent. In metal ammonia complexes of the type $\text{Ca}(\text{NH}_3)_6$, which are metallic substances, the negative electrons are not primarily concerned. The experimental data on which the foregoing conclusions are based are to be published shortly.

J. F. S.

The Possible Existence of Metallic Compounds in the State of Vapour. A. EUCKEN and O. NEUMANN (*Z. Elektrochem.*, 1922, **28**, 322—324).—Sodium amalgam was distilled at pressures between 5 and 10 mm. of mercury, and the boiling point and corresponding composition of the vapour and liquid phases were determined. The results indicate that, contrary to the suggestion of von Wartenberg (*A.*, 1915, ii, 226), no appreciable amount of a compound of sodium and mercury was formed in the state of vapour at about 500° .

J. S. G. T.

Interaction of Sodium Chloride and Silica. FRANCIS HERBERT CLEWS and HUGH VERNON THOMPSON (*T.*, 1922, **121**, 1442—1448).

Chlorites of Sodium and other Metals. G. R. LEVI (*Gazzetta*, 1922, **52**, i, 417—420; *Atti R. Accad. Lincei*, 1922, [v], **31**, i, 212—216; cf. this vol., i, 527).—The following new chlorites are described. *Sodium chlorite*, $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$, prepared from barium chlorite and sodium sulphate, forms lustrous laminæ, and, when anhydrous, explodes on percussion. *Lithium chlorite*, similarly prepared, forms anhydrous, deliquescent crystals and explodes on percussion. *Calcium chlorite*, prepared from calcium peroxide and chlorine dioxide, explodes on percussion and decomposes completely in contact with a heated wire. *Strontium chlorite*, similarly obtained, explodes on percussion, and in contact with a hot wire decomposes with evolution of heat. *Thallous chlorite* explodes on percussion and decomposes immediately at $70\text{--}80^\circ$.

T. H. P.

Oxidation and Reduction Reactions with Chlorites. GIORGIO RENATO LEVI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 370—373; cf. preceding abstract).—At $180\text{--}200^\circ$, sodium chlorite undergoes decomposition quantitatively in accordance with the equation $3\text{NaClO}_2 = 2\text{NaClO}_3 + \text{NaCl}$. The action of ozone on the salt in aqueous solution yields chlorine dioxide, $2\text{NaClO}_2 + \text{O}_3 + \text{H}_2\text{O} = 2\text{NaOH} + \text{O}_2 + 2\text{ClO}_2$; if the dioxide is not carried away

by the ozone, it reacts either with the sodium hydroxide, $2\text{NaOH} + 2\text{ClO}_2 = \text{NaClO}_2 + \text{NaClO}_3 + \text{H}_2\text{O}$, or with hydrogen peroxide, if this has been formed by the excess of ozone, $2\text{NaOH} + \text{H}_2\text{O}_2 + 2\text{ClO}_2 = 2\text{NaClO}_2 + 2\text{H}_2\text{O} + \text{O}_2$. In aqueous solution, sodium chlorite and nitrite react, with development of heat, forming the chloride and nitrate, $2\text{NaNO}_2 + \text{NaClO}_2 = \text{NaCl} + 2\text{NaNO}_3$. The reaction between a chlorite and a ferrocyanide is expressed by the equation $4\text{K}_4\text{Fe}(\text{CN})_6 + \text{NaClO}_2 + 2\text{H}_2\text{O} = \text{NaCl} + 4\text{K}_3\text{Fe}(\text{CN})_6 + 4\text{KOH}$, and may be rendered complete either by gradual neutralisation of the alkali hydroxide by means of dilute sulphuric acid or by addition of a salt such as magnesium sulphate, magnesium hydroxide being then deposited. With an iodide, sodium chlorite reacts with liberation of iodine, $\text{NaClO}_2 + 4\text{KI} + 2\text{H}_2\text{O} = 4\text{I} + 4\text{KOH} + \text{NaCl}$ (cf. Bray, A., 1906, ii, 222, 223, 278), and here too the reaction may be carried to completion by addition of a substance, such as boric acid, capable of neutralising the alkalinity; if the liquid is heated on a water-bath and in an apparatus which prevents sublimation of the iodine, the reaction may be used for the estimation of a chlorite in presence of a chlorate, which does not liberate iodine under these conditions. In neutral solution, chlorites do not act on alkali bromides, but in presence of sulphuric acid bromine is set free; the behaviour towards bromates is similar. From acid solutions of iodates and periodates no iodine is liberated, oxygenated compounds of chlorine, formed by decomposition of the chlorous acid, being obtained.

In neutral solution sodium chlorite reacts slowly with a sulphite, thus: $2\text{Na}_2\text{SO}_3 + \text{NaClO}_2 = 2\text{Na}_2\text{SO}_4 + \text{NaCl}$; with solutions of free sulphurous acid the corresponding reaction takes place immediately. The reaction, $\text{Na}_2\text{S}_2\text{O}_3 + 2\text{NaClO}_2 + \text{H}_2\text{O} = 2\text{NaCl} + 2\text{NaHSO}_4$, which occurs with development of heat, is complete only when either a slight excess of chlorite is used or the liquid is kept neutral by means of magnesium oxide; otherwise a little sulphurous acid is formed. With thiocyanates, chlorites react principally according to the equation $2\text{NaCNS} + 3\text{NaClO}_2 + 2\text{H}_2\text{O} = 2\text{NaHSO}_4 + 2\text{HCN} + 3\text{NaCl}$, slight excess of chlorite being required for the complete oxidation of the sulphur of the thiocyanate to sulphuric acid. Chlorites oxidise hydrogen sulphide to sulphuric acid, and sodium formate and oxalate to sodium hydrogen carbonate.

T. H. P.

Borates. VI. The System $(\text{NH}_4)_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$ at 45° and at 90° . UMBERTO SBORGI and LELIO FERRI (*Atti R. Accad. Lincei*, 1922, [v], 31, i, 324—329; cf. A., 1921, ii, 580).—In this system at 45° are found the 1 : 5 : 8- and the 1 : 2 : 4-compounds, in addition to the 1 : 4 : 6-compound occurring at 60° ; the first two compounds are able to exist unchanged in presence of pure water, but the 1 : 4 : 6-compound is found only in solutions containing an excess of $(\text{NH}_4)_2\text{O}$ and having temperatures above that of the surrounding air. The same three compounds are formed also at 90° .

T. H. P.

The Electrolytic Preparation of Sodium Perborate. KURT ARNDT and ERNST HANTGE (*Z. Elektrochem.*, 1922, **28**, 263—273).—The conditions under which sodium perborate may be prepared electrolytically have been investigated. It is shown that this salt is most efficiently prepared from a solution of borax and sodium carbonate containing 120 grams of anhydrous sodium carbonate and 30 grams of borax per litre of solution. A small quantity of sodium chromate (0.5 gram per litre) and one drop of turkey red oil added to the electrolyte increases the efficiency, since this reduces the cathodic reduction to a minimum. A large anodic current density is requisite and to obtain this an anode of bright platinum is employed, whilst a water-cooled length of tin tubing serves as cathode. The most suitable current density lies between 10 and 20 amp./dm.², and the most suitable temperature is 14—16°; above this temperature the yield of perborate is greatly reduced. During electrolysis, the bath loses carbon dioxide, and if this loss is not replaced the current yield becomes very poor owing to the large concentration of hydroxyl-ions. With an increasing concentration of the per-salt, the yield decreases during the electrolysis. The analysis of the hydrogen-oxygen gas mixture evolved during the electrolysis shows that a strong decrease in the anodic oxidation is responsible for the falling off of the yield. The merest trace of platinum salt in the electrolyte has a very bad effect on the yield, and the presence of iron in the sodium carbonate has a similar bad effect. Both substances decrease the anodic oxidation and increase the cathodic reduction. The addition of cyanide only partly eliminates the deleterious effect of the iron. The curve produced by plotting the current density against the anodic potential shows a sharp inflexion point at 1.47 volts. This potential is due to the concentration of a higher oxide of platinum, presumably PtO₃, which is formed as a solid solution in the anode material by the discharge of hydroxyl ions. It is likely that this higher oxide, in keeping with its potential and oxidising power, acts as an intermediate product in the formation of sodium perborate. J. F. S.

Structure of Crystals of Lithium and some of its Compounds with Light Elements. II. Lithium Hydride. J. M. BIJVOET and A. KARSEN (Proc. K. Akad. Wetensch. Amsterdam, 1922, **25**, 26—30; cf. A. 1921, ii, 200).—Using the method of Debye and Scheerer, the authors have prepared and investigated the X-ray photographs of lithium hydride. The results show that lithium hydride crystallises in the regular system with four molecules in the elementary cell which has a side of length $a = 4.10 \times 10^{-8}$ cm. The density of lithium hydride is calculated to be 0.76 ± 0.01 . The structure is that of sodium chloride, with positive lithium ions and negative hydrogen ions. Systems of two-electron rings are round both the lithium and hydrogen nuclei with radii $0.05a$ and $0.6a$, respectively, and the planes of which are normal to non-intersecting trigonal axes. J. F. S.

Calcium-Ammonium. E. BOTOLFSSEN (*Bull. Soc. chim.*, 1922, [iv], 31 561—567); cf. cf. Biltz and Hüttig, A., 1921, ii, 201).—Solid calcium-ammonium is formed within the temperature limits -15° and $+30^{\circ}$. The pasty state sometimes recorded in the literature is probably due to the presence of traces of sodium in the calcium used. The author confirms previous work on this compound (*loc. cit.*) in certain respects and finds that when it is heated in a vacuum at about 34° it decomposes explosively, the temperature depending slightly on the vacuum obtained. The products of this decomposition are the nitride and hydride of calcium and hydrogen. It is suggested that calcium is capable of forming a series of compounds with ammonia in much the same way as is iodine. W. G.

The Transformation of Gypsum into Ammonium Sulphate. C. MATIGNON and M. FRÉJACQUES (*Compt. rend.*, 1922, 175, 33—35).—The authors obtained a 96% yield in the interaction of an industrial sample of gypsum with ammonium carbonate (cf. Neumann, A., 1921, ii, 587). The curves giving the velocity of the reaction show the existence of two distinct phases. During the first phase the velocity is slower than in the second phase. The presence of ammonium sulphate in the original solution causes a diminution in the velocity of the reaction, but in all cases equilibrium is complete at the end of two and a half hours. W. G.

Magnesium-Cadmium Alloys. LÉON GUILLET (*Rev. Met.*, 1922, 19, 359—365).—The magnesium-cadmium alloys consist of a series of solid solutions and the compound CdMg, which is soluble in all proportions in either metal. Cadmium increases the hardness of magnesium, but the alloys are malleable up to a content of 55% Cd. With more than this they become brittle at ordinary temperatures, due to the formation of a new solid solution stable below 246° and consisting of the compound CdMg with excess of either magnesium or cadmium [cf. *J. Soc. Chem. Ind.*, 1922, 553A]. A. R. P.

The Quaternary System Potassium Sulphate-Magnesium Sulphate-Ammonium Sulphate-Water. ARNOLD WESTON (*T.*, 1922, 121, 1223—1237).

Chemical and Electrochemical Behaviour of Salts of the Acids of Lead. G. GRUBE (*Z. Elektrochem.*, 1922, 28, 273—289).—Two new methods for the preparation of alkali salts of plumbic acid are described, the first of which consists in the anodic solution of a pure lead anode in a strong solution of alkali hydroxide by means of a direct current of high current density on which is superimposed an alternating current. In the second method, a solution of an alkali plumbite in concentrated alkali hydroxide is submitted to anodic oxidation at a platinum electrode. In both methods the alkali plumbates crystallise from the electrolyte in the pure condition during the electrolysis. The oxidation potentials of the processes

$\text{Pb}^{..} + 2 \oplus \longrightarrow \text{Pb}^{...}$ and $\text{PbO}_2'' + 2 \cdot \text{OH}' + 2 \oplus \longrightarrow \text{PbO}_3'' + \text{H}_2\text{O}$ have been systematically investigated in alkaline solution and also the potential of lead in solutions of alkali plumbite has been measured. It is shown that the normal potential of lead against potassium plumbite in 8.42 *N*-potassium hydroxide at 18° is $\epsilon_h - 0.613$ volt, whilst the normal potential of plumbite-plumbate in potassium hydroxide of the same concentration is $\epsilon_h + 0.208$ volt. From these values the normal potential of lead against alkali plumbate solution is calculated to be $\epsilon_h - 0.203$ volt. In all cases a decrease in the concentration of the alkali hydroxide displaces the potential toward more negative values. The nature of the plumbo-plumbates which separate from highly concentrated solutions of alkali plumbates and plumbites in alkali hydroxides has also been investigated, and it is shown that the composition of the deposit varies with the alkalinity of the solution in the sense that from solutions with a concentration of alkali hydroxide less than 4.9*N*, the compound $\text{Pb}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ separates, whilst from solutions more concentrated than 6.9*N*, Pb_3O_4 separates. Hence it follows that Pb_3O_4 is to be regarded as the lead salt of ortho-plumbic acid, and that in very alkaline solutions of plumbates the anions of meta-plumbic acid, PbO_3'' and ortho-plumbic acid PbO_4'''' , are both present. To ascertain whether the alkali plumbates are salts of the acid $\text{H}_2[\text{Pb}(\text{OH})_6]$ or of H_2PbO_3 , the author has investigated the dehydration of sodium plumbate, $\text{Na}_2\text{PbO}_3 \cdot 3\text{H}_2\text{O}$. It is shown that on heating this salt the water is all expelled without decomposition of the salt, from which the conclusion is drawn that the three molecules of water are to be regarded as water of crystallisation and that sodium plumbate is a salt of metaplumbic acid. J. F. S.

Effect of Grinding on the Apparent Density of Lead Oxides.

O. W. BROWN, S. V. COOK, and J. C. WARNER (*J. Physical Chem.*, 1922, **26**, 477—480).—The apparent density of heavy, crystalline lead oxide is diminished initially by grinding, the minimum value being attained by about ten hours' grinding in a pebble mill making 50 revolutions per minute. Thereafter, the apparent density increases, rapidly at first, to a constant value greater than the initial value. The initial decrease of apparent density is not shown by a light, amorphous lead oxide. J. S. G. T.

Thermal Analysis of the System $\text{Tl}_2\text{O}-\text{B}_2\text{O}_3$. G. CANNERI and R. MORELLI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 109—111; cf. Buchta, A., 1914, ii, 135).—The fusion diagram of this system exhibits three maxima corresponding with thallous metaborate, TlBO_2 , m. p. about 474°; thallous pyroborate, $\text{Tl}_4\text{B}_2\text{O}_5$, m. p. about 434°; and normal thallous borate, Tl_3BO_3 , m. p. 370° (decomp.). T. H. P.

Phenomena of Diffusion in Metals in the Solid State and Cementation of Non-ferrous Metals. II. Cementation of Copper by means of Chromo-manganese. G. SIROVICH and A. CARTOCETI (*Gazzetta*, 1922, **52**, i, 436—442).—By means of

the arrangement previously used (this vol., ii, 68) experiments have been made on the cementation of copper by chromo-manganese containing 30.4% and 63.8% of chromium and manganese respectively. At 900°, the cementation is so intense that, in a few moments a layer of copper-manganese containing more than 20% of manganese is formed; as this alloy melts below 900°, the succeeding experiments were carried out at 800°. Although the iron of the ferro-manganese and the chromium of the chromo-manganese do not migrate to the copper, these metals evidently influence the migration of the manganese; the chromium having a greater effect than the iron. The mechanism of the process of cementation is discussed briefly.

T. H. P.

Action of Sulphur on Cuprous Chloride. FREDERICK WILLIAM PINKARD and WILLIAM WARDLAW (T., 1922, **121**, 1300—1302.)

The Structural Formula of Copper Sulphide. W. GLUUD (*Ber.*, 1922, **55**, [B], 1760—1761; cf. this vol., ii, 446).—If hydrogen sulphide is passed into a 1.5% solution of copper sulphate in ammonia (10%) until only a faint blue colour remains, a variety of copper sulphide is precipitated which yields elementary sulphur on immediate oxidation by air, whereas after preservation for four or five hours it is oxidised to copper sulphate and thiosulphate.

It is suggested that the formulæ Cu_2S and Cu_2S_2 are to be assigned to the two modifications. This conception is in harmony with the known tendency of copper sulphide to pass into cuprous sulphide. The modification which yields free sulphur does not give potassium thiocyanate when treated with potassium cyanide; this reaction is shown strongly by the other variety. The difference is probably shown in the equations (i) $2\text{CuS} + 10\text{KCN} = \text{K}_6\text{Cu}_2\text{C}_8\text{N}_8 + 2\text{K}_2\text{S} + \text{C}_2\text{N}_2$ and $\text{C}_2\text{N}_2 + \text{H}_2\text{O} = \text{HCN} + \text{HCNO}$; (ii) $\text{Cu}_2\text{S}_2 + 8\text{KCN} = \text{K}_6\text{Cu}_2\text{C}_8\text{N}_8 + \text{K}_2\text{S}_2$ and $\text{K}_2\text{S}_2 + \text{KCN} = \text{K}_2\text{S} + \text{KCNS}$.

H. W.

The Dissociation Pressures of Hydrated Double Sulphates. I. Hydrated Cupric Alkali Sulphates. ROBERT MARTIN CAVEN and JOHN FERGUSON (T., 1922, **121**, 1406—1414).

The Alloys of Cerium. LÉON GUILLET (*Rev. Mét.*, 1922, **19**, 352—358).—The constitutional diagrams of alloys of cerium with iron, copper, aluminium, magnesium, bismuth, tin, and silicon are reproduced and discussed. Except in the case of iron in the iron-rich alloys, no solid solutions are formed with any of these metals, but a large number of definite compounds are known, some of which melt at a much higher temperature than either of the constituents; for example, Bi_2Ce_3 melts at 1,630° and CeAl_2 at 1,475°. There are two allotropic modifications of the compounds CeFe_2 and CeAl_4 . As cerium increases the brittleness of metals with which it alloys, it is not suitable for use as a deoxidiser.

A. R. P.

Reactions of Sodium Hydroxide with Salts of Aluminium.

ÉDOUARD GROBET (*J. Chim. physique*, 1922, **19**, 331—335).—Making use of the thermal method of titration previously described (cf. this vol., ii, 578), it is shown that the addition of sodium hydroxide to dilute solutions of aluminium nitrate forms successively aluminium hydroxide, sodium metaluminate, and sodium ortho-aluminate. The addition of sodium hydroxide to dilute solutions of aluminium chloride, aluminium sulphate, and potash alum forms successively aluminium hydroxide, basic sodium aluminate, $\text{Al}(\text{ONa})_2\cdot\text{Al}(\text{OH})_3$, and sodium ortho-aluminate. Sodium hydroxide added to concentrated solutions of aluminium chloride, nitrate, or sulphate produces a basic salt of the type $\text{AlX}_3\cdot\text{Al}(\text{OH})_3$, which is followed by the hydroxide, meta-aluminate and ortho-aluminate. Concentrated solutions of potash alum yield under the same treatment a basic salt, $\text{Al}_2(\text{SO}_4)_3\cdot 2\text{Al}(\text{OH})_3$, aluminium hydroxide, a basic aluminate, $\text{Al}(\text{ONa})_3\cdot\text{Al}(\text{OH})_3$, and the ortho-aluminate.

J. F. S.

Crystal Structures of the Hexa-ammoniates of the Nickel Haloids.

RALPH W. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1922, **44**, 1239—1245).—The crystal structure of the complex compounds of the type $\text{NiX}_2\cdot 6\text{NH}_3$, formed when ammonia is added to solutions of nickel chloride, bromide, and iodide respectively, has been examined by means of X-ray photographs. It is shown that the arrangement of the atoms in the crystals of these substances is such that the salts are strictly isomorphous with those of ammonium platinichloride (this vol., ii, 214). The dimensions of the unit cell and the values of the variable parameters defining the positions of the nitrogen atoms in the chloride and iodide have been estimated. The following values are recorded: $\text{NiCl}_2\cdot 6\text{NH}_3$, side of unit cell 10.09 Å.U.; $\text{NiBr}_2\cdot 6\text{NH}_3$, length of side of unit cell, 10.48 Å.U.; $\text{NiI}_2\cdot 6\text{NH}_3$, length of side of unit cell 11.01 Å.U. In each case there are four molecules in the unit cell. The nickel atoms occupy the position of platinum, and the halogen atoms those of nitrogen in the ammonium platinichloride crystal.

J. F. S.

Composition and Crystal Structure of Nickel Nitrate Hexammoniate.

RALPH W. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1922, **44**, 1260—1266).—From analyses, X-ray spectrum measurements, and considerations of space group arrangements, it is shown that neither of the formulæ $\text{Ni}(\text{NO}_3)_2\cdot 4\text{NH}_3\cdot \text{H}_2\text{O}$, or $\text{Ni}(\text{NO}_3)_2\cdot 4\text{NH}_3\cdot 2\text{H}_2\text{O}$ is correct for the pale blue isotropic octahedra which are obtained when an excess of a concentrated solution of ammonia is added to an aqueous solution of nickel nitrate. The true formula is $\text{Ni}(\text{NO}_3)_2\cdot 6\text{NH}_3$. A study of the Laue photographs of these crystals by the generally applicable methods which use the theory of space groups indicates that they have a structure similar to that of the corresponding complex haloids (preceding abstract), in which the nitrate groups replace the halogen groups, and in which the ammonia groups are related to the nickel atoms in exactly the same

way in both compounds. The position of the atoms of the nitrate groups cannot be determined with great accuracy. Both the symmetry characteristics and the diffraction data permit the same kind of displacement of the nitrate nitrogen atoms as is experienced by the sulphur atoms in pyrites. The unit cube contains four molecules and the length of its side is 10.96 Å.U. J. F. S.

Solubility. VI. Solubility of Ammoniates. FRITZ EPHRAIM and PAUL MOSIMANN (*Ber.*, 1922, **55**, [B], 1608—1619; cf. A., 1921, i, 508).—In a previous communication it has been pointed out that the similarity between dissolved substance and solvent has an important influence on solubility and that salts can achieve this similarity with water as solvent by the formation of hydrates or solvates. An experimental examination of this hypothesis has now been attempted by investigating the solubility in water of salts in which the formation of hydrates is rendered difficult. This can be achieved by occupying the co-ordination positions which would eventually be filled by water with other neutral groups, for example, ammonia. A relationship might therefore be expected between the solubility of a series of ammoniates such as $[\text{Ni}(\text{NH}_3)_6]\text{X}_2$ and their ammonia tension. A difficulty, however, arises, since many of these salts are decomposed by water and their solubility has therefore been determined in aqueous ammonia solution, d^{22}_4 0.950, to which half its volume of alcohol (96%) has been added. With the hexamminenickelo-salts there is a parallelism between solubility and ammonia tension in the series iodide \rightarrow bromide \rightarrow chloride \rightarrow thiocyanate, whilst the perchlorate and formate occupy the expected position in the series; on the other hand, in the series tetrathionate \rightarrow thiosulphate \rightarrow sulphide \rightarrow chloride \rightarrow nitrate \rightarrow chlorate, the solubility increases with decreasing ammonia tension. In general, therefore, there is no parallel between ammonia tension and solubility, at any rate in the cases of the ammoniates of the salts containing oxygen. The experiments have been extended to the ammines of copper and cadmium salts; in the oxygen-free salts, a relationship is observed between ammonia tension and solubility, but it is doubtful if this is more than accidental, since the solubility is so greatly affected by the nature of the medium. The ammines of cobalt and chromium are more suitable, since they dissolve in water to a reasonable extent and are not decomposed thereby. The two series $[\text{Co}(\text{NH}_3)_6]\text{X}_3$ and $[\text{Cr}(\text{NH}_3)_6]\text{X}_3$ are so similar in their general properties that it would be expected to find the solubilities of the salts falling in the same order. This is actually the case to a great extent, but the parallelism is not complete. Particularly in the case of the cobalt compounds, the salts fall into two distinct groups, in which the solubilities are of widely differing orders of magnitude, the boundary lying between the perchlorate and oxalate. Possibly the two portions comprise the true salts and pseudo-salts respectively.

The following compounds have not been described previously :

hexamminecobaltic naphthalene- β -sulphonate $[\text{Co}(\text{NH}_3)_6][\text{C}_{10}\text{H}_7\text{SO}_3]_3$, pale yellow, microscopic needles; *hexamminecobaltic picrate*, $[\text{Co}(\text{NH}_3)_6][\text{O}\cdot\text{C}_6\text{H}_2(\text{NO}_2)_2]_3$, microscopic needles; *hexamminechromic dichromate*, $[\text{Cr}(\text{NH}_3)_6]_2[\text{Cr}_2\text{O}_7]_3$, lustrous, hexagonal needles; *hexamminechromic picrate*, small, matted needles; *hexamminechromic naphthalene- β -sulphonate*, pale yellow, microscopic needles; *hexamminechromic perchlorate*, pale yellow needles; *hexamminechromic chlorate*, slender, pale yellow needles. The hexamminechromic salts resemble the alkaloids in giving *precipitates* with the following reagents: potassium mercuric iodide (slender, yellow needles), potassium bismuth iodide (microcrystalline, reddish-brown powder), sodium cobaltinitrite (very small, reddish-brown crystals). The solubilities of the following hexamminecobalti-salts (gram.-mol. per litre) in water at 9° have been estimated: chloride (0.20), bromide (0.040), iodide (0.015), nitrate (0.033), sulphate (0.015), perchlorate (0.013), chlorate (0.215), chromate (0.00055), dichromate (0.00029), oxalate (0.00069), phosphate (0.00055), naphthalene- β -sulphonate (0.00059), picrate (0.00042). The hexamminechromic salts have the following solubilities at 17.5°: chloride (0.42), bromide (0.118), iodide (0.043), nitrate (0.072), dichromate (0.005), sulphate (0.046), phosphate (0.0032), oxalate (0.00084), picrate (0.00037), naphthalene- β -sulphonate (0.00069), chlorate (0.062), perchlorate (0.0199).

H. W.

Hydrous Oxides. III. HARRY B. WEISER (*J. Physical Chem.*, 1922, **26**, 401—434).—In continuation of previous work (A., 1920, ii, 760), the author has studied the properties of various hydrous chromic oxides prepared under different conditions. The results indicate that no definite hydrates of chromic oxide are formed by precipitating a chromic salt with alkali. The evidence that Guignet's green is a definite hydrate is inconclusive. Hydrous chromic oxide freshly precipitated in the cold is readily soluble in acids, but becomes insoluble on keeping or heating. Between the two extremes of solubility an indefinite number of hydrous oxides exists. By precipitating hydrous chromic oxides at temperatures from 0° to 225°, substances ranging in colour from greyish-blue to bright green have been prepared. Positively charged colloidal hydrous chromic oxide may be prepared by peptising the hydrous oxide with chromic chloride, and by hydrolysis of the chloride or nitrate, but not of the acetate. The negatively charged colloid is prepared by peptising the hydrous oxide with sodium or potassium hydroxides. The properties of the respective colloidal suspensions are discussed, more especially the precipitating and peptising action of alkali salts.

J. S. G. T.

Precipitation from Uranyl Nitrate by means of Sodium Hydroxide. Radioactivity of the Precipitate. PIERRE JOLIBOIS and ROBERT BOSSUET (*Compt. rend.*, 1922, **174**, 1625—1628).—When sodium hydroxide is added to a dilute aqueous solution of uranyl nitrate precipitation only commences when an equimolecular

amount of sodium hydroxide has been added. From this stage up to the addition of two molecules a precipitate is obtained, and if this is filtered off and the filtrate is boiled, a further precipitate is deposited. Either precipitate contains 1.5% or more of sodium hydroxide which is not removed by washing. If more than two molecules of alkali are added precipitation is complete and the precipitate contains still higher percentages of alkali. Radioactivity measurements on the different precipitates show that the intensity of radiation is proportional to the amount of radium present. The first precipitate which is formed contains a very important proportion of the uranium-X, the oxide of which is apparently less basic than that of uranium. W. G.

Solubility in the Solid State of Bismuth and Cadmium in Lead. CLARA DI CAPUA (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 162—164).—By means of the method devised by Plato (A., 1906, ii, 521; 1907, ii, 239), the author has investigated the fusion diagrams of the systems Pb-Bi and Pb-Cd. The results obtained give for the solid solubility of lead in bismuth the value 4% and for that of bismuth the value 34%. For lead in cadmium or cadmium in lead the solid solubility is practically zero; in this system the specific thermal conductivity varies linearly with the composition. T. H. P.

Mineralogical Chemistry.

A New Occurrence of Ilsemaninite. CHAS. W. COOK (*Amer. J. Sci.*, 1922, [v], 4, 50—52).—A large number of molybdenum deposits were examined, but ilsemaninite was detected only at Ouray in Utah (A. 1917, ii, 491) and near Gilson in California. At the latter locality, molybdenite occurs with pyrites in aplite, and is often completely altered to yellow molybdenite. A brown tarnish suggests a first stage in the alteration to molybdenum dioxide; and a later stage to a mixture of dioxide and trioxide is suggested by the presence of a blue material which is insoluble in water. Ilsemaninite, the blue soluble material, is perhaps a hydrated compound of dioxide and trioxide. L. J. S.

Chemical and Spectrochemical Study of Spanish Bismuth Minerals. S. PIÑA DE RÚBIES and F. GILA ESTEBAN (*Anal. Fis. Quím.*, 1921, 19, 347—386; cf. Piña de Rúbies, A., 1921, ii, 267).—A description with chemical analyses and spectrographical data of bismuth minerals occurring in Spain. A series of minerals is described having a chemical composition varying between bismuthospherite, $(\text{BiO})_2\text{CO}_3$, and bismuthite, $\text{BiO}\cdot\text{CO}_3\cdot\text{Bi}(\text{OH})_2$.

Another class of minerals includes oruetite, Bi_8TeS_4 , and anti-moniferous bismuthine. Oruetite and similar minerals are probably eutectic mixtures of bismuth, tetradymite, Bi_2Te_3 , and bismuthine, Bi_2S_3 . The carbonate minerals of the first series may be derived from the oruetite minerals. Native bismuth, scheelite, and molybdenite are also described.

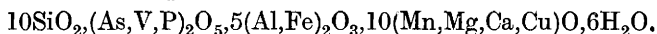
G. W. R.

Ardennite from Ceres, in the Ala Valley (Piedmont).

FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 147—151).—This mineral occurs, intimately associated with piedmontite and mixed with various other species, in aggregates of colophony-brown, vitreous fibres or rods, often twisted or bent. The crystals exhibit marked pleochroism and the other optical characters observed with the ardennite found in the Belgian Ardennes, and have the following percentage composition :

SiO_2 .	As_2O_5 .	P_2O_5 .	V_2O_5 .	Al_2O_3 .	Fe_2O_3 .	CuO .	CaO .	SrO .	BaO .
29.53	10.30	0.12	0.25	22.40	3.11	0.75	5.61	trace	trace
MnO .	NiO .	MgO .	Na_2O .	K_2O .	$\text{H}_2\text{O}-$.	$\text{H}_2\text{O}+$.	Total.		
18.76	0.04	4.03	0.07	0.12	0.12	5.42	100.63		

These results correspond well with the formula



The mineral is almost pure arsenioardennite, the proportion of vanadioardennite being very small.¹

T. H. P.

The Melting of Potash Felspar. G. W. MOREY and N. L. BOWEN (*Amer. J. Sci*, 1922, **4**, 1—21).—A pure synthetic orthoclase was prepared by crystallising glass of the composition KAlSi_3O_8 in a bomb containing water vapour, and this material was used for determining the melting point of the pure substance. The temperature usually given for the melting point, determined on natural crystals, is 1200° . It was found that orthoclase has no true melting point. When kept for a week at 1200° , it forms a glass which, under the microscope, is seen to have a cross-lined structure. At higher temperatures, the structure becomes more distinct and develops into typical leucite crystals. The temperature range of incongruent melting, in which leucite crystals are in equilibrium with liquid, is $1170-1530^\circ$. Three natural potash feldspars showed the same behaviour, namely, microcline from N. Carolina, sanidine from Laacher See, and adularia from St. Gotthard, but in these the upper limit was lowered somewhat by the foreign matter present. It follows that orthoclase must be considered as a binary compound in the leucite-silica ($\text{KAlSi}_2\text{O}_6-\text{SiO}_2$) system. The general form of the diagram of this system is shown, but only a few points on it have yet been accurately determined. The incongruent melting of orthoclase is of particular importance for the theory of rock formation. It shows that leucite can form from a liquid containing an adequate amount of silica, or even excess, for orthoclase formation and that a mass

may have leucite as early crystals (phenocrysts) together with free silica as late crystals (ground-mass). The regular behaviour of leucite in breaking up into orthoclase and nephelite suggests that the early separation of leucite may afford a key to the origin of many nephelitic rocks as well as of leucite rocks. E. H. R.

Tridymite from the Euganean Hills, Italy. EDOARDO BILLOWS (*Mem. Accad. Lincei*, 1922, [v], **13**, 506—524).—A detailed crystallographic description of tridymite from the trachyte of Zovon in the Euganean Hills near Padua. The crystals are cloudy and now consist of an aggregate of quartz. L. J. S.

Analytical Chemistry.

Behaviour of Platinum on Strong Ignition. D. BALAREFF (*Chem. Ztg.*, 1922, **46**, 573).—On heating either new or carefully cleaned old platinum crucibles in a blast flame or over a powerful Teclu burner, a fairly constant loss in weight of 0.6 mg. per hour was noticed, whilst the side of the crucible nearest the blast was considerably brighter than that more remote. No experiments were made, however, to find an explanation of the loss.

A. R. P.

Heavy Liquids for the Separation of Minerals. ENRICO CLERICI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 116—118; cf. A., 1911, ii, 257).—The following three liquids, useful for the mechanical separation of minerals of different densities, are colourless and may be diluted and recovered: Aqueous barium bromomercurate solution d^{11} 3.11, d^{18} 3.14. Saturated aqueous thallium formate solution, d^{10} 3.31, d^{20} 3.40, d^{50} 4.10. Aqueous solution of thallium formate and thallium malonate in equal proportions, d^{10} 4.00, d^{50} 4.70, $d^{\text{about } 100}$ above 5. Thallium formate, melting at 95° to a highly mobile liquid, may also be used, and a mixture of thallium formate and malonate in equal amounts melts below 95° and has d above 5. Fused thallium formate has d below 5, but it dissolves powdered thallium carbonate, giving a liquid with d above 5.

T. H. P.

A New Physico-chemical Method of Volumetric Analysis applied to some Problems of Inorganic Chemistry. PAUL DUTOIT and ED. GROBET (*J. Chim. physique*, 1922, **19**, 324—327).—A method is described by which solutions of acids may be titrated

with bases using a thermometer graduated in $1/100^\circ$ as indicator. The solution to be titrated is placed in a small Dewar vessel, which stands in a somewhat larger Dewar vessel, a mechanical stirrer is placed in the solution, and the alkali is added at regular intervals in amounts which cause the temperature to increase by not more than 0.02° . The burette is surrounded by asbestos paper and the stopcock is operated by a long pair of pincers. The number of c.c. of alkali added are plotted as abscissæ and the temperature after each addition as ordinate, and the points joined. It is found that the end-point is marked by a decided change of direction in the curve. Not only is this point fixed by the curve, but all other points at which a change in the nature of the reaction occurs are fixed. Thus with sulphuric acid the points corresponding with the completion of the formation of the hydrogen sulphate and the normal sulphate are both accurately shown. In the titration of phosphoric acid with sodium hydroxide the points where the formation of NaH_2PO_4 , Na_2HPO_4 , and Na_3PO_4 , respectively, is complete are well marked. In the titration of normal sodium phosphate with nitric acid, the points where the formation of Na_2HPO_4 , NaH_2PO_4 , and H_3PO_4 is complete are clearly marked. The titration of the nitrates of zinc, lead, and magnesium by this method indicates the completion of the formation of definite basic salts, and in the case of the two first-named metals, of zincates and plumbites, respectively. Titration of salts of cobalt, copper, and nickel with ammonia in the same way indicates the formation of the various ammonia complexes. This method yields identical results with those obtained by electrometric and electroconductivity titrations and in addition it also indicates the formation of derivatives which these methods do not.

J. F. S.

Simple Method of Electrometric Titration in Acidimetry and Alkalimetry. PAUL FRANCIS SHARP and F. H. MACDOUGALL (*J. Amer. Chem. Soc.*, 1922, **44**, 1193—1196).—The object of the work described is the preparation of a number of constant and reproducible electrodes which are electrometrically equivalent to hydrogen electrodes dipping in solutions of various known hydrogen-ion concentrations. Such electrodes are extremely useful in cases where it is necessary to titrate a solution of an acid to an end-point which shall have a definite hydrogen-ion concentration. In such a case, the half cell containing a hydrogen electrode and the solution being titrated is connected with the electrode which has the same potential difference as the hydrogen electrode will have when the titration is completed. A solution of alkali is then run into the acid until a galvanometer indicates that the total cell, comparison electrode|sat. KCl|titration liquid| H_2Pt , has a zero *E.M.F.* The following are the comparison electrodes together with the potential against a normal calomel electrode and the equivalent hydrogen-ion concentration :

HgPb—	
(12—12.5%)	0.52 c.c. KI in 100 c.c. solution ; <i>E.M.F.</i> 0.5195 = $10^{-4}N\text{-H}$
„	2.90 c.c. KI „ 100 „ „ 0.5609 = $10^{-4.7}N\text{-H}$
„	6.14 c.c. KI „ 100 „ „ 0.5786 = $10^{-5}N\text{-H}$
„	67.50 c.c. KI, in 100 „ „ 0.6378 = $10^{-6}N\text{-H}$
HgCd—	
(12—12.5%)	100 c.c. CdSO ₄ + 0.2 c.c. KI „ 0.6967 = $10^{-7}N\text{-H}$!
„	10 c.c. CdSO ₄ + 10 c.c. KI in 100 c.c. sol. <i>E.M.F.</i> 0.7560 = $10^{-8}N\text{-H}$
„	100 c.c. CdSO ₄ + 26.40 c.c. KI <i>E.M.F.</i> 0.8151 = $10^{-9}N\text{-H}$
„	2c.c. CdSO ₄ + 48.7c.c. KI in 100c.c. sol. <i>E.M.F.</i> 0.8743 = $10^{-10}N\text{-H}$

The number of c.c. of potassium iodide and cadmium sulphate refer, respectively, to 2.0*N*- and 0.5*N*-solutions, respectively (cf. Pinkhof A., 1920, ii, 121). J. F. S.

The Use of Potassium Ferrocyanide in Potentiometric Titrations. II. The Potentiometric Titration of Zinc. I. M. KOLTHOFF (*Rec. trav. chim.*, 1922, 41, 425—437).—The possibility of this titration has been established for some time (Koninck and Prost, A., 1896, ii, 675), but no worker has yet stated the degree of accuracy with which determinations may be made (cf. Bichowsky, A., 1917, ii, 219). The author recommends the use of a solution of potassium ferrocyanide, the concentration of which is 1/40 mol., to this is added 1 gram per litre of potassium ferricyanide. The standardisation of the zinc solution for the control experiments, which is described in detail, is a matter of difficulty; in previous work sufficient attention does not seem to have been directed to accuracy in this respect. The titration is best carried out at 70°, as at this temperature the reaction is quicker and the change in potential which denotes the end-point is greater. As the results obtained in neutral solution are too low, 1—2 c.c. of 4*N*-sulphuric acid should be added. Excess, however, should be avoided, otherwise the precipitate of potassium zinc ferrocyanide is partly dissolved and the change in potential at the end-point diminished. In such a solution 0.2 mg. of zinc may be determined within 1%. In presence of potassium sulphate at 70% and of ammonium sulphate at ordinary temperatures, results are obtained which are 0.5% too high; the latter salt at 70° has the reverse effect, which is also given by ammonium chloride. The titration may be carried out speedily and accurately in the inverse direction. H. J. E.

Estimation of Chlorine in Organic Compounds. J. KLIMONT (*Chem. Ztg.*, 1922, 46, 521—522).—Attempts were made to estimate chlorine in organic compounds by boiling the latter with alcoholic potassium hydroxide solution under a reflux apparatus and titrating the excess of alkali subsequently with standard acid. Acetylene dichloride, monochlorohydrin, monochloroacetone, dichloroacetone, α -chloronaphthalene, dichloronaphthalene, bornyl chloride, and pinene hydrochloride yielded either low or untrustworthy results; trichloroethane, acetylene tetrachloride, and α -dibromohydrin yielded high results, whilst monochloroacetic acid gave a correct result. W. P. S.

Estimation of Free Chlorine and Hypochlorous Acid in Concentrated Salt Solutions. M. C. TAYLOR and C. A. GAMMAL (*J. Ind. Eng. Chem.*, 1922, **14**, 632—635).—The estimation of free chlorine and hypochlorous acid in concentrated salt solutions, which may contain either sodium hypochlorite or hydrochloric acid, is usually carried out by estimations of total "available" chlorine, and of free chlorine by an aeration process. The latter, however, is inaccurate owing to decomposition of hypochlorous acid or of hypochlorite during aeration. It is now shown that the rate of the removal of the free chlorine is a linear function of the amount present at any moment, whilst when all free chlorine has been removed the rate of removal varies as the square of the amount of hypochlorous acid present. The curves obtained by plotting the rate of removal of chlorine against the total amount removed as measured by absorption in potassium iodide solution and titration with thiosulphate will therefore be two distinct lines having a point of intersection, the abscissa of which is the free chlorine initially present as such. To obtain the amount of chlorine initially present as hypochlorous acid and hydrochloric acid, the increase in acidity after aeration is determined by means of potassium iodide-iodate solution in terms of thiosulphate solution, and this is equal to the actual loss of chlorine during aeration due to such reactions as $\text{HOCl} \rightarrow \text{HCl} + \text{O}$. G. F. M.

Estimation of the Chlorometric Degree of Bleaching Chlorides. J. ROYER (*Ann. Falsif.*, 1922, **15**, 146—148).—For the estimation of available chlorine in bleaching solutions the method of Poncius is recommended as being rapid and exact. It consists in titrating the solution with standard potassium iodide in the presence of sodium hydrogen carbonate. The first reaction consists in the oxidation of the iodide to iodate, but as soon as the free chlorine has been used up the next drop of iodide solution reacts with the iodate with the liberation of free iodine, which is indicated by starch paste. W. G.

Electrometric Titrations with Silver Nitrate. Estimation of Chlorides, Bromides and Iodides, and of Iodides in the Presence of Chlorides and Bromides. I. M. KOLTHOFF (*Z. anal. Chem.*, 1922, **61**, 229—240).—In most cases the solubility of the silver compound indicates whether the end-point of a titration with silver nitrate solution may be ascertained electrometrically. The method is trustworthy for chlorides, iodides, and bromides, even in very low concentration, and iodides may be titrated in ammoniacal solution in the presence of chlorides and bromides. Certain complex salts, such as ferrocyanides, pyrophosphates, etc., cannot be estimated by the method, although with ferricyanides and thiocyanates the results obtained are accurate. The method may also be used for the estimation of cyanides, chromates, oxalates, tartrates, succinates, and salicylates. W. P. S.

Estimation of Minute Amounts of Gaseous Oxygen and its Application to Respiratory Air. HOWARD M. SHEAFF (*J. Biol. Chem.*, 1922, **52**, 35—50).—The method is intended mainly for use in following the oxygen consumption of plant and animal tissue under different conditions. By means of the apparatus, which is described and illustrated in the original, it is stated that oxygen can be estimated in amounts as small as 1×10^{-7} gram. The method depends on the conversion of the oxygen, in the presence of nitric oxide and sodium hydroxide, into sodium nitrite, and the estimation of the latter colorimetrically by means of sulphanilic acid and α -naphthylamine. E. S.

The Oxygen-absorption and Concentration of Pyrogallol Solutions used in Gas Analysis. FRITZ HOFMANN (*Z. angew. Chem.*, 1922, **35**, 325—328).—The absorptive powers of solutions of pyrogallol and potassium hydroxide of all proportions are tabulated in a Gibbs triangular diagram for the ternary system pyrogallol, potassium hydroxide, and water. A line of maximum absorptions was found to correspond with mixtures containing pyrogallol and potassium hydroxide in the proportions 3 to 2. The field to one side of the line, corresponding with a smaller proportion of the latter, falls sharply in power of absorption. The optimum proportion is given as pyrogallol 20 parts, potassium hydroxide 20 parts, and water 60 parts. H. M.

Rapid Estimation of Sulphur. I. LUIGI LOSANA (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 204—206).—The method here described depends on the fact that, if a compound containing sulphur is heated with powdered iron in absence of air, the sulphur in the residual mass is liberated completely as hydrogen sulphide on subsequent treatment with hydrochloric acid. This gas is absorbed by zinc acetate solution and the sulphide thus formed estimated by titration with iodine solution. Tests made on flowers of sulphur and on copper, lead, barium, and cobalt sulphates gave excellent results. The method is applicable also to the estimation of sulphur in organic compounds, but the latter must previously be heated with copper oxide or lead chromate in a porcelain crucible, or, if the organic compound is volatile, in a narrow hard glass tube, in which it is covered with a deep layer of the oxidising material [cf. *J. Soc. Chem. Ind.*, 1922, 614A]. T. H. P.

The Kleemann Modification of the Kjeldhal Process. FRANTIŠEK SKUTIL (*Chem. Listy*, 1922, **16**, 173—177).—The various methods of estimating the nitrogen of foodstuffs and manures, using modifications of the Kjeldhal process, are reviewed, and the advantages of the Kleemann modification (*Z. angew. Chem.*, 1921, **34**, 625) pointed out. Results obtained by a modification of this method are found to be in satisfactory agreement with those obtained by the standard analytical method used in Czecho-Slovakia. This method differs from that of Kleemann in that, after the addition of mercury, 30% of hydrogen peroxide is added, and then the

concentrated sulphuric acid, slowly, and with cooling. After some time, the contents of the flask are heated until a deep coloration appears. Finally, anhydrous potassium sulphate is added, and the process completed. R. T.

The Estimation of the Total Non-protein Nitrogen of Serum. Comparative Study of Trichloroacetic and Metaphosphoric Acids as Protein Precipitants. PAUL CRISTOL (*Bull. Soc. Chim. Biol.*, 1922, 4, 267—271).—Higher values are obtained for total non-protein nitrogen when proteins are precipitated by means of metaphosphoric acid than when trichloroacetic acid is used for this purpose. This is due to the partial hydrolysis of the proteins by the former reagent. E. S.

The Estimation of Non-protein Nitrogen in Blood. ERIC PONDER. (*Biochem. J.*, 1922, 16, 368—369).—Blood (0.2 c.c.) is added to water (1 c.c.) and the pipette used is washed out twice, each time with a further 0.2 c.c. of water. The protein is precipitated with 0.2 c.c. of a 10% solution of sodium tungstate and 0.2 c.c. of 2/3N-sulphuric acid as in Folin's method for the preparation of blood filtrates. 0.5 C.c. of this filtrate is boiled very gently with 0.2 c.c. of a digestion mixture diluted 1 in 4. The digestion mixture consists of 50 c.c. of a 5% copper sulphate solution, 100 c.c. of 85% phosphoric acid, and 300 c.c. of pure sulphuric acid. After boiling for two minutes, water is added to make the volume 3.5 c.c., and the solution is directly nesslerised and compared with a standard solution of ammonium sulphate. W. O. K.

Detection and Estimation of Nitrate Nitrogen in Urine and Serum. O. NOLTE (*Z. anal. Chem.*, 1922, 61, 278—282).—The presence of nitrates may be detected by means of the diphenylamine reaction or by the less sensitive ferrous sulphate reaction; the diphenylamine reaction, however, is obtained with oxidising substances other than nitrates. For the estimation of nitrates in urine, the Schlösing-Grandeau gasometric method appears to be the most trustworthy, but the nitric oxide content of the volume of gas obtained must be estimated subsequently. W. P. S.

Analytical Determination of Oxides of Nitrogen in Gas Mixtures. CHARLES L. BURDICK (*J. Ind. Eng. Chem.*, 1922, 14, 308—310).—Mixtures of nitrogen peroxide and nitric oxide are absorbed in dilute alkali in accordance with the equations $3\text{NO}_2 + 2\text{NaOH} = 2\text{NaNO}_3 + \text{NO} + \text{H}_2\text{O}$ and $\text{NO} + \text{NO}_2 + 2\text{NaOH} = 2\text{NaNO}_2 + \text{H}_2\text{O}$. If previous to absorption there is a development of mist in consequence of cooling, the nitrogen peroxide present in the hot gas will be partly converted into nitric acid and nitric oxide. An absorption apparatus must therefore provide for the measurement of nitric oxide passing through the alkali unabsorbed. The absorption bulb in the apparatus described is a tube containing a number of glass bells with side perforations placed vertically above one another and with the inlet tube passing down through

their central axes. This is filled with a known volume of $N/10$ alkali hydroxide free from carbonate diluted as required. The gas passes through this into an aspirator, in which it is treated with hydrogen peroxide, absorbed in excess of alkali hydroxide, and estimated as usual. The solution in the absorption bulb is titrated with $N/10$ -sulphuric acid, using a few drops of a solution of methyl-red in $N/100$ -alkali hydroxide as indicator. To the neutralised solution a known excess of permanganate with 5 c.c. of sulphuric acid are added, the solution is left for a few minutes, a slight excess of ferrous sulphate added, and the excess titrated back. If there is no acid mist present and if A c.c. of alkali and P c.c. of permanganate are neutralised in the absorber, it will be seen that of this $(3A + P)/2$ c.c. of alkali hydroxide have been neutralised by nitrogen peroxide and the total alkali hydroxide— $(3A + P)/2$ c.c. by nitric oxide.

If nitric acid mist is present, it is absorbed as nitrate in the bulb and is measured by the excess of alkali hydroxide neutralised over the nitrite formed, whilst the nitrite formed contains twice the quantity of nitrogen present as nitrogen peroxide. If more than 5% of excess oxygen is present in the gas mixture, a correction for oxidation during the passage of the gas through the sampling tube should be applied.

C. I.

A Possible Source of Error in the Bell-Doisy Method for the Estimation of Phosphates in Blood Plasma. W. DENIS and L. VON MEYSENBUG (*J. Biol. Chem.*, 1922, **52**, 1—3).—The method of Bell and Doisy (*A.*, 1920, ii, 769) for the estimation of phosphates in blood gives accurate results when applied to serum, but low values are obtained when plasma is used. Serum should therefore be used for this estimation; if, however, plasma is used, the accuracy may be increased by restricting the amount of anti-coagulant and increasing the quantities of molybdic acid and quinol.

E. S.

Microchemical Investigation of Arsenic. ARNALDO PIUTTI and ENRICO BOGGIO-LERA (*Mem. Accad. Lincei*, 1922, [v], **13**, 475—479).—In the detection of arsenic in very small proportions, good results are obtained by using a reagent composed of 1 c.c. of 3% ammonium molybdate solution, 10 c.c. of 3.4% ammonium nitrate solution, and 39 c.c. of 40% nitric acid solution. With liquids containing 0.02—0.004 mg. of arsenic per c.c., this reagent is used directly, but for lower concentrations of arsenic, the reagent is diluted five times with 40% nitric acid. A drop of the arsenic solution yields characteristic microscopic crystals when evaporated with a drop of the reagent. As little as 0.00005 mg. of arsenic is detectable in this way.

T. H. P.

Estimation of Arsenic Acid. L. ROSENTHALER (*Z. anal. Chem.*, 1922, **61**, 222—229).—Diffused light does not interfere in the iodometric estimation of arsenic acid, but atmospheric oxygen

reacts with the hydriodic acid formed, yielding further quantities of free iodine. This may be prevented by adding 5 grams of sodium hydrogen carbonate before the potassium iodide is introduced. The titration solution should contain at least 16% of hydrochloric acid or 33.3% of sulphuric acid. When sulphuric acid is used, the following procedure should be adopted. The iodate solution is treated with concentrated sulphuric acid in quantity sufficient to make the concentration of the latter 33.3%, the mixture is cooled, and 5 grams of sodium hydrogen carbonate are added in small quantities at a time; concentrated potassium iodide solution is now added, and the iodine is titrated with $N/10$ -thiosulphate solution. A precipitate which forms on the addition of the iodide consists chiefly of arsenic tri-iodide, and should be dissolved by adding a small quantity of water before the titration is commenced.

W. P. S.

Iodometric Estimation of Arsenic and Antimony Sulphides. FERDINAND NIKOLAI (*Z. anal. Chem.*, 1922, **61**, 257—272).—Arsenites and the corresponding antimony salts may be estimated volumetrically by adding their solutions to an excess of standard iodine solution containing dilute acetic acid and sodium acetate and then titrating the excess of iodine with thiosulphate solution. Arsenic trisulphide, or antimony trisulphide, may be titrated by dissolving it in sodium hydroxide solution and adding this solution to iodine solution containing acetic acid and sodium acetate, with subsequent titration of the excess of iodine. The alkaline solution of the sulphide is oxidised readily by atmospheric oxygen, but this may be prevented, or the rate of oxidation retarded to a considerable extent, by the addition of a small quantity of gelatin.

W. P. S.

Tests of an Iodine Pentoxide Indicator for Carbon Monoxide. S. H. KATZ and J. J. BLOOMFIELD (*J. Ind. Eng. Chem.*, 1922, **14**, 304—306).—The "Hoolamite" carbon monoxide indicator consists of a glass tube containing granulated pumice impregnated with 1 part of iodine pentoxide to 5 parts of fuming sulphuric acid (60% SO_3). The gas is drawn through cotton-wool filters and a tube of activated charcoal into a rubber hand bulb and discharged through the tube containing the pumice. The colour produced on the latter is matched with a series of permanent colours in a sealed glass tube. A series of tests with a large number of observers showed that by this instrument a minimum concentration of 0.07% of carbon monoxide can be detected, and that a rough quantitative estimation of higher concentrations can be made. In the absence of the activated charcoal most hydrocarbons, hydrogen sulphide, and hydrogen chloride interfere; methane, chlorine, carbon dioxide, sulphur dioxide, and some other gases do not. The "Hoolamite" tube may be used for six to eight estimations, after which it deteriorates.

C. I.

The Direct Estimation of Small Quantities of Radium by the Penetrating Rays. B. SZILARD (*Compt. rend.*, 1922, **174**, 1695—1698).—The electrometer previously described (*ibid.*, 1922, **174**, 1618) has been modified so as to provide a transportable instrument working without either a high tension battery or a projection mirror. By means of it rapid measurements can be made of the penetrating rays. The sensitiveness of the instrument corresponds with 10^{-4} U.E.S.

W. G.

Ash-alkalinity (of Foodstuffs). B. PFYL. (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 313—339).—To utilise the titration values of the ash of foodstuffs as indications of their composition, it is necessary to choose the values, to be determined in such a way that they are definite and as independent as possible of chance circumstances, and to employ simple and unexceptionable methods for determining them. The chemical processes taking place during the incineration of foodstuffs have to be considered more closely than has been done in the past, and the necessity for avoiding loss of mineral acids and for the conversion of the whole of the phosphorus into tribasic phosphate must be kept in view. In many cases this can only be attained by the addition of a measured quantity of alkali before incineration. The most useful values to be determined are (a) the intrinsic alkalinity, (b) the methyl-orange alkalinity, and (c) the total phosphate of the ash. The first may be defined as the excess, expressed in milli-equivalents, of the kations Na^+ , K^+ , Ca^{++} , Mg^{++} , which remains after combination with the anions PO_4''' , SO_4'' , Cl' for O'' , and the weakly acid anions CO_3'' , SiO_3'' , BO_2' , MnO_3'' , MnO_4'' , AlO_2'' . If such excess does not exist, the difference is expressed as "intrinsic acidity." (b) is the excess, expressed in milli-equivalents, of the same four kations which remains after combination with the anions $\text{H}_2\text{PO}_4'$, SO_4'' , and Cl' for O'' , and the above enumerated weakly acid anions. The absence of such excess is indicated as methyl-orange acidity. (c) The total phosphates is expressed in milli-equivalents of PO_4''' . These three values can be obtained by titration against methyl-orange, followed by a titration against phenolphthalein. Full details of simple methods of carrying out the above determinations are given; these are the result of many years of experience, and are founded on sound scientific principles. Modifications necessary in special cases and precautions and corrections to be applied where special accuracy is needed are also indicated. The above three values are usually calculated to 100 grams of dry food-stuff or 1 litre of liquid, but occasionally to 1 gram of ash or 1 gram of ash soluble in hydrochloric acid. In cases of adulteration, one or other of these values is affected. Methods proposed by others for the determination and presentation of ash-alkalinity are criticised.

H. C. R.

Atkinson's Process for the Estimation of Potassium in the Presence of Sodium, Magnesium, Sulphates, and Phosphates. S. J. WATSON (*Analyst*, 1922, **47**, 285—288).—The

process is considered unsatisfactory because the compensating errors necessary to overcome the loss due to the solution of some potassium perchlorate do not occur to an extent sufficient to balance this loss, and the quantity of methyl alcohol and perchloric acid used is too large to make the process economical. Keeping the contents of the beaker at the boiling point for an hour, whilst perhaps necessary to ensure complete solution of undesirable substances, must also favour the solution of potassium perchlorate itself.

H. C. R.

The Estimation of Calcium in Blood. ARTHUR ROBERT LING and JOHN HERBERT BUSHILL (*Biochem. J.*, 1922, **16**, 403—406).—Two to 5 c.c. of blood are incinerated in a platinum dish, treated with 1.5 c.c. of concentrated hydrochloric acid, and washed into a special centrifuge tube. After adjusting the reaction, the calcium is precipitated with oxalic acid and ammonium oxalate. The calcium oxalate is centrifuged and washed, sulphuric acid is added, and the oxalic acid titrated with permanganate.

W. O. K.

A Colorimetric Method for the Estimation of Small Amounts of Magnesium. F. S. HAMMETT and E. T. ADAMS (*J. Biol. Chem.*, 1922, **52**, 211—215).—The method is designed for application to urine, blood, and tissue extracts and is a modification of Kramer and Tisdall's method (*A.*, 1921, ii, 595). The precipitate of ammonium magnesium phosphate obtained in the latter method is dissolved in 0.01*N*-hydrochloric acid and the phosphorus estimated colorimetrically by Bell and Doisy's method (*A.*, 1920, ii, 769). The value for magnesium is then calculated from this result.

E. S.

Volumetric Estimation of Lead Peroxide in Miniums. Practical Modification of Diehl's Method. A. BONIS

(*Ann. Falsif.*, 1922, **15**, 157—159).—The following modified procedure for Diehl's method of estimating lead peroxide in samples of minium is advocated. Half a gram of the sample is macerated with 2.5 c.c. of nitric acid (*d* 1.080) and the mixture is washed into a conical flask with 25 c.c. of a saturated solution of sodium acetate. To this is added 10 c.c. of a 12% solution of potassium iodide in saturated sodium acetate, and the whole is well shaken, and the iodine liberated is titrated with *N*/10-thiosulphate solution. If the sample of minium contains iron oxide, instead of titrating the free iodine an excess of standard thiosulphate is added and the whole is made up to 100 c.c. with the saturated sodium acetate solution. After filtering, an aliquot portion of the filtrate is titrated back with *N*/10-iodine solution.

W. G.

Rapid Electro-analysis. A. KLING and A. LASSIEUR (*Ann. Chim. Analyt.*, 1922, **4**, 171—177).—For the rapid electrolytic deposition of copper or zinc a silver cathode is recommended,

together with an anode of platinum alloyed with iridium or rhodium. The silver cathode is readily cleaned without loss in weight by immersion in a cold solution of 10 grams of trichloroacetic acid in 50 c.c. of strong ammonia and 50 c.c. of water. Copper is deposited from a sulphate solution acidified with nitric acid and containing 5 grams of sodium metaphosphate if iron is present. Zinc is deposited from a solution containing sodium acetate and 5 c.c. of acetic acid per 100 c.c., together with 10 c.c. of a saturated solution of sodium fluoride if iron is present; large quantities of iron should, however, be separated. Lead may be deposited on the anode as peroxide from a solution containing 15 c.c. of nitric acid per 100 c.c., or as metal on the cathode by electrolysis at 70° with 5 amperes a solution containing less than 0.4 gram of lead and 3 c.c. of nitric acid (d 1.3), 2.5 grams of crystallised gallic acid, and 5 c.c. of 95% alcohol in 100 c.c. total bulk. Antimony may be electrolysed from a solution containing 80 c.c. of sodium sulphide solution (d 1.14), 60 c.c. of water, and 5 grams of potassium cyanide by a current of 5 amperes at 60–70°, or from a boiling solution containing 20 c.c. of hydrochloric acid and 4 grams of hydroxylamine hydrochloride in 130 c.c. of water. The latter solution, with the addition of 10 grams of ammonium oxalate, may be used for the deposition of tin. The above methods are adapted to the rapid analysis of brasses, bronzes, and white metals [cf. *J. Soc. Chem. Ind.*, 1922, 551A]. A. R. P.

Iodometric Estimation of Copper in the Presence of Iron.

A. WÖBER (*Z. angew. Chem.*, 1922, **35**, 336–337).—Solutions containing copper salts in the presence of ferrous iron always contain a small amount of cuprous ions. These cannot be oxidised by nitric acid or hydrogen peroxide in ammoniacal solution, as the small amount of nitrites formed interferes with the subsequent titration. The solution is therefore made ammoniacal and treated with a current of air at 70°, whereby all the copper dissolves as cupric salt and the iron is precipitated as ferric hydroxide, which is collected, re-dissolved and re-precipitated to recover the adsorbed copper. The combined filtrate is boiled to expel ammonia, acidified, treated with potassium iodide, and titrated as usual [cf. *J. Soc. Chem. Ind.*, 1922, 545A]. A. R. P.

Separation of Aluminium from Iron by means of o-Phenetidine. K. CHALUPNY and K. BREISCH (*Z. angew. Chem.*, 1922, **35**, 233–234).—The solution containing the iron and aluminium salts is slightly acidified with hydrochloric acid and treated with a current of hydrogen sulphide for ten minutes; carbon dioxide is then passed through the solution until all excess of hydrogen sulphide has been expelled. These operations are carried out in a flask closed with a cork and provided with inlet and outlet tubes. Ammonium carbonate is then added until a precipitate forms, the latter is dissolved by the addition of dilute hydrochloric acid, and an excess of 5% alcoholic phenetidine

solution is added. The flask is closed, the contents are heated at 80° , and the precipitate is then collected, washed with hot, dilute ammonium nitrate solution, ignited, and weighed as aluminum oxide. If copper and other metals are present with the iron and aluminium, the copper must be separated electrolytically, the iron and aluminium then precipitated as basic acetates, the latter dissolved in dilute hydrochloric acid, and the solution used for the separation of the iron and aluminium as described. It is essential that the iron should be present in the ferrous state; ferric salts yield a precipitate with phenetidine solution. W. P. S.

Gravimetric Analysis. XXV. Estimation of Manganese. L. W. WINKLER (*Z. angew. Chem.*, 1922, **35**, 234—235; cf. A., 1921, ii, 656).—The manganese is precipitated as manganese ammonium phosphate, the method being that described previously (*loc. cit.*) for the estimation of cadmium. Small corrections are applied to the weight of precipitate obtained; for instance, 1 mg. is deducted when the precipitate weighs 0.2 to 0.3 gram. The presence of potassium chloride does not interfere, but sodium chloride must not be present. W. P. S.

Oxidation of Manganese to Permanganate in Alkaline Solution. J. HESLINGA (*Chem. Weekblad*, 1922, **19**, 274).—Manganese in ores and alloys is readily detected by heating the solution with potassium hydroxide and excess of copper sulphate (which acts as a catalyst), and adding a few drops of a mixture of bromine water and potassium hydroxide; the violet coloration due to permanganate develops at once. 0.005 Mg. of manganese may be detected. The reaction is not suitable for quantitative estimation, since it is only complete where very small quantities of manganese are present; also the presence of iron affects the colour, probably by formation of potassium ferrate.

The catalytic action of the copper oxide is probably due to its tendency to form easily dissociated oxygen compounds, and its tendency to form compounds with manganese hydroxide. More copper than manganese must be present, otherwise the catalyst remains in this combination. S. I. L.

The Adsorption of Iron by Precipitates of Manganese Dioxide. MAX GELOSO (*Compt. rend.*, 1922, **174**, 1629—1631; cf. Nicolardot, Geloso and Réglade, A., 1920, ii, 334).—When manganese is precipitated as its dioxide by the addition of ammonium persulphate to an acid solution of manganese sulphate containing some iron salt, the amount of iron adsorbed by the precipitate varies directly with the amounts of iron and manganese present in the solution and inversely with the acidity. The presence of ammonium sulphate has no effect. The iron adsorbed is mostly in the form of hydroxide. W. G.

Estimation of Chromium in Steels. LUIGI LOSANA and ENRICO CAROZZI (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 197—200).—Gravimetric methods for estimating chromium in steel give good

results but are too tedious for industrial use, and colorimetric methods are not to be recommended. Provided that attention is directed to various points, satisfactory results are obtained by Stead's method, in which the chromium is oxidised by means of nitric acid and by permanganate to chromic acid and this is treated with ferrous sulphate, the excess of the latter being titrated with permanganate. Modifications are suggested which render the ammonium persulphate method more rapid and exact [cf. *J. Soc. Chem. Ind.*, 1922, 594A].

T. H. P.

New Qualitative Test for Uranium. HAROLD D. BUELL (*J. Ind. Eng. Chem.*, 1922, **14**, 593).—Uranium may be detected in slags or ores by preparing a nitric acid solution of the material, too great an excess of acid being avoided, and adding an excess of granulated zinc. When the reaction with the acid has subsided, a yellow deposit will appear on the zinc if uranium is present. Gold, platinum, thorium, lead, tungsten, titanium, chromium, mercury, and copper do not interfere with the test. Iron and vanadium only interfere if present in large quantities, and in that case the spent liquid is removed, and the zinc and the deposit are again treated with nitric acid. The deposit dissolves, but reappears when the acid is again exhausted, and vanadium and iron remain in solution. As regards the delicacy of the test, in a solution of pure uranyl nitrate it was possible to detect 0.88 mg. of uranium per c.c. The test is not applicable in presence of sulphuric or hydrochloric acids. The yellow deposit is apparently the hydrated trioxide, $\text{UO}_3 \cdot 2\text{H}_2\text{O}$.

G. F. M.

Colorimetric Estimation of Vanadium in Steel. A. KROPF (*Z. angew. Chem.*, 1922, **35**, 366—367).—The steel is dissolved in a mixture of nine parts of sulphuric and one part of phosphoric acid to prevent separation of tungstic acid. The solution is oxidised first with nitric acid, then with ammonium persulphate to destroy carbonaceous matter, and the colour produced by hydrogen peroxide in this solution is matched with that produced by a known amount of vanadium pentoxide added to a solution containing approximately equal amounts of chromium, nickel, and hydrogen peroxide [cf. *J. Soc. Chem. Ind.*, 1922, 594A.]

A. R. P.

Rapid Detection of Bismuth in Urine and in Saliva. DOMENICO GANASSINI (*Boll. Chim. Farm.*, 1922, **61**, 321—326).—For the detection in urine of small proportions of bismuth, which is administered in the form of sodium or potassium bismuthotartarate (cf. Sazerac and Levaditi, this vol., i, 89) in cases of syphilis, good results are obtained by means of stannous chloride solution, prepared by dissolving 10 grams of the crystallised salt in 10 c.c. of concentrated hydrochloric acid and heating the liquid with a few pieces of tin on a water-bath until it becomes almost clear (cf. Vanino and Treubert, A., 1898, ii, 461). Ten c.c. of the urine are treated with 2 c.c. of this reagent and then with 5 c.c.

of 20% sodium hydroxide solution, and the whole is shaken. If the urine contains salts of bismuth, these undergo reduction to the metal, which is deposited with the precipitated calcium and magnesium phosphates and gradually colours these brown or black; in some cases, also, the supernatant liquid becomes brown owing to dissolution of part of the bismuth in the colloidal condition. Saliva may be tested similarly. That the dark precipitate actually contains bismuth may be shown by conversion of a little of it into the vivid red bismuth rubidium iodide, $\text{BiI}_3 \cdot 2\text{RbI} \cdot 2.5\text{H}_2\text{O}$, and microscopic examination of this.

Nylander's test for dextrose (A., 1884, 1433) may be used inversely as a test for bismuth, but is not so sensitive as that given above.

T. H. P.

Estimation of Minute Quantities of Methane. ERNST MURMANN (*Oesterr. Chem.-Ztg.*, 1922, 25, 90).—The estimation of small quantities of methane, involving the absorption of the carbon dioxide derived therefrom in baryta solution, has hitherto required two or more absorption flasks to ensure the complete removal of carbon dioxide from the gases owing to the short time in which the bubbles are in contact with the liquid. One ordinary Erlenmeyer flask only is sufficient, however, if the gases are led into the baryta solution through a capillary tube and 0.5—1.0 c.c. of 1% gelatin solution is added to the liquid so as to make a foam on the surface which increases the duration of contact of the gases and the absorbent solution to at least thirty seconds, and renders absorption thereby complete. The capillary may conveniently be fixed into the flask through the straight arm of a T-piece fitted into a rubber stopper, and the connexion made gas-tight with a piece of rubber tube. The artifice may also be useful for other cases where complete absorption of a gas by a liquid is required.

G. F. M.

The Estimation of Benzene in Gases. E. BERL (*Z. angew. Chem.*, 1922, 35, 332).—The benzene is absorbed by carbon, which is then heated at 100—120° in a current of steam (in a salt-bath). A small amount of benzene remains behind, and therefore a test is made with carbon containing benzene to control the results. The burette filled with water in which the benzene is collected is provided with an overflow in such a manner that the benzene remains in the burette. This method is simpler and better than that by which the benzene is washed out of the gases with light petroleum.

H. M.

Some New Colour Reactions of Cholesterol. LOUIS KAHLBERG (*J. Biol. Chem.*, 1922, 52, 217—225).—Cholesterol dissolves in arsenic trichloride to a pink solution changing to cherry-red; isocholesterol yields a cobalt blue solution changing through violet, purple, and dark red to dark green; phytosterol, however, dissolves to a colourless solution. The colours are discharged by the addition of solvents such as benzene, toluene, and

chloroform. The colour reactions are also obtained with hot solutions of arsenious oxide in concentrated hydrochloric acid, but are not so permanent as with the anhydrous chloride. Coloured solutions, which are not, however, sufficiently characteristic to be used for distinguishing between the sterols, are also obtained with certain other acid chlorides. E. S.

Analytical Observations on the True Blood-sugar Value in Normal and Pathological Individuals. WILHELM STEPP (*Arch. expt. Path. Pharm.*, 1922, 90, 105—128).—A series of analyses of blood-sugar was carried out in the following way: the proteins were removed with phosphotungstic acid and the sugar estimated by a reduction method (that of Bertrand or Laquenne); a further amount of the filtrate was freed from phosphotungstic acid with lead acetate, the excess of lead removed, and the solution concentrated; the concentrated fluid was analysed for sugar by a reduction method, by fermentation, and polarimetrically.

The values obtained by the reduction methods on the untreated filtrate were 20% to 100% higher than those obtained on the filtrate after concentration; the difference was greatest in cases where there was nitrogen retention, and was proved to be not due to loss of sugar in the process of analysis.

The agreement between the results obtained by the three methods on the concentrated filtrate was, on the whole, good, the polarimetric and fermentation methods giving especially close agreement. It is suggested that nitrogenous reducing substances are carried down in the process of removing the excess of phosphotungstic acid, and that the lower values obtained after this treatment represent the true concentration of sugar in the blood.

C. R. H.

The Inversion of Sucrose in the Alkaline Copper Solution. E. CANALS (*Bull. Soc. chim.*, 1922, [iv], 31, 583—588).—Results indicate that sucrose is slowly hydrolysed during the estimation of reducing sugars in its presence by means of some form of Fehling's solution. The actual amount of sucrose hydrolysed increases with the concentration of the sucrose, with the time of heating, and with the temperature at which the liquid is kept. It is essential therefore to make a blank estimation, and it is advisable to heat by immersion in a water-bath. W. G.

Estimation of Humus by Oxidation with Chromic Acid. A. GEHRING (*Z. anal. Chem.*, 1922, 61, 273—278).—The soil is first treated with dilute sulphuric acid in a flask through which a current of air free from carbon dioxide is passed. When all carbon dioxide produced by the decomposition of carbonates has been expelled, potassium dichromate is added to the flask and the mixture is heated; the carbon dioxide and other gases resulting from the oxidation of the organic matter are passed through a combustion tube containing copper oxide and lead chromate, and the carbon dioxide is then absorbed in potash bulbs. W. P. S.

Oxidation with Mixtures of Sulphuric Acid and Chromates. L. J. SIMON (*Compt. rend.*, 1922, **174**, 1706—1708).—For the wet combustion of organic compounds by means of chromic acid, the most satisfactory results are obtained by the use of concentrated sulphuric acid and silver chromate, using about 15 c.c. of the acid and 12 grams of the chromate for about 0.1 gram of substance. This oxidising mixture may be used for the combustion of acetates or acetyl derivatives, theoretical results being obtained. W. G.

Analysis of Acetic Anhydride. C. EDWARD SAGE (*Perf. Essent. Oil Rec.*, 1922, **13**, 172).—In the method described by Reclaire (this vol., ii, 532) for the estimation of acetic anhydride, the phenolphthalein used as indicator seems with certain samples to be peculiarly insensitive. The actual cause of this is obscure, but the peculiarity seems to run parallel with the development of the iodoform reaction when the sample in question is tested with sodium hydroxide and iodine. The unknown impurity giving this reaction may be traced back to the original acetic acid from which the anhydride was prepared, and it seems to be associated with faults in odour which sometimes develop in products prepared from the anhydride, for example, aspirin, or synthetic "acetyl" perfumes. The insensitiveness of phenolphthalein above mentioned may be overcome, and a sharp end-point obtained if the titration is made by adding an excess of $N/2$ -hydroxide, keeping for some time without heating until hydrolysis is complete, then adding a known quantity of $N/2$ -acid and finishing off the titration with more $N/2$ -hydroxide. By this procedure errors due to heating under reflux will also be eliminated. G. F. M.

Estimation of Fatty Acids (and Cholesterol) in Small Amounts of Blood Plasma. W. R. BLOOR, K. F. PELKAN, and D. M. ALLEN (*J. Biol. Chem.*, 1922, **52**, 191—205).—Bloor's method (A., 1914, ii, 392) for the estimation of fatty acids in blood probably gives incorrect results owing to the different nephelometric values which the various fatty acids and cholesterol possess (cf. Csonka, A., 1918, ii, 277). To overcome this two modifications are suggested: (1) the separation of cholesterol from the fatty acids and the separate estimation of the two fractions thus obtained (cf. A., 1916, ii, 275), (2) the use of a standard, consisting of 60% oleic and 40% palmitic acid, which melts at approximately the same temperature as the mixture obtained from blood. Using these modifications, the results are accurate to within 5%. E. S.

Estimation of Small Amounts of Lactic Acid. S. W. CLAUSEN (*J. Biol. Chem.*, 1922, **52**, 263—280).—The method of Fürth and Charnass is slightly modified. Lactic acid is decomposed either by acid permanganate at 95° or by 50% sulphuric acid at 140°, the aldehyde produced being swept into excess of sodium hydrogen sulphite. The excess of the sulphite is removed by addition of iodine, the end-point being adjusted to a definite blue

to starch. Saturated sodium hydrogen carbonate is then added until the blue coloration is just discharged, and the sulphite of the aldehyde bisulphite compound titrated with standard iodine, the end-point being determined by a blank control. The errors which arise when the method is applied to blood or urine may be reduced, but not entirely eliminated, by first extracting the lactic acid from the protein-free filtrate by ether, using a special extraction apparatus. E. S.

Detection and Estimation of Oxalic Acid and its Use in Standardising Iodine and Silver Solutions. L. ROSENTHALER, (*Z. anal. Chem.*, 1922, **61**, 219—222).—Iodine is liberated when potassium iodate solution is heated with the addition of a small quantity of oxalic acid; the reaction may be obtained with 3mg. of oxalic acid and permits of the detection of the latter in the presence of tartaric and malic acids which reduce the iodate much more slowly. Oxalic acid and oxalates may be estimated by heating their dilute sulphuric acid solution with an excess of standard iodate solution until all free iodine has been expelled, cooling the mixture, and titrating the excess of iodate with thiosulphate solution after the addition of potassium iodide. It is proposed to use sodium oxalate for the standardisation of iodine solutions and of silver nitrate solutions; in the latter case, a known quantity of the oxalate is treated with a slight excess of silver nitrate solution, the mixture diluted to a definite volume, filtered, and the excess of silver titrated in an aliquot portion of the filtrate with thio-cyanate solution. W. P. S.

Oxidation of Oxalic Acid in the Absence of other Acids. J. C. WITT. (*J. Physical Chem.*, 1922, **26**, 435—446).—It is shown that oxalic acid may be titrated with potassium permanganate without the addition of any other acid, the oxalic acid functioning both as reducing agent and acid. The end-point is marked by the appearance of turbidity followed by a slight permanent precipitate and is affected by the temperature of titration, the concentration, and the presence of electrolytes. When a solution of an oxalate is titrated in the presence of sulphuric acid, the colloid precipitating power of the sulphate-ion is effective in the presence of a fairly high concentration of the hydrogen-ion, and hence the quantity of sulphuric acid required is much greater than the theoretical value. J. S. G. T.

Standard Method for the Estimation of Soap in Wool. BRITISH RESEARCH ASSOCIATION FOR THE WOOLLEN AND WORSTED INDUSTRIES (*Trans. Text. Inst.*, 1922, **13**, 143—149).—Traces of soap left on a woollen fabric may cause serious disturbances in dyeing, and consequently may require estimation. It is shown that extraction at the boiling point with neutral absolute alcohol, in a glass apparatus with ground-in joints, satisfactorily removes the soaps and free fatty acids from the material. J. C. W.

Olive Oils and the Villavecchia Reaction. JEAN PRAX (*Ann. Falsif.*, 1922, **15**, 159—161).—It has been shown previously (*ibid.*, 1921, **14**, 270) that certain olive oils, particularly Tunisian, give a red coloration with Villavecchia's reagent, similar to that given by an olive oil adulterated with sesamé oil. This abnormal reaction is not obtained if such an oil is shaken with its own volume of 90% alcohol containing 10% of ammonia and the alcohol and ammonia then evaporated on a water-bath before applying the test. It is now shown that it is as a result of the action of the ammonia that these abnormal oils no longer give the red coloration with the Villavecchia reagent. W. G.

The Orcinol Reaction with Furfuraldehyde. Application to the Colorimetric Estimation of Small Quantities of Furfuraldehyde. PAUL FLEURY and GABRIEL POIROT (*Bull. Soc. Chim. Biol.*, 1922, **4**, 252—266).—For the estimation, 1 c.c. of the furfuraldehyde solution and 5 c.c. of a hydrochloric acid reagent (*d.* 1.19 and containing about 60 mg. of ferric chloride per litre) are added successively to 4 c.c. of an orcinol reagent (1 gram of orcinol in 1600 c.c. of glacial acetic acid). The mixture is then heated for one minute on a water-bath, left for half an hour at the ordinary temperature, and the blue coloration compared with that produced in a standard solution treated simultaneously in the same manner. The standard solution contains 0.1 mg. of furfuraldehyde per c.c.; that to be estimated should contain between 0.01 and 0.30 mg. E. S.

A Cause of Error in the Application of the Colour Test for Acetone. ANTONIO TROISE (*Ann. Chim. Analyt.*, 1922, **4**, 177—178).—On testing a sample of urine for acetone by means of ammonia and sodium nitroprusside in acetic acid (Lieben's reaction) the characteristic violet colour was obtained, although the distillate did not give the reaction. The cause of the colour was found to be the presence of istycine (1.8 dihydroxyanthraquinone) which had been taken medicinally. A. R. P.

Differentiation and Estimation of Saponins. L. KOFLER (*Z. Unters. Nahr. Genussm.*, 1922, **43**, 278—287).—The usual methods of investigation do not suffice to arrive at the identity of a saponin when it is not available in the pure state. The author makes use of the foaming power in addition to the hæmolytic action of saponins. The "foam number" is obtained by shaking up 10 c.c. of each of a series of solutions of different concentrations in test-tubes 16 mm. internal width for fifteen seconds and allowing them to remain for fifteen minutes. The foam number is given by the dilution in that tube in which the foam stands 1 cm. high. The hæmolytic index is determined in the usual way, the details of which are specified. If the hæmolytic index is divided by the foam number, a quotient is obtained which is independent of the state of purity of the saponin. This quotient has a characteristic value for each of the six different saponins investigated, varying

from zero in the case of glycyrrhizin to 10 in the case of Merck's digitonin. By this means saponins separated from artificial lemonades by Brunner's method (*ibid.*, 1902, **5**, 1197; 1908, **16**, 165; 1912, **23**, 566; 1914, **27**, 192) can be readily identified and quantitatively estimated by comparing the hæmolytic index and foam value obtained with those tabulated for the saponin in question. It would be possible to specify a maximum value for the "poison/foam" quotient which should not be exceeded by the saponins used in food-stuffs. The figure 1.0 or 0.5 is suggested.

H. C. R.

The Defecation of Blood for the Estimation of Carbamide.

AL. IONESCU (*Bul. Soc. Chim. Romania*, 1922, **4**, 13—17).—The defecating agent recommended consists of a saturated aqueous solution of sodium chloride to which has been added 10% of glacial acetic acid. To the serum an equal volume of this reagent is added and the mixture is heated to boiling and filtered. The filtrate is made slightly alkaline with sodium hydroxide and the carbamide estimated in an aliquot portion by the hypobromite method.

W. G.

The Testing of Foodstuffs for Vitamins.

J. C. DRUMMOND and A. F. WATSON (*Analyst*, 1922, **47**, 235—246).—Details are given of the method of carrying out physiological tests on rats for the presence of the three vitamins in foodstuffs. Young healthy rats of not more than 50 grams body weight are fed on a ration of purified foodstuffs from which all traces of the vitamin to be tested for have been removed. These rations are specified for each of the three vitamins. When the rats have shown no further increment of weight for fourteen days, the substance to be tested is administered in a daily ration of known weight. The method has been used to show that samples of butter vary very considerably in the amount of vitamin they contain.

The amount of vitamin-B in milk depends entirely on the food of the cow. The monkey is the best animal for testing for vitamin-C, but the guinea pig is generally used. Testing is rendered more difficult by the fact that the guinea pig is entirely herbivorous. The potency of the food supplement added is judged from the daily dose necessary to prevent the onset of, or to cure established, scurvy. The antiscorbutic value of milk is dependent on the diet of the animals. Lemon juice possesses a very much higher antiscorbutic potency than lime juice.

H. C. R.

The Necessity of Checking the Quality of Sodium Tungstate used in the System of Blood Analysis.

OTTO FOLIN (*J. Biol. Chem.*, 1922, **51**, 419—420).—Specimens of sodium tungstate which are not alkaline to phenolphthalein contain complex tungstates. They may be made suitable for use in the author's system of blood analysis by addition of the requisite quantity of alkali.

E. S.

General and Physical Chemistry.

The Luminescence of Incandescent Solids. E. L. NICHOLS and H. L. HOWES (*Physical Rev.*, 1922, **19**, 300—318).—Certain oxides, when heated to temperatures lying within a definite and sometimes narrow range, emit radiation in a limited region of the spectrum far in excess of the radiation emitted in that region by a black body at the same temperature. The effect is ascribed to luminescence, and is particularly marked in the case of the blue radiation from columbium oxide; the blue glow is also shown by the oxides of glucinum, magnesium, calcium, aluminium, silicon, and zirconium. Intensity-temperature curves for the red, green, and blue radiations from the oxides of samarium, gadolinium, gallium, columbium, erbium, cerium, praseodymium, and neodymium show that all except cerium emit a blue or greenish-blue glow, and all but columbium and neodymium have one or two red, green, and blue outbursts above 1000°. Luminescence is essentially different from temperature radiation, and the effect for any oxide is sensitive to slight impurities. It is considered that luminescence is probably a phenomenon of instability associated with a chemical change such as oxidation, or with the physical disturbances which the oxides undergo as they are heated.
A. A. E.

Optics of Disperse Systems. V. I. LIFSCHITZ and GEORG BECK (*Kolloid Z.*, 1922, **31**, 13—15; cf. A., 1920, ii, 137).—A number of misprints and errors of calculation contained in a previous paper (*loc. cit.*) are corrected. Tables of the recalculated values are given and a repetition of the measurements of the refractive index of arsenic trisulphide sol has brought the authors' measurements into agreement with those of Wintgen. The discrepancy previously found was due to a film of the arsenic sulphide separating on the prism. It is also shown that the influence of the degree of dispersion on the refraction is very small in comparison with the influence of constitution.
J. F. S.

The Mass of the Particles that Emit the Spectrum of Carbon Monoxide. M. DUFFIEUX (*Compt. rend.*, 1922, **175**, 159—161).—On the supposition that the widening of the spectral lines emitted by a luminous gas is solely due to thermal vibration, the limit of the interference fringes which can be obtained with these lines is given by the equation $N = K\sqrt{M/T}$, where K is a constant, T the absolute temperature, and M the mass of the luminous particles on the atomic weight scale. This method was applied to an investigation of the origin of the spectra of nitrogen and carbon monoxide. The values found for N for the nitrogen lines, 3998 and 4200, were 270,000 and 274,000, respectively, whilst very concordant results averaging 313,000 were found for four of

the carbon monoxide bands, and 260,000 for the fifth band, 4123. Adopting on the one hand Lord Rayleigh's value for K , namely, 1.37, as an upper limit, and, alternatively, Fabry and Buisson's, 1.22, as the lower limit, M for nitrogen becomes 11.6 or 14.5, and for carbon monoxide 15.3 or 18.3 for the four bands, and 10.6 or 13.2 for the fifth band. The conclusion is drawn that the two bands of nitrogen are emitted by atomic nitrogen (14), and that the four bands 5610, 5198, 4833, and 4509 are due to atomic oxygen (16), whilst the fifth band is due to carbon atoms (12), the masses of all these atoms falling well within the upper and lower limiting values obtained for M .
G. F. M.

The Excitation of the Enhanced Spectra of Sodium and Potassium in a Low Voltage Arc. PAUL D. FOOTE, W. F. MEGGERS, and F. L. MOHLER (*Astrophys. J.*, 1922, 55, 145—161; cf. this vol., ii, 4).—It is shown that the quantum theory requires that the enhanced spectra of sodium and potassium should be excited at comparatively low voltages. The experimental results demonstrate that this is the case, and clearly show the three-stage development in the spectra of these elements, namely, (1) the single pair stage, 2.1 to 5.1 volts for sodium; 1.6 to 4.3 volts for potassium; (2) the arc spectrum stage, 5.1 to 30 volts for sodium; 4.3 to 20 volts for potassium; (3) the enhanced spectrum stage, above 30 volts for sodium; above 20 volts for potassium.

A. A. E.

The Difference between Series Spectra of Isotopes. P. EHRENFEST (*Nature*, 1922, 109, 745—746; cf. following abstract).—A criticism of the use of Bohr's formula for the change in frequency, ν , due to the motion of the nucleus, in the case of atoms in which several electrons move round the nucleus. The formula $\nu_2 : \nu_1 = M_2 / M_2 + m : M_1 / M_1 + m$, where M_1 , M_2 , and m are, respectively, the masses of the nuclei of the isotopes and of the electron, and ν_1 and ν_2 the frequencies of the corresponding lines, cannot be true in general in such cases, although it will probably be possible to derive a sufficiently approximate formula for the case of the p - and d -motions of lithium; this must be very difficult, however, for the case of the $1.5S$ -path.

A. A. E.

The Difference between Series Spectra of Isotopes. N. BOHR (*Nature*, 1922, 109, 746; cf. preceding abstract).—It is admitted that the effect of the mass of the nucleus on the spectrum of an atom containing more than one electron is a complex problem; not only may the mass effect disappear completely in such cases, but also, in the case of the motions actually met with in the emission of the series spectra, this effect may be different from that calculated for an atom with one electron. It is shown that the problem differs essentially from the problem of two bodies in celestial mechanics. The discrepancies, observed by Merton, in the wave-lengths of certain lines in the spectra of lead isotopes are considered with reference to the mass effect, and to the possibility of their being due to a slight difference in the field of force

surrounding the nucleus, arising from the difference in the internal nuclear structure of the lead isotopes. A. A. E.

The Difference between Series Spectra of Isotopes. J. W. NICHOLSON (*Nature*, 1922, **110**, 37; cf. preceding abstracts).—The differences found by McLennan in the spectra of the lithium isotopes are three times as great as those calculated by Bohr's formula. This large separation cannot be explained by the quantum theory, and it is suggested that the new series may be a combination series or a spark series. In an investigation on some of the simpler possible orbits in a lithium atom with only two electrons, a specially simple class of orbits was found. The principal spark-line of lithium has a value very close to λ 6708, the red line shown in the ordinary spectrum. The results appear to indicate that when there are many electrons in an atom, a ratio roughly of order 1/10 exists between the orbital radii of the two outer consecutive electrons. An immediate consequence is that the Bohr formula would never be very far wrong in its use for a rough determination of the separation to be looked for in the spectra of isotopes.

A. A. E.

The Vacuum-spark Spectra of the Metals. EDNA CARTER (*Astrophys. J.*, 1922, **55**, 162—164).—Vacuum-spark spectra of calcium, magnesium, cadmium, titanium, and iron were obtained, the iron spectrum being also photographed on a dyed film from λ 4000 to λ 6600 Å.; the new spectra show no striking new characteristics. The vacuum-spark spectrum of calcium and magnesium is practically identical with the spark spectrum in air; with cadmium, and particularly with titanium, the arc lines are more intense. In the case of iron, the vacuum-spark spectrum is more like the arc spectrum than the spark spectrum. In general, the vacuum-spark spectra resemble the luminescence spectra produced by cathode-ray bombardment in a high vacuum; the conditions of emission in the two cases are considered to be very similar.

A. A. E.

The Limits of Absorption L of the Elements Barium to Antimony. LINDSAY (*Compt. rend.*, 1922, **175**, 150—151).—The limits of absorption, L , of the elements barium, caesium, iodine, tellurium, and antimony were measured by means of a vacuum spectrograph, using a prism of calcite, and a 0.1 mm. slit. The current used was between 10 and 50 milliamperes, at such a voltage that the second order did not appear in the spectral region studied, for example, 8000 volts for antimony. The screens consisted of a thin sheet of paper which had been dipped in a saturated solution of a suitable compound of the element. The following results, expressed in units of 10^{-11} cm., were obtained.

	L_1 .	L_2 .	L_3 .
Barium	2357.7	2199.5	2060.2
Cæsium	2467.8	2307.3	2160.5
Iodine	2712.4	2548.3	2381.9
Tellurium	2847.0	2683.7	2502.6
Antimony	2994.5	2831.0	2632.7

A comparison of the values of the Sommerfeld doublet (expressed as $1/\lambda$) for the limits of absorption (L_2-L_1) and the two lines $\beta_1-\alpha_2$ measured by Hjalmar shows a very satisfactory agreement.
G. F. M.

The Variations of the Spectrum of the Mercury Arc with the Conditions of Emission. ST. PROCOPIŮ (*Compt. rend.*, 1922, **175**, 217—219).—If the arc is produced in a vacuum with a current of 14—15 volts and 1.9 amperes, the spectrum contains more lines towards the extremity of the ultra-violet than if a more powerful current (65 volts, 3.5 amperes) is used with a correspondingly increased vapour density. Under both conditions of current, the cathodic spectrum is richer in lines than the anodic, and with the higher voltage the cathodic lines become diffuse, sometimes so much so as to form a continuous spectrum. If the arc is struck in air, under water, or especially in coal gas, the lines of the two secondary series are weakened and widened compared with the lines of the vacuum arc, this being the more pronounced the higher the position of the line in the series. The line 2537 appears strongly inverted in the three media, and a number of lines are strengthened, notably 3984, 2857, 2848, and 2224. The author considers that the widening of the lines is related to the Stark effect and explainable by the assumption of an intermolecular electric field, whilst the weakening or disappearance of certain lines when the arc is struck in air, water, etc., may be explained by Bohr's theory.

G. F. M.

Fine Structure of Röntgen Spectra. ADOLF SMEKAL (*Sitzungsber. Akad. Wiss. Wien*, 1921, **130**, 25—30; from *Chem. Zentr.*, 1922, i, 240; cf. A., 1921, ii, 292, 615).—The scheme for the L series can only be tested for tungsten since in this case alone are sufficient experimental data available. There are five M layers and at least five N layers.

G. W. R.

The Absorption Spectrum of Potassium Permanganate. A. HAGENBACH and R. PERCY (*Helv. Chim. Acta*, 1922, **5**, 454—468).—Spectrophotometric measurements were made of the absorption of aqueous potassium permanganate solutions at twelve dilutions from 2^{-6} to 2^{-17} mol. per litre at sixty-one points in the visible spectrum between wave-lengths 438 and 701 $\mu\mu$. From the results, curves were plotted in which the percentage absorption was plotted against the wave-length at each dilution, and from the curves obtained the positions of the absorption bands were deduced. New figures are given for the wave-lengths of the eight known bands, differing slightly in some instances from those given by Formánek. The new figures are 4388, 4537, 4695, 4866, 5050, 5249, 5461, 5695. These bands are related in such a manner that there is a constant difference between the oscillation frequencies of successive members of the group. This law has not previously been observed to hold for an inorganic substance. The broad band which Formánek ascribed to the wave-length 6370 has been resolved into four bands at 5949, 6264, 6528, 6862. These then

form a continuous series with the other eight bands. The Beer-Lambert law was found to hold within the limits of 5%. E. H. R.

Structure of the Second Cyanogen Band. JUNZŌ ÔKUBO (*Sci. Rep. Tôhoku Imp. Univ.*, 1922, **11**, 55—86).—The second cyanogen band radiated by the ordinary carbon arc in air was examined under higher dispersion and resolving power than that used by previous investigators. The wave-length of all lines lying between the first head at λ 4216 Å. and λ 3900 Å. (about 1555 in all) were measured and calculated in international units. This band contains many doublet lines with close components, some of which have been previously described as singlets. Three remarkable series were traced, one triplet series beginning from the first head and two closed doublet series beginning from the second head. The intensity distribution in these series is described. The wave-length of the heads of cyanogen bands were measured and some simple relations are shown to exist between the differences in the ratios of the wave numbers of the heads; for example, the differences in the ratios for successive heads are generally in an arithmetical progression. T. H. B.

Absorption Spectra of Triphenylmethane Colouring Matters. EMILIO ADINOLFI (*Atti R. Accad. Lincei*, 1922, [v], **31**, i, 461—464).—The author has shown (*Rend. Accad. Sci. Fis. Mat. Napoli*, 1921, [iii], **27**) that triphenylmethane colouring matters, when dissolved in water, alcohol, ether, benzene, glycerol, toluene, or xylene, exhibit absorption curves of similar types with maxima which undergo gradual displacement as the molecular weight of the solvent increases. Solutions of 19 of these colouring matters in water and in methyl, ethyl, isobutyl, and amyl alcohols have now been examined spectroscopically by the diffusion method (A., 1920, ii, 720), the positions of the mid-points of the two absorption bands being tabulated. With the alcoholic solutions the velocity of diffusion is greater than with those in other solvents, this velocity diminishing as the molecular weight of the alcohol increases. The diffusion of some of the compounds examined is characterised by two distinct phases: the first consists in a rapid propagation of the coloration with a very low gradient of the concentration, the spectrum showing only one of the characteristic bands which assumes constant breadth; the original surface of separation remains and gives rise to a second, slower diffusion, as a result of which the absorption curve characteristic of this group of compounds becomes complete. That this phenomenon of double diffusion appears to be due to two different atomic groupings is supported by other evidence to be published later.

The gradual displacement of the maxima of the absorption curves as the molecular mass of the alcoholic solvent increases is observed with all the compounds examined with the exception of uranine and rhodamine-B. T. H. P.

The Calculation of the Colour of the Azo-dyes and Related Coloured Substances. JAMES MOIR (T., 1922, **121**, 1555—1562).

Absorption Spectra of Benzeneazophenol and its Derivatives. ALPHEUS W. SMITH and C. E. BOORD (*J. Amer. Chem. Soc.*, 1922, **44**, 1449—1455).—The absorption spectra of benzeneazophenol and each of the three isomeric tolueneazophenols, chlorobenzeneazophenols, and nitrobenzeneazophenols have been measured in alcohol and in alcohol containing sodium hydroxide. The measurements were made by the visual method and in all cases continuous absorption curves were obtained. It is shown that the substitution products absorb light more strongly in the visible region than does benzeneazophenol, and the alkali salts more strongly than the free dyes. The order of absorption for the isomerides in the dilutions examined is para > meta > ortho, except in the case of the nitro-derivatives, when it becomes para > ortho > meta. The deviation of the latter derivatives may be due to a difference in structure. The changes in absorption brought about by substitution are discussed briefly in the light of McClelland's mutual induction theory of absorption of light. J. F. S.

Disturbance of the Power of Fluorescing of Fluorescent Solutions by Light, and the Photochemical Equivalent Law. PETER PRINGSHEIM (*Z. Physik*, 1922, **10**, 176—184).—The change in the intensity of the fluorescence of fluorescein, eosin, and other substances in aqueous, alcohol, glycerol, and amyl alcohol solutions, when submitted to an intense beam of light, has been investigated. It is shown that the disturbance of the power of fluorescence, discovered by Perrin (*A.*, 1918, ii, 418; 1919, ii, 177) and investigated by Wood (*Proc. Roy. Soc.*, 1921, [A], **99**, 362; this vol., ii, 334) is due to the concentration of the acting light, a result also obtained by Wood. Of two solutions of equal concentration, that with the weaker fluorescence is changed more rapidly than the other, and of two solutions with the same intensity of fluorescence and with identical absorption and fluorescence spectra, the one may be changed more rapidly than the other and thereby a different product produced. The fluorescence spectrum of a newly-formed substance is displaced in the same sense as the absorption spectrum of this substance. The intensity of fluorescence is not markedly changed at low temperatures, but the chemical reaction is practically inhibited. For these reasons, the hypothesis of Perrin (*loc. cit.*), according to which fluorescence is an attendant phenomenon of chemical change, cannot be maintained. On the other hand, there is the second possibility, that either fluorescence or chemical change is of importance for the validity of the photochemical equivalent law. J. F. S.

The Influence of Constitution on the Rotatory Power of Optically Active Substances. XV. A New Constant for Calculating the Curve of Rotation-dispersion. H. RUPE (*Annalen*, 1922, **428**, 188—198).—In place of the customary magnitudes $\lambda\alpha$ and λ_0^2 , it is now proposed to use $\lambda\alpha$ and λ_0 , and, in particular, their product, $\lambda\alpha \cdot \lambda_0 = k$, which is termed the "Rotation-Dispersion Product," and is signified by the letters "*P.R.D.*" It is shown (by reference to camphor derivatives) that the *P.R.D.*'s

exhibit a fair degree of constancy for a series of substances of the same "optical type." C. K. I.

Molecular Ælotropy in Liquids. C. V. RAMAN (*Nature*, 1922, **110**, 11).—In experiments with many liquids on the molecular scattering of light, the scattered beam in a direction transverse to the primary rays shows a large admixture with unpolarised light. It is therefore suggested that the polarised and unpolarised parts of molecularly scattered light may arise in two distinct ways, the former being a mass effect, and the latter a molecular effect. Passing from the condition of vapour to that of liquid considerably increases the ratio of unpolarised to polarised light, as has been experimentally shown in the cases of ethyl ether, benzene, and chloroform; such increase would naturally be in proportion to the number of molecules per unit volume. Moreover, when a substance is in the state of vapour under small pressures, both the positions and orientations of its molecules are absolutely at random, and assuming the molecules to be ælotropic, the degree of imperfection of polarisation of the light scattered by it may be calculated; in the liquid state, however, the packing of the molecules is so close that their ordering in space is no longer at random, but the orientations may still be considered to be arbitrary. Viewed in this way, the same results are obtained. A. A. E.

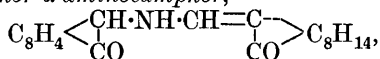
The Rotatory Power of Crystals and Molecular Rotatory Power. LOUIS LONGCHAMON (*Compt. rend.*, 1922, **175**, 174—177).—A comparison of the crystalline rotatory power with the molecular rotatory power expressed as $[\alpha]d/100$, where $[\alpha]$ is the specific molecular rotation, and d the density of the crystal, showed with the substances examined, including camphor, sucrose, rubidium, and ammonium tartrates, and ammonium molybdomalate, no definite constant relationship. On the other hand, the rotatory dispersions, that is to say, the ratio of the rotations for two given spectral lines, exhibited practically constant values, in spite of great variations in the rotatory power in passing from the liquid to the crystalline state. In the case of camphor, remarkably constant values were obtained for the rotatory dispersion in solution in ethyl ether, and in hexane, and in the liquid, gaseous, and crystalline states. If it is admitted with Traube and Landolt that there is a structural rotatory power in crystals superimposed on a molecular rotatory power, the former must therefore present the same rotatory dispersion as the latter, which, a priori, does not seem reasonable. The only alternative to this is that there is no structural rotatory power, and the rotatory power of the crystal is therefore the molecular rotatory power in a determined direction, it being established that the rotation is variable with the direction of observation. The rotatory dispersion, however, is in all cases independent of the direction of observation. G. F. M.

A Case of Total Anomalous Rotation-Dispersion. H. RUPE and H. SCHMID (*Helv. Chim. Acta*, 1922, **5**, 437—443).—Tschugaev and Glinin (*A.*, 1912, ii, 1020) consider that the cause of anomalous

rotation-dispersion is to be found in the influence of the optical superposition of several asymmetric carbon atoms on an absorption band in the ultra-violet. The authors dispute this hypothesis, and suggest that the phenomenon is due to the disturbing influence of unsaturated residues on the asymmetric carbon atom. In agreement with this view, they find that triphenylmethyl- α -aminocamphor exhibits total anomalous rotation-dispersion in benzene and in acetone solution, whilst the condensation product of α -aminocamphor with hydroxymethylenecamphor is normal.

α -Triphenylmethylaminocamphor is prepared by condensing triphenylchloromethane with α -aminocamphor, m. p. 153–154°, $[\alpha]_C - 1.34^\circ$, $[\alpha]_D - 1.68^\circ$, $[\alpha]_{Hg} - 1.68$ ($\lambda = 546.3$), $[\alpha]_F - 2.13^\circ$ in benzene.

Methylenecamphor- α -aminocamphor,



forms white to pale yellow leaflets, m. p. 228–230° (decomp.); $[\alpha]_C + 90.51^\circ$, $[\alpha]_D + 121.8^\circ$, $[\alpha]_{Hg} + 151.7^\circ$, $[\alpha]_F + 211.4^\circ$ in benzene.
E. H. R.

Coagulation of Colloids by Sunlight. P. B. GANGULY and N. R. DHAR (*Kolloid Z.*, 1922, **31**, 16–19).—The action of sunlight on colloidal gold, silver, platinum, copper, sulphur, selenium, a number of colloidal sulphides, hydroxides, and complex colloidal solutions, both pure and in the presence of protecting colloids, has been investigated. In most cases, it is shown that sunlight increases the rate of coagulation. In the case of the metallic sulphides, the sensitiveness toward sunlight follows the order: arsenic, cadmium, mercury, and antimony sulphide, whilst in the presence of gelatin as protecting colloid the order is: nickel, platinum, zinc, gold, iron, cobalt, and silver sulphide. In the case of a manganese dioxide sol containing 0.3 gram of manganese dioxide per litre, sunlight has the same coagulating action as 2.5 c.c. of a 2*N*-solution of copper sulphate acting on 25 c.c. of the sol. Colloidal solutions of stannous, bismuth, lead, manganese, and ferrous sulphides, when acted on by sunlight in the presence of air, are oxidised with the formation of colloidal sulphur, which on further action of light is coagulated.
J. F. S.

Decomposition of Iodoform in Solutions by Means of Radiant Energy. E. H. BUTLER (*Chem. News*, 1922, **125**, 38–39).—Iodoform in benzene or carbon tetrachloride solutions is decomposed by light, but in alcoholic solution there is no decomposition.
J. F. S.

Thermotropy. JOSÉ RODRÍGUEZ MOURELO (*Anal. Fis. Quím.*, 1922, **20**, 139–145).—Some experiments are recorded on the effect of heat on the phototropy of certain sulphides. Phototropy is diminished by low temperatures and increases with rise of temperature up to a maximum, after which it diminishes. Phototropy may, under certain conditions, be induced by simple heating in the absence of light.
G. W. R.

Conductivity of the Latent Image. A. G. RABINOVICH (*J. Physical Chem.*, 1922, **26**, 577—590).—With the object of furnishing evidence as to the nature of the undeveloped photographic image, the author has determined the electrical resistance of celluloid photographic films and silver bromide gelatin emulsions both before and after illumination. The results show that the resistance undergoes no change measurable by the most sensitive methods, and consequently this method throws no light on the nature of the latent image. The electrical conductivity of a dry film 5×10 mm. at $18-20^\circ$ is of the order 10^{-11} /ohm cm. and the temperature coefficient about 10% per degree, whilst the specific conductivity of a silver bromide gelatin emulsion at 22° is 8.0×10^{-4} ohm $^{-1}$ and the temperature coefficient 3% per degree.

J. F. S.

Absorption and Dispersion of Radiation. FRITZ WEIGERT (*Z. physikal. Chem.*, 1922, **44**, 414—444).—A theoretical paper in which the absorption and dispersion of radiation are considered in the light of modern work. The experimental results of the effects of linearly polarised light on the different photo-sensitive systems and the adaptation of the system to the colour of the exciting radiation are mainly considered. It is shown that for these effects not a single molecule, but always a whole system of numerous unordered and closely-packed molecules of different types, is responsible. The actual process of adsorption, which is closely connected with the adaptation, can only occur through the simultaneous action of different molecules or molecular groupings. The combination of the individual parts of such a closely packed aggregate occurs through electrons in an internal photo-electric effect, in which an electron from a molecule is projected in the direction of the radiation with an energy given by the relationship $1/2mv^2 = h\nu$, and taken up by an electron receiver. The frequency and direction of the absorbed radiation is determined by the distance between the two molecules and their relative orientation; since almost all combinations are possible, the adaptation to the colour and direction of the radiation is practically unlimited. The absorption spectrum varies with the spatial arrangement and the relative proportion of the electron emitter and receiver, in the sense that the bands are displaced toward the red when the proportion of receivers is greater than that of emitters, and toward the blue when the proportion is the reverse. It is possible by spectrometric measurements to differentiate the two constituents. The inconstancy of the absorption of the chief coloured substances, the finely divided disperse systems, organic dyes, and inorganic complex compounds can be shown in the case of the photo-chlorides, cyanin collodion layers, and the blue copper-ammonia complexes respectively. In all these cases, Beer's law does not hold, and the reason for this is to be found in the method of action of the electron emitters and receivers, so that here a perfectly general phenomenon is to be found. The emitters expel their electrons with an energy $h\nu$ when they encounter a radiation of frequency ν in a perfectly

definite phase, which probably is the maximum of the magnetic displacement. The electron then probably takes a cometary path, and if, at the limit of its path, it meets an electron receiver it stays there, and the system now richer by one energy quantum takes from the radiation the amount of energy still failing. In the more likely case where the electron does not meet with a receiver, it returns to the emitting molecule and thereby emits an impulse wave of the frequency ν . This impulse is, however, emitted with a certain delay, which is equal to the time of flight of the electron. During the passage of radiation through a material system, a diminution of the light velocity is recorded which is greater the greater the frequency, for the electron has a longer path and the time of flight is longer. Here is to be found a meaning for normal dispersion. When the time of flight is exactly a half period of the radiation, the emitted impulse destroys the exciting radiation entirely by interference. If this corresponds with the characteristic frequency of the substance, then the radiation does not pass through the medium, and a zero velocity of light and an infinitely large index of refraction are observed. When the time of flight is only a little larger than the half period, then it appears as though the emitted wave commences before the exciting radiation disappears. Here there is an apparent increase in the velocity of light and abnormal dispersion. This repeats itself when the time of flight t_ν is equal to an odd multiple of the half period which is expressed by the formula $t_\nu = (n - 1/2)1/\nu$. The abnormal dispersion of spectrum lines is probably explained by this formula, when for n the natural series of numbers is inserted.

J. F. S.

Determination of the Velocity of the α -Rays of Polonium. (MLLE) IRÈNE CURIE (*Compt. rend.*, 1922, **175**, 220—222).—The velocity of emission of the α -rays of polonium was determined by the magnetic deviation method, the distance between the impressions produced by the α -rays on a photographic plate in the presence and in the absence of the magnetic field being measured with great precision by means of the instrument used for spectrographic measurements, from which it was calculated that the velocity of the rays is 1593×10^9 cm. per second, and the ratio of the emission velocities of the α -rays of polonium compared with those of radium-*C* is accordingly 0.829. This is in close agreement with the value 0.826 given for the ratio of the cube roots of the penetrating power of the α -rays of these two elements.

G. F. M.

α -Particles as Detonators. G. H. HENDERSON (*Nature*, 1922, **109**, 749).—If it is considered that when an α -particle passes through matter, the matter in its proximity is momentarily raised to a high temperature, the detonation of certain unstable substances would be expected to take place on exposure to the action of these particles. Air-dried nitrogen iodide is detonated in this way. The detonation is not caused by the first α -particle which happens to strike the substance, but appears to be a probability effect.

A. A. E.

Multiple Valency in the Ionisation by α -Rays. T. R. WILKINS (*Physical Rev.*, 1922, **19**, 210—220; cf. Millikan, Gottschalk, and Kelly, *ibid.*, 1920, **15**, 157; *Proc. Nat. Acad. Sci.*, 1919, **5**, 591).—Slight modifications were introduced into Millikan's oil-drop method for determination of the valency of individual ions, polonium being used instead of radium bromide as a source of α -rays. In air, not more than 3% of the positive ions could have been doubly charged; the number was probably considerably smaller. In helium, a determination was made of the variation of the number of "doubles" with the range; the maximum proportion was found to be about 10% for the range of maximum ionising power. The corresponding figure for hydrogen was 0.5%. The relative stopping power for α -rays of air and helium was found to be about 3.8, a result which is in agreement with the Bragg-Kleeman law. A. A. E.

Theory of Röntgen Spectra. II. ADOLF SMEKAL (*Sitzungsber. Akad. Wiss. Wien*, 1920, **129**, 635—660; from *Chem. Zentr.*, 1922, i, 240).—The error introduced by the use of the Loschmidt number in the standard value for the lattice constant of sodium chloride is considered. Attention is also directed to a theoretical L_{α} arrangement which takes account of the relativity correction. The hypothesis used in the proof of the electron ring theory may be reduced to Bohr's frequency hypothesis. The presence of three electrons in the K ring follows qualitatively from the assumption of a spacial arrangement of electrons in the sheath. The determination of the quantum conditions of the L and M electrons permits the number of L and M absorption edges to be obtained. G. W. R.

Röntgen Spectra and Chemical Valency. GREGOR WENTZEL (*Naturwissenschaften*, 1922, **10**, 464—468).—A discussion of the dependence of the K absorption limits of chlorine and phosphorus on the valency as observed by Lindh (*Compt. rend.*, 1921, **172**, 1175) and Bergengren (A., 1920, ii, 654). It is probable that the properties of the K limits of titanium, vanadium, and chromium reported by Fricke (A., 1921, ii, 6) are due in so far as this structure extends to the weaker part to the presence of ions of different valency. The structure of the K - β line of the light elements is explained similarly (cf. Hjalmar, A., 1920, ii, 655; 1921, ii, 145, 292). CHEMICAL ABSTRACTS.

Radium Synthesis of Carbon Compounds from Air. F. HARRISON GLEW (*Nature*, 1922, **109**, 714).—Quartz or glass fibres, supported immediately above an uncovered radioactive surface, the whole being enclosed in a box in a dark room, become covered in a few days with a white, viscid liquid, tending to form droplets. Prolonged exposure causes increase in size of the droplets, coloration to dark brown, and a tendency to solidify with irregular contraction. The gaseous emanation of radium seems to be necessary, since deposits cannot be obtained by using α -, β -, or γ -rays, either separately or in combination. A chemical examination of the products has not yet been made. A. A. E.

An Attempt to Influence the Rate of Radioactive Disintegration by Use of Penetrating Radiation. G. HEVESY (*Nature*, 1922, **110**, 216; cf. Ellis, this vol., ii, 339).—It is assumed that the emission of γ -rays from the nucleus of the atom precedes the disintegration process. If, therefore, the nucleus could be induced to take up a γ -ray impulse supplied by an exterior source, it would mean a change in its stability, and so most probably a change in the rate of its disintegration. Experiments with uranium in radioactive equilibrium with uranium-*X*, and with radium-*D* in equilibrium with radium-*E*, failed to show a change in β -radiation greater than 0.1% and 0.2%, respectively. A. A. E.

Measurement of the Resonance, Radiation, and Ionisation Potentials of Several Gases and Vapours. PAUL EDWARD BOUCHER (*Physical Rev.*, 1922, **19**, 189—209; cf. Mohler and Foote, A., 1920, ii, 464).—A modification of Compton's variable-area electrode was employed. The resonance potentials were obtained from the difference in voltage between successive peaks of the resonance curves; the ionisation potentials from the Lenard current-voltage curves corrected as to zero by the resonance curves; the relative importance of radiation and ionisation at various voltages from the ratio of the Lenard currents obtained with the plate to the corresponding currents obtained with the gauze electrode having only one-fourth the area. The critical resonance potentials, potentials at which radiation is predominant, and ionisation potentials, in volts, accurate to about ± 0.1 volt except in the case of toluene, are as follows: hydrogen, 10.1, 10.1—13.6, 13.6, and 15.6; nitrogen, 8.4, 8.4—15.8, 15.8; oxygen, 8.0, none, 14.0; ethyl ether, 6.6, 8.1—10.1, 13.6; benzene, 6.0, none, 9.6; toluene, 6.2 ± 0.2 , none, 8.5 ± 0.5 ; xylene, 6.5, none, 10.0; chloroform, 6.5, none, 11.5. A. A. E.

The Effect of Oxygen and Hydrogen on the Emission of Electrons from Hot Platinum. LAURICE L. LOCKROW (*Physical Rev.*, 1922, **19**, 97—113).—By using a tube with a platinum cylinder surrounding a V-shaped filament, it was found that the effect of oxygen and air was slightly to decrease the emission, the observations of Richardson, Wilson, and others being thereby confirmed. The effect is, however, temporary and is not due to the formation of heavy ions, neither is there evidence of the formation of an oxide of platinum. Pure hydrogen probably has no effect on the emission from pure platinum, the observed effects, although considerable, being ascribed to impurities. Richardson's constants for pure platinum were found to be: $A=9900$; $b=52000$, whence the thermionic work function for platinum is 4.46 volts. These values are lower than those obtained by other methods, and are subject to errors inherent in the resistance method of measuring temperatures. A. A. E.

Behaviour of Free Electrons toward Gas Molecules. H. B. WAHLIN (*Physical Rev.*, 1922, **19**, 173—186).—To account for the appearance of abnormal negative mobilities at low pressures,

Wellisch (*Amer. J. Sci.*, 1915, [iv], **39**, 583; 1917, [iv], **44**, 1; A., 1917, ii, 352) assumes that in order to form an ion an electron must have more than a certain amount of energy, whilst Thomson (*Phil. Mag.*, 1915, [vi], **30**, 321) considers that it must have made, on the average, n impacts. The author finds that when the energy of the electrons is increased the number of ions is not increased; hence Thomson's theory is preferred. The Thomson constant n was determined for carbon monoxide, ammonia, ethylene, acetylene, ethane, ethyl chloride, and chlorine. The results, which depend on the values assumed for the mobility of the electron in the various gases, indicate a progressive decrease in the value of n in the above order from about 10^8 for carbon monoxide to 10^3 or less for chlorine. It is concluded that electronegative gases attach electrons more readily than do electropositive gases, and that the degree of saturation of hydrocarbons has but little effect. The mobility of negative ions in chlorine, ethane, and ethylene was found by Rutherford's method to be, respectively, 0.73, 1.30, and 0.91 cm./sec./volt/cm. at atmospheric pressure. A. A. E.

Piezo-electricity of Potassium Sodium Tartrate Crystals.

E. KILBURN SCOTT (*Trans. Faraday Soc.*, 1922, **17**, 748—752).—An account of the piezo-electric properties of Rochelle salt crystals, based on the recent work of A. McLean Nicolson. Suitable crystals are best prepared by the hurried cooling of a saturated solution of potassium sodium tartrate, in which a temperature gradient is established and seed crystals are immersed. Piezo-electric properties are best developed in crystals having one side slightly concave and the other convex, and in which the "hour-glass" marking is developed. An average-sized crystal weighs 100 grams. The piezo-electric effect is very pronounced when the crystal is dried in 90% alcohol for twenty-four hours, then in 100% alcohol for about four hours, and afterwards baked at 40° for several days. In the case of crystals showing the "hour-glass" structure, the piezo-electric effect is best developed by the application of a twisting couple about the principal axis of the crystal. Potentials as high as 500 volts can be developed, and the crystals are readily applicable to the reproduction and transmission of sounds.

J. S. G. T.

The Electrodeless Discharge in certain Vapours.

J. K. ROBERTSON (*Physical Rev.*, 1922, **19**, 470—477; cf. A., 1921, ii, 668).—The effect of the discharge, which was produced by electromagnetic induction, varied with the vapour pressure and with the *E.M.F.* Potassium at 250—300° gave a bright ring with a spectrum including seven or more members of each subordinate series. Sodium above 300° gave a bright yellow discharge showing the *D*-lines, four members of the diffuse series, and three members of the sharp series. Lithium up to 500° gave only a feeble discharge due to impurities. Kowalski's observations in the case of mercury were confirmed and extended. A white ring discharge (at 70—110°), at first dazzling, became fainter and was followed (at 110—115°) by a green glow of which the spectrum showed

a few lines superimposed on a continuous band extending from the violet to the yellow. The glow may be associated with poly-atomic molecules formed at the higher vapour pressures. Iodine at -5° to $+5^{\circ}$ gave a pale yellow ring showing a band spectrum, changing with increase in the spark gap to a green, pink-bordered ring with a line spectrum. The change may be due to dissociation of molecules into atoms. It is suggested that the method may be applied to the investigation of isotopy. A. A. E.

Construction of Platinum Film Electrodes and their Method of Use. A. EILERT (*Z. angew. Chem.*, 1922, **35**, 445—446).—The method of preparing durable electrodes from burnt-in layers of platinum is described. A thin piece of platinum wire is sealed into the end of a glass tube and while the glass is still soft pushed inward, so that a deep depression is produced. This is allowed to cool and then coated with one of the numerous platinising liquids in such a way that both the outside walls of the tube and the walls of the depression are thickly coated. The tube is then heated, at first cautiously and then to the softening point. In this way, a layer of platinum is burnt into the glass and is in good contact with the platinum wire. A drop of mercury inside the tube makes contact with the rest of the apparatus. Measurements are given to show the durability and permanence of such electrodes. J. F. S.

Construction of Platinum Film Electrodes and their Method of Use. A. EILERT (*Z. angew. Chem.*, 1922, **35**, 452—455).—Examples are given of the application of the film electrodes described in the preceding abstract. Only in the case of film electrodes used in the electro-analysis of metals do the films require periodical renewal. A simplified method of electrometric titration of solutions of salts of weak acids is described. J. S. G. T.

Sodium Amalgam Electrode for the Determination of Sodium Ion [Concentration]. BENJAMIN S. NEUHAUSEN (*J. Amer. Chem. Soc.*, 1922, **44**, 1411—1416).—The trustworthiness of a sodium amalgam electrode for the measurement of the concentration of sodium ions has been investigated by measuring cells of the type $\text{NaHg}|\text{NaCl}(c)||\text{sat. KCl}||\text{sat. KCl, Hg}_2\text{Cl}_2|\text{Hg}$ at 25° . Further measurements have also been made with sodium chloride containing various amounts of potassium, ammonium, calcium, and zinc chlorides. The electrode was made up in a vessel similar to that employed by Lewis and Kraus (*A.*, 1910, ii, 1027), except that at the bottom of the vessel there was a tap for draining off the amalgam which had dropped from the electrode. An amalgam containing about 0.16% of sodium was used and measurements were made against the normal electrode. The following values were obtained for the concentrations of sodium chloride stated: 0.20*N*, 2.1483 volt; 0.10*N*, 2.1650 (2.1649); 0.02*N*, 2.2035 (2.2042); 0.01*N*, 2.2198 (2.2213); the values in brackets are the *E.M.F.* values calculated from the value obtained for the 0.20*N*-solution. Further readings were made in each case at five-minute intervals to see how rapidly

the electrode lost its sodium, and then a new surface was produced and a further reading made. The following figures show the type of change: 0.2*N*-sodium chloride, voltage at start, 2.1482; after five minute intervals, 2.1482, 2.1480, 2.1476, 2.1470, 2.1460; new surface, 2.1483. Long series of measurements are recorded for solutions containing the salts mentioned above, gelatin, serum, and proteins and no difficulties were observed in the work.

J. F. S.

Modification of the Clark Hydrogen Electrode Vessel to permit Accurate Temperature Control. GLENN E. CULLEN (*J. Biol. Chem.*, 1922, **52**, 521—524).—The Clark electrode vessel (A., 1916, ii, 75) is provided with an additional opening by means of which a thermometer may be inserted in the solution. E. S.

Electrolysis of Aqueous Solutions of Alkali Nitrites with a Lead Anode, and an Electrometric Determination of the Constitution of the Complex Ion formed. F. H. JEFFERY (*Trans. Faraday Soc.*, 1922, **17**, 709—718).—In continuation of previous work on the electrolysis of aqueous sodium nitrite solutions employing a silver or copper anode (A., 1920, ii, 662; 1921, ii, 374), the author has investigated the phenomena occurring when a pure lead anode is employed in such electrolysis. A cathode of smooth platinum was used. The strength of the anolyte solution varied from 6.9 grams to 27.6 grams of sodium nitrite per 100 grams of water. The temperature was maintained at 17—18°, and the anode area was 100 sq. cm. The current ranged from 0.099 to 0.77 ampere. Lead was in no case deposited on the cathode, but was dissolved at the anode, forming a complex ion which gave a bright orange colour to the anolyte. For small concentrations of lead in alkali nitrite solutions, probably the only plumbo-nitrite complex formed is $[\text{Pb}(\text{NO}_2)_4]^{''}$. Crystals of $\text{Pb}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ are in equilibrium with solutions obtained from anolytes of certain concentrations. Solid solutions derived from aqueous solutions containing potassium-, nitrate-, and nitrite-ions and the plumbo-nitrite complex are orange-coloured, but more red than the orange of lead nitrite. It is suggested that the complex exists as a definite atomic group in such crystals. J. S. G. T.

Electrolysis of Sodium Silicate Solutions. JAMES FREDERICK SPENCER and KATHLEEN PROUD (*Kolloid Z.*, 1922, **31**, 36—37).—Orthosilicic acid may be prepared by the electrolysis of a 50% solution of sodium silicate in a divided cell, using a heavy anode current density. The cathode employed was a platinum dish 7.5 cm. in diameter, and this contained a small porous pot which held the anode, a coil of platinum wire of 1.80 cm.² surface. A current of 9 amperes was used, and this fell rapidly until no current passed, due to the formation of an insulating layer of orthosilicic acid on the anode. On bending the wire, the deposit fell away and the current again passed. The product is glass-like in appearance, entirely insoluble in water, and stable in the air.

J. F. S.

The Electrochemistry of Non-aqueous Solutions. I. Measurement of Current-density and Potential Difference in the Electrolysis of Metallic Salts in Pyridine. ROBERT MÜLLER (*Monatsh.*, 1922, **43**, 67—74).—A form of electrolytic cell suitable for these measurements is described, and the preparation of an appropriate standard electrode investigated. The element $\text{Ag}/0.1N\text{-AgNO}_3$ in pyridine has a potential (measured with reference to the calomel electrode) of +0.28 volt ($H=0$), and the element $\text{Ag}/0.1N\text{-AgNO}_3$ in pyridine/ NH_4NO_3 saturated solution in pyridine, has +0.26 volt ($H=0$). C. K. I.

The Electrochemistry of Non-aqueous Solutions. II. Decomposition Potential and Electrode Potentials in the Electrolysis of Pyridine Solutions of Silver Nitrate, and the Potential of Silver in these Solutions. ROBERT MÜLLER and ALOIS DUSCHEK (*Monatsh.*, 1922, **43**, 75—80; cf. preceding abstract).—The decomposition potentials are: $0.1N\text{-AgNO}_3$, 2.15 volts; $N\text{-AgNO}_3$, 2.05 volts; saturated- AgNO_3 , 1.95 volts. The silver potentials (invariant with current density) are: $\text{Ag}/0.1N\text{-AgNO}_3$, +0.24 volt; $\text{Ag}/N\text{-AgNO}_3$, +0.33 volt; $\text{Ag}/\text{saturated AgNO}_3$, +0.33 volt referred to the hydrogen electrode. The anodic potential differences are functions of the current density for each of the above concentrations. C. K. I.

Variations in the Magnetic Susceptibility of Oxychromic Salts with Addition of Sulphuric Acid. B. CABRERA and S. PIÑA DE RUBIES (*Anal. Fis. Quím.*, 1922, **20**, 175—181).—The effect of the addition of sulphuric acid to solutions of an oxychromic salt is twofold and results in a depression followed by an elevation of the magnetic constant. In the experiments recorded the variations of the magnetic constant of solutions of an oxychromic salt with time were followed for different values of the ratio H^+/Cr^{+++} . For high values of this ratio, the change is so rapid that only the elevation in the magnetic constant is noticeable. For low values of the ratio, the initial depression is clearly shown by the experimental curves. G. W. R.

A New Adjustable Thermostat for all Temperatures between 0° and 100° . SAMUEL JUDD LEWIS and FLORENCE MARY WOOD (*Trans. Faraday Soc.*, 1922, **17**, 696—700).—A form of thermostat employing a toluene-mercury thermo-regulator of the type due to Barnes and to Gouy is described. The individual parts of the apparatus were independently mounted on a framework extending the length of the thermostat. The surface of the mercury used in the electrical relay employed was covered with glycerol. The dimensions of the thermostat were $24'' \times 16'' \times 14''$, and any desired temperature was attained from cold in an hour and a half. After a further half hour, the temperature did not vary by more than 0.01° . J. S. G. T.

Electric Heating and Controlling Apparatus for a small Thermostat. S. O. RAWLING (*J. Soc. Chem. Ind.*, 1922, **41**, 250—251T).—An electric heating and controlling apparatus is

described by means of which the steady temperature of a small thermostat may be speedily fixed at any point between 25° and 40° without making troublesome readjustments of the apparatus. The current is supplied through two resistances, R_1 and R_2 , in series to the heating resistance, and a toluene or calcium chloride regulator is so arranged that the second resistance may be cut out or left in the circuit as the temperature demands. The resistance R_1 is of such a size that when the current passes through it and the heater alone too much heat is developed, but when the current passes through R_1 , R_2 , and the heater, insufficient heat is supplied to keep the temperature at the required point. The thermostat consists of a long bulb from the neck of which a side arm slopes downward and connects with the middle of a U-tube. The U-tube itself is divided into two parts by means of a glass seal through which a platinum wire is fused. One arm of the U-tube is provided with a short length of capillary tubing of about 1 mm. bore. A side tube is fitted above the top of the capillary and a rubber stopper fitted into the widened end of the U-tube carries a platinum electrode, which projects about 1.5 cm. into the capillary tube. The upper end of the tube leading from the main bulb is fitted with a glass tap, K , of fairly wide bore and very well fitting. To fill the regulator mercury is poured into the U-tube so that its level is about half-way up the capillary tube; the toluene is then placed in the bulb; electrical terminals are provided by the platinum wire dipping into the capillary and by a copper wire dipping into the other arm of the U-tube. These electrodes are connected with a small relay which cuts out or inserts the resistance R_2 in the circuit. Adjustment is effected by bringing the bath to the required temperature with the tap, K , open. The tap is then closed and the electrode tip adjusted to the surface of the mercury in the capillary. This regulator works extremely well, and with a bath of 27 litres it is capable of keeping the temperature constant to 0.02° at 25° . Calculations are given to show how the values of R_1 and R_2 may be arrived at for any particular temperature.

J. F. S.

The Specific Heats of some Sulphides Used in Metallurgy, with Special Reference to High Temperatures. K. BORNE-MANN and O. HENGSTENBERG (*Mitt. Metallhütt. Inst. Tech. Hochschule Breslau*, 1920, 18 pp.).—By means of Oberhoffer's vacuum method improved by substituting a Nernst metal calorimeter for the Bunsen ice calorimeter, the specific heats of the quartz used as container and of several sulphides were determined. The figures for quartz (to 1400°) agree best with those of Magnus (A., 1913, ii, 103) but also satisfactorily with those of White (A., 1909, ii, 966) and of Wüst. Results at 100° intervals given in tabular and graphic form can be summarised as follows: galena, $0-600^{\circ}$, $0.0500-0.0540$; cuprous sulphide, $0-900^{\circ}$, $0.1432-0.1369$; iron sulphide, $0-1200^{\circ}$, $0.1664-0.2216$ (heat of fusion calculated as 60 cal. per gram); magnetic pyrites, $0-100^{\circ}$, 0.1531 ; pyrites, $0-100^{\circ}$, 0.1284 ; zinc blende, $0-900^{\circ}$, $0.1249-0.1351$; Emser blende,

0—900°, 0.1187—0.1311; Annam blende, 0—900°, 0.1131—0.1287. In zinc blendes containing much iron the relation between temperature and the average specific heats suggests a reciprocal solubility of ferrous sulphide and zinc sulphide at high temperatures. Between 720° and 760° the iron-zinc blendes showed two transition points not thus far known and these were confirmed by thermal analysis.

CHEMICAL ABSTRACTS.

The Energy of Gaseous Molecules. J. R. PARTINGTON (*Trans. Faraday Soc.*, 1922, **17**, 734—741).—The experimental values of the molecular heats at constant volume of various monatomic, diatomic, and polyatomic gases are critically reviewed in the light of the equipartition of energy theory. It is suggested that exchange of energy in molecular collisions may occur in quanta, the energy being likewise distributed among the various degrees of freedom. The author discusses the translational energy of gaseous molecules, when the frequency in the energy quantum relation $\epsilon=h\nu$ is identified with the mean value of the collision frequency. It is suggested that although the translational energy is almost exactly equal to the equipartition value, at the ordinary temperature, the rotational energy may depend on the former through a whole-multiple relation existing between the respective frequencies. Vibrational frequencies are, as in the case of solid bodies, assumed to be independent of temperature. The values, deduced from experimental data, of the internal molecular heat of hydrogen at various temperatures, are compared with theoretical values calculated by means of the formulæ given respectively by Einstein, Nernst and Lindemann, Nernst, and an empirical formula of the author, in the form $\beta\nu'=6541/\sqrt{T}$, where ν' is the rotational frequency, equal to 1000 ν , where ν is the translational frequency. The energy of the hydrogen and nitrogen molecules is considered from the point of view of Bohr's theory of atomic structure, as developed by Krüger (*Ann. Physik*, 1916, **50**, 346; **51**, 450). The theory indicates the molecular heat of nitrogen to be higher than that of hydrogen and less affected by temperature.

J. S. G. T.

Melting Interval of certain Undercooled Liquids. The Use of Liquid Air as a Refrigerant. JOHN BRIGHT FERGUSON (*J. Physical Chem.*, 1922, **26**, 549—552).—It has been previously noted by McIntosh and Edson (*A.*, 1916, ii, 230) that solids formed by the sudden chilling of aqueous solutions of salts and acids do not show a melting interval extending from the eutectic point to the temperature at which such a liquid solution would be in equilibrium with a trace of pure ice, but rather melted exactly at this temperature. These authors prepared constant temperature baths by using such chilled materials. The present author has prepared and investigated a number of such chilled materials (glasses) from solutions of sodium chloride and hydrochloric acid. It is shown that the constant temperatures obtained on melting the glasses are dependent on the particular experimental conditions.

In the case of salt solution glasses, these temperatures approach the liquidus temperature, but are always below it. The analysis of the residual slushes left on partial melting indicate that the salt solution glasses may persist for some time at temperatures above the liquidus temperature. Since there does not appear to be an exact relation between the melting temperatures and the liquidus temperatures, the use of such glasses for constant temperature baths cannot be regarded as of general application. One explanation of the constant temperature obtained with these glasses is that this temperature is the point at which the heat absorbed by the melting glass exactly equals the heat of partial crystallisation of the excess component together with the heat lost through the walls of the container. The heat given out when unit weight of the excess component crystallises is probably very great when compared with the heat absorbed when unit weight of the glass melts. If the glass melts slowly, a constant temperature would result which would be near the liquidus temperature, but, on the other hand, if the glass melts quickly the constant temperature would be considerably below the liquidus temperature. When liquid air is used to "freeze" a solution, it is shown that the true melting curve may be obscured by the presence of the glass in the melting mass.

J. F. S.

Vapour Pressures and Heats of Vaporisation of Non-associated Liquids. F. SPENCER MORTIMER (*J. Amer. Chem. Soc.*, 1922, **44**, 1429—1435).—A theoretical paper in which empirical methods for evaluating the constants in the vapour pressure and sublimation pressure equations: $\log P_v = C_v - S_v/T$ and $\log P_s = C_s - S_s/T$ are given and their significance is discussed. It is shown that S_v , the slope of the $\log Pvs. 1/T$ curves is, for normal liquids, given by the expression $S_v = -68 + 4.877T_b + 0.0005T_b^2$. It is demonstrated from existing experimental data that the molecular heat of vaporisation is equal to $4.23S_v$ rather than $4.58S_v$, the value generally adopted. It is shown that the values of the molecular latent heats of vaporisation calculated from the equation $L_v = 4.23S_v$ are generally in better agreement with the experimental results than those calculated from the equations put forward by Trouton, Bingham, or Nernst. This advantage is especially noticeable when the equations are applied to substances boiling at high temperatures. Thus in the case of cadmium $T_b = 1057^\circ$, $L_{obs.} = 23480$, $L_{calc.} = 4.58S_v = 26300$, $L_{calc.} = 4.23S_v = 23920$; (Trouton) 22720; (Bingham) 30200; (Nernst) 22550. The thermodynamical equations connecting heats of vaporisation, heats of sublimation and heats of fusion and the relationships with vapour pressure and sublimation pressure are briefly reviewed and empirical methods for calculating each from the freezing and boiling points are put forward for normal liquids.

J. F. S.

The Heat of Formation of Aluminium Nitride. FR. FICHTER and ERNST JENNY (*Helv. Chim. Acta*, 1922, **5**, 448—454).—The aluminium nitride used for the experiments was prepared from aluminium bronze and contained about 91% of AlN and 0.5%

of silicon, the remainder being alumina. The heat of combustion was measured in a bomb calorimeter, the nitride being mixed with a proportion of benzoic acid to facilitate combustion. The heat of combustion found for the reaction $2\text{AlN} + 3\text{O} = \text{Al}_2\text{O}_3 + \text{N}_2$ was 258.2 (254.8) Cal. Subtracting this from the heat of combustion of aluminium, $2\text{Al} + 3\text{O} = \text{Al}_2\text{O}_3 + 380.2$ Cal., the value for the heat of formation of aluminium nitride is $\text{Al} + \text{N} = \text{AlN} + 61.0$ (62.7) Cal. The figure in brackets is the corrected value, assuming that all the silicon present in the nitride was in the elementary form. The value found is considerably higher than that obtained by previous workers, 55—56 Cal. E. H. R.

The Graphitic Conception of Aromatic Carbon. A. L. VON STEIGER (*Ber.*, 1922, **55**, [B], 1968—1979).—It has been shown previously that the heats of combustion of aromatic hydrocarbons can be calculated on the assumption that all aromatic C—C and C—H linkings are equivalent but differ from the corresponding aliphatic linkings. The value for the aromatic C—C linking which is thus deduced agrees very closely with that of the graphite main linking and thus important evidence of the graphitic conception of aromatic carbon, as postulated by Debye and Scherrer, is adduced. Attempts to apply similar methods to the calculation of molecular refractions have also been described (A., 1921, ii, 473), and it has been found that the results, based on linking constants, harmonise better with the observed values than do those calculated by Brühl's summation method. These results have been criticised adversely by von Auwers (this vol., ii, 98), who has pointed out that an incorrect value has been adopted for the molecular refraction of naphthalene; this is admitted, but it is pointed out that, although the deviation from strict additivity is thereby rendered more pronounced, the superiority of the newer method of calculation still remains.

The molecular refractions of the alkylbenzenes have been examined. With a compound such as ethylbenzene, the summation for the phenyl group is effected with aromatic, that of the ethyl radicle with aliphatic, constants; the character of the C—C linking joining the two halves of the molecule remains undecided, but is assumed provisionally to be of an aliphatic nature. The agreement between the calculated and observed values for the lower benzene homologues is very satisfactory; with the methyl compounds, depressions are observed which become more marked as the methyl groups are in closer proximity to one another and thus attain their maximum in compounds such as 1:2:3:4-tetra-methylbenzene.

The communication concludes with a reply to the criticisms of Wibaut (this vol., ii, 239) and von Weinberg (A., 1921, ii, 668, 669). H. W.

The Heat of Combustion of Benzoic Acid, Cane-sugar, and Naphthalene. W. SWIENTOSŁAWSKI and [MLLE] H. STARCZEWSKA (*Bull. Soc. chim.*, 1922, [iv], **33**, 654—667).—A survey of previous work on the subject reveals discrepancies between the

results obtained by various workers (cf. Wrede, A., 1910, ii, 1038; Roth, A., 1910, ii, 584; Swientoslawski, A., 1915, ii, 315, and 1921 ii, 679; Dickinson, *Bull. Bur. Stand.*, 1915, **11**, 190; Richards, A., 1920, ii, 589; Jessy, this vol., ii, 1041; Henning, A., 1921, ii, 379; Verkade, this vol., ii, 474). Further measurements made by the authors are here compared with those of Dickinson and Verkade, and the opinions expressed by the latter (*loc. cit.*) as to the advisability of choosing benzoic acid as the standard substance are now supported by fresh experimental evidence. Reference is made to the consideration of this subject by the International Conference of Pure and Applied Chemistry, Lyons, 1922.

H. J. E.

Heat Developed on Mixing Sulphuric Acid, Nitric Acid, and Water. J. W. McDAVID (*J. Soc. Chem. Ind.*, 1922, **41**, 246—250r).—The heat developed on mixing various proportions of the following pairs of substances: 49.2% nitric acid and 96.16% sulphuric acid, 20.0% nitric acid and 96.16% sulphuric acid, 96.8% nitric acid and 60.0% sulphuric acid, 96.8% nitric acid and 99.5% sulphuric acid, and a mixed acid containing 49.8% sulphuric acid, 48.4% nitric acid, and 1.8% water with water, has been determined calorimetrically. From the results obtained together with Thomsen's values for the heat of dilution of sulphuric and nitric acids respectively ("Thermochemistry," Thomsen, Burke, p. 76), triangular diagrams have been constructed whereby the heat developed on making any mixture of the three substances may be obtained.

J. F. S.

Compressibility of Exhausted Flasks in the Determinations of the Densities of Gases. E. MOLES and R. MIRAVALLÉS (*Anal. Fis. Quím.*, 1922, **20**, 104—116).—The contraction of flasks used in the determinations of gas densities due to atmospheric pressure may be expressed by the empirical formula $x = 17.5 \cdot V/W \times 10^{-6}$, where x is the contraction per litre of volume, V the volume of the flask, and W its weight. Measurements made on six flasks by three methods showed good agreement of observed values with values calculated from the formula.

G. W. R.

The Compressibility at 0° and less than 1 Atmosphere and the Divergence from Avogadro's Law of Several Gases. PH. A. GUYE and T. BATUECAS (*Helv. Chim. Acta*, 1922, **5**, 532—543).—To determine accurately the molecular weight of a gas by physico-chemical methods, it is necessary to know accurately the weight of a normal litre, L_0 , of the gas and its divergence from Avogadro's law, $1 + \lambda$. A method is described for measuring with great precision the compressibility of a gas at 0°, from which $1 + \lambda$ can be calculated. The apparatus consisted of three cylindrical glass bulbs of approximately equal volume, accurately calibrated, in a vertical column, connected together by capillary tubing and at the top communicating with a barometer. The volume of the gas was measured in this apparatus at approximately 1, $\frac{1}{2}$, and $\frac{1}{3}$ atmosphere. Experiments were made with oxygen, hydrogen,

and carbon dioxide. The divergence from Avogadro's law was calculated from the formula $1+\lambda=(pv)_0/(pv)_1$ (cf. Guye, A., 1919, ii, 318).

The oxygen used was prepared by three different methods, from potassium permanganate, from a mixture of sodium and potassium chlorates, and electrolytically. The mean value obtained for $1+\lambda$ was 1.00085 ± 0.00002 , and the coefficient of compressibility per cm. is 11.3×10^{-6} . Taking $L_0=1.42891$, the value of the gas constant R is 22.414. Hydrogen was prepared by the action of concentrated potassium hydroxide on aluminium and also electrolytically. The mean value found for $1+\lambda$ was 0.99935 ± 0.00002 , which, taking $L_0=0.089858$, gives for the atomic weight of hydrogen 1.0077. The coefficient of compressibility is -8.6×10^{-6} . Carbon dioxide was prepared by heating pure sodium hydrogen carbonate and by the combustion of sucrose. The mean value of $1+\lambda$ was 1.00706 ± 0.00004 ; taking $L_0=1.97685$, this gives as the atomic weight of carbon 11.998, somewhat less than the value accepted by the International Committee, 12.05, but in good agreement with the probable correct value 12.00. The coefficient of compressibility is 92.2×10^{-6} . E. H. R.

The Compressibility at 0° and less than 1 Atmosphere and the Divergence from Avogadro's Law of Several Gases.

II. Ethylene. T. BATUECAS (*Helv. Chim. Acta*, 1922, 5, 544—546; cf. preceding abstract).—Ethylene was prepared by the action of sulphuric acid on ethyl alcohol and by the catalytic action of heated alumina on ethyl alcohol vapour. The mean value found for $1+\lambda$ was 1.00780 ± 0.00004 ; taking $L_0=1.26401$, the molecular weight is found to be 28.032, and the atomic weight of carbon 12.000. The coefficient of compressibility is 102×10^{-6} .

E. H. R.

Measurement of Surface Tension. ROBERT B. ELDER (*J. Physical Chem.*, 1922, 26, 558—562).—A theoretical paper in which the author discusses the measurement of surface tension in connexion with the work of Ferguson (A., 1914, ii, 768) and of Bhatnagar (A., 1921, ii, 169). It is shown that although the numerical values of the latter author are very close to those of Ferguson, the method used involves a number of errors which are partly compensating. The method and errors are discussed.

J. F. S.

Method for the Determination of the Surface of Adsorbing Powders. FRITZ PANETH and WALTER VORWERK (*Z. physikal. Chem.*, 1922, 101, 445—479).—The authors have put forward a rapid and trustworthy method for determining the surface of an adsorbing powder. The method is based on the following considerations. When a sparingly soluble powder is shaken with its saturated solution there will be an exchange of molecules between the surface of the powder and the solution; if it were possible to identify the molecules of the substance in solution, or at least a portion of them, then the partition of these between the solution

and surface could be determined, and at equilibrium the ratio of the identified molecules on the surface to the identified molecules in solution will be equal to the ratio of the total molecules on the surface to the total molecules in solution. This process can be actually carried out for substances which have isotopes; thus in the case of lead sulphate, thorium-*B* can be used and will constitute the identified molecules. The process can be followed by an electroscope and represented by the equation $\text{Isotope(ads)}/\text{Isotope(sol)} = \text{Element(surf)}/\text{Element(sol)}$. The ratio of the isotope adsorbed to the isotope in solution can be determined from the change in the β -ray activity of the solution, and the amount of lead in solution can be determined by analysis, hence, Element(surf) , that is, the weight of the surface layer, can be calculated. Using this method, the weight of the surface layer of one gram of various specimens of lead sulphate and lead chromate has been determined. The values obtained in grams of lead per gram of material are: lead sulphate 6.4×10^{-4} and lead chromate 69.2×10^{-4} . These values have been controlled by microscopic examination and found to be somewhat larger than the microscopic values, but of the same dimensions.

J. F. S.

Thickness of the Adsorbed Layer in the Adsorption of Dyes by Crystals. FRITZ PANETH and WALTER VORWERK (*Z. physikal. Chem.*, 1922, **101**, 480—488).—The adsorption of ponceau-2R by lead sulphate has been determined and from the amount adsorbed and the dimensions of the surface of the lead sulphate (cf. preceding abstract), it is shown that the adsorbed layer is one molecule thick.

J. F. S.

The Sorption of Carbonyl Chloride by Beechwood Charcoal. HUGH MILLS BUNBURY (*T.*, 1922, **121**, 1525—1528).

The Relation between Adsorption and Electrolytic Dissociation. M. A. RAKUSIN (*Biochem. Z.*, 1922, **130**, 282—285).—When a porous pot is immersed in solutions of sucrose or sodium chloride, the concentration of the solution increases owing to negative adsorption. This is correlated with the general adsorption of colloids and non-adsorption of electrolytes. H. K.

Chemical Adsorption. G. STADNIKOFF (*Kolloid Z.*, 1922, **31**, 19—32).—The author differentiates four types of adsorption: (1) solution adsorption, which is represented by Henry's law, $c_2 = kc_1$; (2) chemical adsorption, represented by the equation $c_2 = \sigma c_1 / (1 + \sigma_1 c_1)$; (3) combined adsorption, represented by the equation $c_2 = kc_1 + \sigma c_1 / (1 + \sigma_1 c_1)$, and (4) exchange adsorption, represented by $(mc_2 \cdot c'_1 v) / (mc'_2 \cdot c_1 v) = k$; or $c_2 c'_1 / c'_2 c_1 = k$. The author is of the opinion that chemical adsorption can only be definitely proved in the case of an adsorbent of definite composition possessing either marked acid or basic properties, adsorbing either base or acid from solution. With the object of ascertaining whether or no a chemical explanation for adsorption is possible, the adsorption of sulphuric, hydrochloric, nitric, and acetic acids and mixtures of two of these acids and also of iodine by aniline-black, prepared both

by the use of potassium dichromate and of potassium persulphate, has been investigated. In the case of sulphuric acid, the maximum adsorption is two molecules of sulphuric acid to one of aniline-black, and the adsorption is entirely reversible. The limiting value of the adsorption of hydrochloric acid is three molecules of hydrochloric acid to one molecule of aniline-black and in this case the formula for chemical adsorption is fully followed. The limiting adsorption of acetic acid is two molecules of the acid to one of the adsorbent, whilst in the case of the adsorption of iodine, twelve iodine atoms are adsorbed to each molecule of aniline-black, that is two iodine atoms to each quinonoid nitrogen atom of the tri-quinonoid aniline-black. The experimental results of other authors have been recalculated from the point of view of chemical adsorption (cf. Willstätter and Dorogi, A., 1909, i, 535, 975). J. F. S.

Dissociation of Hydrogen in a Tungsten Furnace and Low Voltage Arcs in Monatomic Gases. O. S. DUFFENBACK (*Science*, 1922, **55**, 210—211).—A furnace consisting of a cylinder of thin sheet tungsten, and an axial tungsten filament, both heated electrically, was used to determine the voltages at which the arc was struck and broken. The results were in agreement with those required by Bohr's theory for the ionising (13·52 volts) and radiating (10·14 volts) potentials of the hydrogen atom, and the potential (16·4 volts) which, according to Bohr's theory, is approximately that necessary to accelerate an electron so that it will dissociate the molecule and ionise one of the atoms on impact. Calculated values for the percentage of monatomic hydrogen in equilibrium with diatomic hydrogen at temperatures from 1000° K. to 3000° K. appeared to be confirmed by the experimental results. A. A. E.

Formation and Dissociation of some Polyhalogen Compounds of Hydrogen in Aqueous Solution. PRIYADARANJAN RÂY and PULIN VIHARA SARKAR (T., 1922, **121**, 1449—1455).

Dissociation of Glucinum Sulphate. (MLE) G. MARCHAL (*Compt. rend.*, 1922, **175**, 270—272).—Glucinum sulphate decomposes under the influence of heat according to the equations $\text{GISO}_4 = \text{GIO} + \text{SO}_3$, and $2\text{SO}_3 \rightleftharpoons 2\text{SO}_2 + \text{O}_2$, and the total equilibrium pressure corresponding with temperatures from 590—830° was measured by means of a mercury manometer, the anhydrous sulphate being heated in an electric furnace in a previously exhausted porcelain tube, and the temperature measured with a le Chatelier platinum-rhodium couple. Utilising the known equation for the equilibrium of dissociation of sulphur trioxide, the partial pressures of sulphur trioxide, sulphur dioxide, and oxygen were calculated from the data obtained. The complete results are recorded in tabular form and include the following values for the partial pressures of sulphur trioxide, sulphur dioxide, and oxygen, respectively: at 700°, 3·30, 6·34, and 3·17 cm.; at 750°, 9·12, 18·24, and 9·12 cm., and at 785°, 17·23, 35·58, and 17·79 cm. Utilising the pressures at the above temperatures, the equilibrium equation was found to be $\log p_{\text{SO}_3} = -14907/T - 14·1 \log T + 57·97$, and the results obtained for other

temperatures from this equation agreed well with the pressures actually observed. The heat of dissociation of glucinum sulphate was calculated to be -53.5 cal. by comparison with that of copper sulphate and its decomposition pressures as determined by Plüddemann (*Diss.*, Berlin, 1907). G. F. M.

Thermostat Arrangement for the Determination of the Effect of Temperature on Diffusion. L. W. ÖHOLM (*Hyllnings-skrift tillägnad Ossian Aschan*, 1920, 9—17).—Experiments were carried out with potassium chloride and sugar solution ($0.25N$, $0.5N$, and N) in a rectangular copper vessel with glass sides, in which the circulation was maintained by a propeller driven by an electric motor supported so as to prevent any shaking of the thermostat; the temperature was constant to $\pm 0.15^\circ$. In the equation $\alpha = A + B \log k$, where α is the temperature coefficient, A and B are constants, and k is the diffusion coefficient, α for potassium chloride between 13.5° and 29.5° was found to have an average value of 0.025 , and for sugar between 13.7° and 28.7° the average value was 0.033 . CHEMICAL ABSTRACTS.

The Determination of Molecular Weight by means of Osmotic Pressure. FOIX (*Bull. Soc. chim.*, 1922, [iv], 33, 653—654).—The author has measured osmotic pressures without using semi-permeable membranes in order to eliminate errors due to imperfections in the membrane. A solution is placed together with pure solvent in a closed system at constant temperature. If the weight of the solution remains constant, the distance between the free surfaces of the two liquids will be equal to the height of the corresponding osmotic column, since, for a perfect osmometer in a closed space, when equilibrium is reached the vapour should be in equilibrium both with the surface of the solution at the top of the column and with the pure solvent at its base. It is claimed that the method is successful, although it is difficult to maintain constant temperatures over the long period of time required to effect the measurement. H. J. E.

Solubility of Gases in Liquids. B. S. NEUHAUSEN (*J. Physical Chem.*, 1922, 26, 553—557).—The author has plotted the solubility data for ammonia, hydrogen chloride, sulphur dioxide, and carbon dioxide in methyl alcohol and ethyl alcohol and from the results shows that the formula $V = K(P\sigma/\bar{P}_0)^{1/n}$ is applicable to the solubility of these gases in the solvents named, as was previously (this vol., ii, 264) shown for aqueous solutions. The values of the constants K and $1/n$ are given for all three solvents. J. F. S.

Melting Point, Latent Heat of Fusion, and Solubility. F. SPENCER MORTIMER (*J. Amer. Chem. Soc.*, 1922, 44, 1416—1429).—A theoretical paper in which a method of calculating the solubility of substances forming non-ideal solutions is described. It is shown that for those systems which do not form molecular complexes or solid solutions the ratio of the experimental to the ideal slope of the $\log Nvs. 1/T$ curves is a factor which may be determined by a graphical method. Three methods are described

whereby the ideal slope of the $\log Nvs. 1/T$ curves for any solute may be found. It is pointed out that the solubility or melting-point method of determining the latent heat of fusion of organic compounds gives very accurate results when interpreted in the light of the principles laid down in the paper. Some generalisations in connexion with the nature of binary systems obtained with various types of mixtures are put forward. The uses of these principles in determining the choice of a solvent for crystallisations and molecular-weight determinations are suggested. J. F. S.

Reactions in Fused Salt Media. II. Solvolysis. J. F. G. HICKS and WALLACE A. CRAIG (*J. Physical Chem.*, 1922, **26**, 563—576; cf. this vol., ii, 147).—The authors have investigated the reactions which occur when lead chromate, lead oxide, silver chromate, and barium chromate, respectively, are dissolved in molten sodium chloride and in an equimolecular mixture of sodium and potassium nitrates at various temperatures up to about 850°. For comparative purposes the hydrolysis of lead chromate in water has been investigated both at ordinary pressure and under increased pressure. It is shown that the solvolysis of lead, silver, and barium chromates by a fused equimolecular mixture of sodium and potassium nitrates represents states of equilibrium analogous to hydrolysis. Of these reactions, the solvolysis of lead chromate is the most complete and that of silver chromate the least complete. The regularity with which the constants of solvolysis vary between consecutive observations follows the same order, and the marked irregularity in the case of silver chromate suggests the possibility of another factor entering into the reaction. The solvolysis of lead chromate by fused sodium chloride also represents a true state of equilibrium, whilst in the case of silver chromate the reaction goes to completion. In the solvolytic reactions studied, equilibrium is reached in about one hundred minutes, and the constants of solvolysis may be calculated with a fair degree of accuracy. The solvolysis of lead oxide by fused sodium chloride proceeds to completion at 850—870°, and that of silver chromate is also complete at the same temperature, but here the reaction occurs much more rapidly. The present work indicates that lead chromate and litharge combine by simple molecular addition after part of the former has undergone solvolysis in the nitrate flux. In other words, the red basic lead chromates are higher order compounds. The relatively small degree of solvolysis of lead chromate and the practically complete solvolysis of lead oxide by the same reagent under the same conditions explains the failure to obtain red basic lead chromates when a fusion containing lead chromate, lead oxide, and sodium chloride is rapidly cooled, and also the appearance of the red basic lead chromates when a similar fusion is slowly cooled. The results confirm the assumption of the dissociation $Pb_2CrO_5 \rightleftharpoons PbO + PbCrO_4$. This assumption was previously (*loc. cit.*) offered as an explanation of the failure to obtain red basic lead chromates when a fusion containing lead oxide, lead chromate, and sodium chloride was poured into water and agrees well with the evidence offered by

the thermal equilibrium diagram plotted for the system lead chromate-lead oxide. J. F. S.

Theory of Recrystallisation. H. ALTERTHUM (*Z. Elektrochem.*, 1922, **28**, 347—356).—The present views of recrystallisation are considered and nucleus formation and growth are regarded as a consequence of a thermodynamic instability. It is shown that the energy changes which accompany the cold working of a metallic crystal may be divided into reversible and irreversible changes, and the different degrees of working as a continuous series of different modifications. On the basis of Boltzmann's theory of probability, a formula is developed which expresses the number of nuclei of a recrystallised metal as a function of the temperature and the degree of working, which is in excellent agreement with the experimental results of Czochralski (A., 1917, ii, 302). From the same point of view, a continuous series of modifications, which differ in the degree of dispersity, is assumed and a similar formula is derived for the number of nuclei in recrystallisation by absorption of other crystals. The proportionality factors are attributed, in part, to causes which are not thermodynamic, and the possible changes of these during the process of recrystallisation are discussed. J. F. S.

Loosening of Crystal Lattices. G. VON HEVESY (*Z. physikal. Chem.*, 1922, **101**, 337—352).—The transport of material, that is, diffusion and electrolytic transport, in crystals is rendered possible by the gradual loosening of the crystal lattice by an increase of temperature. As a measure of the loosening tendency of a crystal, the dimensions of the change in electrical conductivity between solid and liquid at the melting point serve as the most suitable standard. This value is extraordinarily divergent for different substances, varying relatively from 1 for silver iodide to 20,000 for sodium nitrate. A close relationship exists between the loosening tendency and the electro-affinity of the ions which form the crystal. The greater the work necessary to convert the ions of a crystal into the neutral condition, the smaller is the tendency of the lattice to loosen. From this it follows that the loosening of the lattice is brought about by a disturbance of the normal condition of individual ions constituting the crystal. The increase in electrical conductivity which solid electrolytes undergo when illuminated is regarded as due to a loosening of the lattice which increases the mobility of the ions already present in the electrolyte, and the transport of electricity by electrons is regarded as a limiting case of this phenomenon. The relationship between the loosening and the overstepping of the Dulong and Petit value of the atomic heat at higher temperatures is discussed and the overstepping regarded as a preliminary condition of the melting process. J. F. S.

Röntgenographic Determination of Crystal Arrangement. M. POLÁNYI (*Naturwiss.*, 1922, **10**, 411—416).—Röntgenographic methods must be employed to determine whether a crystal lattice is changed by elongation of a single crystal. By means of a fila-

ment diagram it was found that for a zinc crystal (1) the lattice changes its orientation with respect to the longitudinal axis when elongated; (2) in the section drawn out to a flat band (cf. Schiebold, *Z. Physik*, 1922, **9**, 180; Carpenter and Elam, this vol., ii, 69; Gomperz, *Z. Physik*, 1922, **8**, 184) the angle that the hexagonal axis of the crystal lattice makes with the longitudinal axis changes from 10° to 18° , and (3) the cylindrical filaments resulting from further elongation of the flat bands have the same orientation of their lattices as the flat bands. It is maintained that this same kind of shift in the orientation of the lattice occurs in a zinc wire as in the individual crystal.

CHEMICAL ABSTRACTS.

Graphical Determination of Hexagonal and Tetragonal Crystal Structures from X-Ray Data. ALBERT W. HULL and WHEELER P. DAVEY (*Physical Rev.*, 1921, **17**, 549—570).—A graphical method of interpreting X-ray patterns of powders is described, for each type of lattice the logarithms of the theoretical spacings of the different planes being plotted as functions of the axial ratio. A number of graphs are reproduced for comparison with observed spacings. Three specific arrangements have been given for each system, namely, simple prism, centred, and face-centred arrangements in the cubic and tetragonal systems, and simple prism, close packed, and rhombohedral arrangements in the hexagonal system. Since (1) all possible arrangements of atoms in the cubic, tetragonal, or hexagonal systems may be obtained by the combination of one or more identical simple space lattices of cubes, right tetragonal prisms, and right 60° triangular prisms, respectively, and (2) the intermeshing of two or more identical lattices weakens or causes to disappear some of the lines due to a single lattice, but can add no new lines, it follows that the above, and all other possible arrangements, are obtained from the simple tetragonal and triangular prism lattices, respectively, by simply omitting part of the lines. The cubic forms may be found on either the tetragonal or hexagonal plots, whilst for the orthorhombic, monoclinic, and triclinic systems the relative crystal spacings must be expressed as a function of two, three, and five variables, respectively; a simple approximate method is, however, indicated.

Zinc is shown to be a hexagonal close-packed assemblage of prolate spheroids, with axial ratio 1.860 and the side of the unit triangle 2.760 Å. Cadmium has a similar structure, the corresponding measurements being 1.89 and 2.980. Indium has a structure very similar to that of aluminium (cubic close-packed), namely, a tetragonal close-packed arrangement of prolate spheroids, with axial ratio 1.06 and a unit square of side 4.58 Å. A. A. E.

X-Ray Crystal Analysis of Metals. ALBERT W. HULL (*Physical Rev.*, 1921, **17**, 571—588; cf. *ibid.*, 1917, **10**, 661; *Proc. Amer. Inst. Elec. Eng.*, 1919, **38**, 1171; A., 1919, ii, 470; 1920, ii, 546; 1921, ii, 38, and preceding abstract).—The crystal structure of thirteen common metals has been determined. The lattices of chromium, molybdenum, and tantalum are body-centred cubes with sides 2.895, 3.143, and 3.272 Å., respectively; cobalt (α form),

nickel, rhodium, palladium, iridium, and platinum have face-centred cubic lattices with sides of cubes 3·554, 3·540, 3·820, 3·950, 3·805, and 3·930 Å., respectively; cobalt (β form), zinc, cadmium, and ruthenium have hexagonal lattices of the close-packed type with axial ratios 1·63, 1·86, 1·89, and 1·59, respectively, and with triangular sides 2·514, 2·670, 2·960, and 2·686 Å., respectively; indium has a face-centred tetragonal lattice with axial ratio 1·06 and side of elementary prism 4·58 Å. The structures of cadmium, zinc, and indium are close-packed arrangements of solid prolate spheroids, whilst that of ruthenium is a close-packed arrangement of oblate spheroids.

A. A. E.

Coagulation of Colloids. ARNE WESTGREN and JOSEF REITSTÖTTER (*J. Physical Chem.*, 1922, 26, 537—548).—A theoretical paper in which the authors summarise Smoluchowski's kinetic hypothesis of coagulation (A., 1917, ii, 297) and give an account of the work which has been published with the object of substantiating this hypothesis.

J. F. S.

Protecting Colloids. XII. Gelatin as Protecting Colloid. II. Colloidal Selenium. A. GUTBIER and R. EMSLANDER (*Kolloid Z.*, 1922, 31, 33—36; cf. A., 1921, ii, 693; this vol., ii, 142, 283, 485).—The stabilising action of gelatin on colloidal solutions of selenium has been investigated. A very stable selenium sol may be prepared by dissolving 2—3 grams of selenium dioxide in a litre of 0·1% gelatin solution made up in chloroform water and slowly reducing at 18—25° with a solution of hydrazine hydrate (1 : 1000), taking care that the reduction is stopped before the last of the dioxide is reduced. The solution is then dialysed and preserved under a layer of chloroform. The solution is red in colour, quite clear and very stable at ordinary temperatures, but on heating a red, amorphous precipitate separates. Sols prepared as above have been preserved without change for eight years. The addition of hydrochloric acid or sodium hydroxide in small concentrations to the protected colloid causes the system to be more stable to freezing than the protected colloid without the addition of electrolyte. Sodium chloride causes the solutions to change to a lighter colour, but exerts no further action on the protected colloid. The colour change is attributed to the formation of a stable complex, salt-glutin-selenium.

J. F. S.

An Inhibition Period in the Separation of an Emulsion. T. C. NUGENT (*Trans. Faraday Soc.*, 1922, 17, 703—707).—The author has investigated the de-emulsifying action of sodium hydroxide solution on emulsions of benzene in water, containing 50% by volume of benzene and not less than 0·1% of gelatin as stabiliser. If sodium hydroxide is added immediately after production of the emulsion, de-emulsification commences at once. If the emulsion is left undisturbed for some time prior to adding the sodium hydroxide solution, de-emulsification is inhibited for a period following such addition. The inhibition period depends on the interval between the production of the emulsion and the addition of the sodium hydroxide

solution. It is suggested that the stability of the emulsion increases with its age owing to the gradual formation of protective layers of the stabilising agent about the benzene particles. J. S. G. T.

Precipitation of Metals by Hydrogen Sulphide. G. McP. SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 1500—1502).—A theoretical paper in which the author suggests that should it be thought best to regard the formation of sulphide precipitates from the ionic point of view alone, then the hydrogen sulphide (HS')-ion should be regarded as the active participating ion, and not the sulphide (S')-ion. In support of this statement, it is shown that a 0.2*N*-solution of hydrochloric acid containing 0.2*N*-hydrogen sulphide contains in 5 c.c., 3×10^{20} non-ionised molecules of hydrogen sulphide, 15×10^{13} hydrogen sulphide ions, and only one sulphide ion. A further extreme case due to Knox (*A.*, 1908, ii, 830) is considered; according to this author, mercuric sulphide has a solubility product 2.8×10^{-54} , from which it follows that the maximum concentration of mercuric and sulphide ions is 1.7×10^{-27} in a saturated solution of mercuric sulphide, that is, one individual mercuric or sulphide ion in 1000 litres of solution, which implies that to maintain anything like equilibrium these ions must move with the velocity of light, a condition which is not fulfilled. J. F. S.

Force of Adhesion in Solutions. III. Partition of Substances between two Solvents. NIKOLAI SCHILOV, LIDIE LEPIN, MARIE JANTSCHAK, and MICHAEL DUBININ (*Z. physikal. Chem.*, 1922, **101**, 353—402; cf. this vol., ii, 350).—A very large number of partition coefficients have been determined at temperatures ranging from 10° to 40°. These include: formic acid, acetic, propionic, succinic, benzoic, oxalic, tartaric, and nitric acids between ethyl ether and water; acetic, propionic, isobutyric, benzoic, mandelic, salicylic, trichloroacetic, and trichlorobutyric acids between benzene and water; iodine, pyridine, benzoic, and picric acids between toluene and water; benzoic and acetic acids between xylene and water; iodine, acetic, propionic, isobutyric, benzoic, and salicylic acids between chloroform and water; mandelic and benzoic acids between anisole and water; benzoic acid between phenetole and water; succinic acid between amyl ether and water; benzoic acid between light petroleum and water, and trichloroacetic and trichlorobutyric acids between amylene and water. It is shown that because of the mutual influence on solubility the use of the Henry-Dalton law, in connexion with the partition of substances between two liquid phases, is extremely limited, and the law therefore represents an ideal limiting condition which rarely occurs. The difference between dilute and concentrated solutions is not fundamental, but only quantitative. The partition coefficient is generally dependent on the total concentration of the solute, and the constancy of this quantity cannot alone be taken as a proof of the Henry-Dalton law, because mutual compensating volume changes in the liquids can occur, as has been actually shown in the present experiments. The limiting value of the partition coefficient at large concentrations of the solute is

not, in general, determined by the ratio of the individual solubilities in the two solvents, but by the ratio of the concentrations of the two phases at the triple point, solid-liquid-liquid. The partition data are readily presented graphically if the relative concentrations of the solute in the individual phases are plotted as a function of the total concentration. In this way, for each partition two coupled isotherms are obtained which in many cases have characteristic forms and serve to differentiate the various types. The partition coefficient can be expressed by the general approximation formula $K = C_1/C_2^n = C_1/C_2^{\log \beta_1 / \log \beta_2}$, in which β_1 and β_2 are defined by the change of concentration of the individual phases brought about by definite changes in the total concentration of the solute. The index n therefore becomes any suitable figure, and only in a few special cases has it a stoichiometric significance. In many of the cases examined now and previously the mean values of β_1 , β_2 , and n for the region of larger concentrations are approximately constant and may be followed up to the triple point. The partition of substances which are infinitely soluble in both phases is determined by the dissolving power of both solvents with respect to the solute. The coupled isotherms are convergent and meet at the critical mixture point of the two phases. This phenomenon can be investigated by partition and mixing experiments and furnishes information about the dependence of the dissolving power of water and organic solvents on constitution. Experiments on the kinetics of partition show definitely that with respect to the equilibrium concentrations partition is a time reaction of the first order. The slow diffusion process of the solute through the interface and through the concentrated layers which adhere to the interface is determinative of the velocity as in the case of heterogeneous systems of solid and liquid. The velocity constants obtained are to a degree proportional to the number of rotations per minutes of the reaction vessels and independent of the absolute amount of substance diffusing.

J. F. S.

System $\text{Na}_2\text{O}-\text{CO}_2-\text{NaCl}-\text{H}_2\text{O}$, considered as two Four Component Systems. F. A. FREETH (*Phil. Trans.*, 1922, [A], 223, 35—87).—The solubility relations in the systems $\text{Na}_2\text{CO}_3-\text{NaCl}-\text{H}_2\text{O}$; $\text{Na}_2\text{CO}_3-\text{NaOH}-\text{H}_2\text{O}$; $\text{Na}_2\text{CO}_3-\text{NaHCO}_3-\text{H}_2\text{O}$; $\text{NaOH}-\text{NaCl}-\text{H}_2\text{O}$; $\text{NaHCO}_3-\text{NaCl}-\text{H}_2\text{O}$; $\text{Na}_2\text{CO}_3-\text{NaOH}-\text{NaCl}-\text{H}_2\text{O}$ and $\text{Na}_2\text{CO}_3-\text{NaHCO}_3-\text{NaCl}-\text{H}_2\text{O}$ have been experimentally determined at 0° , 10° , 15° , 20° , 25° , 30° , 35° , 45° , and 60° . Numerous tables of the results and diagrams representing the relationships are included in the paper, from which the composition and quantity of the stable phases formed from any mixture of the components may be deduced.

J. F. S.

Liesegang's Phenomenon and Precipitate Formation. N. G. CHATTERJI and N. R. DHAR (*Kolloid Z.*, 1922, 31, 15—16).—In continuation of work previously published (this vol., ii, 205), it is shown that the peptisation of insoluble hydroxides of iron, cobalt, uranium, and thorium may also be brought about by

gelatin, agar, glue, gum arabic, and starch in the manner previously employed with glycerol. In the case of peptisation by glycerol, it is shown that this is governed by the concentration of the reacting substances. Thus glycerol does not peptise ferric hydroxide in the presence of concentrated solutions of ferric chloride. The authors describe experiments to show that the formation of Liesegang rings is closely connected with the above-named actions, and that here also the concentration of the reacting solutions is an important factor.

J. F. S.

Velocity of Chemical Change in Solid Substances. C. N. HINSELWOOD and E. J. BOWEN (*Z. physikal. Chem.*, 1922, **101**, 504—505).—A discussion of Sieverts and Theberath's conclusions on the velocity of chemical reactions in solid systems (this vol., ii, 360), and a reference to the author's experimental work on the same subject (A., 1920, ii, 743; 1921, ii, 443; T., 1921, **119**, 721).

J. F. S.

Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. II. Reaction of Permanganate and Formic Acid in Neutral Solution. JOSEF HOLLUTA and NIKOLAUS WEISER (*Z. physikal. Chem.*, 1922, **101**, 489—497; cf. this vol., ii, 448).—The reduction of potassium permanganate in neutral solution by formic acid has been examined at 17° and 26.75°. It is shown that the disturbances observed in the reductions carried out in acid solution disappear in neutral solutions; these disturbances are observed down to acid concentrations 0.001*N*, and are greatest at the start of the action. The reduction in acid solutions is represented by the equations $2(\text{MnO}_4' + \text{HCO}_2' + \text{H}_2\text{O} = \text{MnO}_4'' + \text{CO}_3'' + 3\text{H}')$ and $2\text{MnO}_4'' + \text{HCO}_2' + 7\text{H}' = 2\text{Mn}(\text{OH})_4 + \text{CO}_2$. The temperature coefficient of the reaction is 1.88, a perfectly normal value which is very close to the value observed for the action in dilute acid solutions (*loc. cit.*).

J. F. S.

Antioxidants and Antioxygenisers. A. SEYEWETZ and P. SISLEY (*Bull. Soc. chim.*, 1922, [iv], **33**, 672—676).—A review of the subject in which reference is made to the work of Bigelow (A., 1898, ii, 506), Titoff (A., 1904, ii, 113), Lumière and Seyewetz (A., 1905, ii, 379), Sisley (*Rev. gén. mat. col.*, 1911, 337), and Moureu and Dufraisse. The suggestion is made that the term antioxygeniser (*antioxygène*) applied by the last named is less suitable than antioxidant (*antioxydant*) suggested by Lumière and Seyewetz.

H. J. E.

Catalysis with Special Reference to Newer Theories of Chemical Action. I. The Radiation Theory of Chemical Action. (1) Radiation and Chemistry. JEAN PERRIN. (2) **The Radiation Hypothesis of Chemical Reactivity and some of its Applications.** W. C. McC. LEWIS. (3) **A Theory of Chemical Reaction and Reactivity.** E. C. C. BALY. (4) **Is a True Unimolecular Action Possible?** T. MARTIN LOWRY (*Trans. Faraday Soc.*, 1922, **17**, 546—572, 573—587, 588—595, 596—597).—(1) A review of the author's radio-chemical theory of reactions

("Les Atomes," 1913; A., 1919, ii, 177), which is in accord with the laws of Arrhenius and of Planck. Experimental verification of the theory is derived from a consideration of the phenomena of photochemistry, luminescence, and organic fluorescence. The theory is extended to the phenomena of radioactivity.

(2) A review of the author's application of the quantum radiation hypothesis to the investigation of the mode whereby energy necessary to produce chemical change in catalytic or non-catalytic processes is communicated to the reactant unit (cf. T., 1914, 105, 2330; 1915, 107, 233; 1916, 109, 796; 1918, 113, 471; 1920, 117, 1120).

(3) Chemical reaction between atoms is conceived as consisting in the joint loss of an equal amount of energy by the reacting atoms, whereby a stable molecule is produced. The atoms in combination retain their individuality as absorbers or radiators of energy. The least possible amount of energy that the molecule can lose is a multiple of the least common integral multiple of the frequency quanta of its component atoms. The theory is confirmed by the phenomena observed in the photochemical combination of hydrogen and chlorine, and the possibility of the existence of two samples of a gas, for example, ammonia in apparent thermal equilibrium but in different molecular phases.

(4) The author contends that none of the actions to which the radiation hypothesis has been applied involves only a single molecule. The application of the hypothesis to cases of radioactive disintegration and bombardment by α -particles, where single molecules are involved, is unnecessary. The foundation of the radiation hypothesis is consequently doubtful.

J. S. G. T.

Catalysis with Special Reference to Newer Theories of Chemical Action. II. Heterogeneous Reactions. (1) **Chemical Reactions on Surfaces.** (2) **The Mechanism of the Catalytic Action of Platinum in the Reactions $2\text{CO} + \text{O}_2 = 2\text{CO}_2$, and $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$.** IRVING LANGMUIR (*Trans. Faraday Soc.*, 1922, 17, 607—620, 621—654).—(1) The author reviews his theory of adsorption at solid surfaces and the modus operandi of chemical reactions occurring thereat. Films adsorbed at solid surfaces are exceedingly stable, are unimolecular in thickness, and are oriented with regard to the adsorbing surface. Adsorption occurs as the result of a time lag between condensation and evaporation occurring at the surface. The orientation of the molecules on the adsorbing surface is a vital factor in determining the activity of the surface towards reacting gases. Differences in the geometrical arrangement of the atoms in the surface are responsible for the activation of catalysts effected by the action that occurs on them. Reactions between separate phases of constant composition occur only at the boundaries of phases.

(2) A detailed account is given of a theoretical and experimental investigation of the conditions determining the combination of (a) carbon monoxide and oxygen, and (b) hydrogen and oxygen, occurring at a smooth platinum surface. In the case of the former

reaction, for the range of temperatures $500\text{--}700^\circ\text{K.}$, the platinum surface is nearly completely covered by a unimolecular carbon monoxide film and reaction occurs only when carbon monoxide molecules strike oxygen atoms which have become adsorbed in the spaces left vacant by the evaporation of carbon monoxide molecules. For the range of temperatures $750\text{--}1050^\circ\text{K.}$, the surface is nearly covered with oxygen when there is an excess of oxygen, and the reaction velocity is limited by the rate at which carbon monoxide molecules strike the surface. With an excess of carbon monoxide, the surface is largely bare, and the reaction velocity is limited by the rate at which oxygen molecules strike the surface. In the case of the reaction between hydrogen and oxygen, at low temperatures ($300\text{--}600^\circ\text{K.}$), the reaction velocity depends on the previous treatment of the platinum. With relatively inactive platinum, the results resemble those obtained with carbon monoxide and oxygen, the reaction velocity being roughly proportional to the pressure of oxygen and inversely to that of the hydrogen. At temperatures between 700°K. and 1900°K. , the results correspond closely with those obtained with carbon monoxide and oxygen. At these temperatures, the reaction is not sensitive to the previous treatment of the platinum. Adsorbed oxygen atoms are very reactive towards hydrogen, whilst under certain conditions adsorbed hydrogen atoms are relatively inactive towards oxygen molecules.

J. S. G. T.

Induced Reactions and Negative Catalysis. N. R. DHAR and N. N. MITTRA (*Trans. Faraday Soc.*, 1922, **17**, 676—680).—The phenomenon of induced reaction studied by Dhar (T., 1917, **111**, 690) is shown to be of general occurrence. Negative catalysis, due probably to the formation of intermediate compounds, occurs in oxidation reactions when the catalyst is readily oxidisable. It is concluded that one chemical change will promote or induce another chemical change of the same type.

J. S. G. T.

Adsorption and its Bearing on Catalysis. MARCEL GUICHARD (*Bull. Soc. chim.*, 1922, [iv], **33**, 647—653).—A study of the effect of variation of surface on catalytic activity. In the case of silica, a diagram is given showing the different amounts of water vapour adsorbed at various temperatures and constant pressure by the catalyst after preliminary heating to different temperatures; increase in the temperature of preliminary heating decreases activity in adsorption. Similar results are obtained in the case of finely divided nickel and also for various solids in respect of iodine vapour. The author concludes that the conditions which tend to decrease the amount of vapour adsorbed by a powdered solid are the elevation of equilibrium temperature and the lowering of equilibrium pressure, both being reversible; further, the temperature and duration of heating to which the solid has been subjected beforehand produce an effect which is irreversible. Reasons are given for the inference that the preliminary heating results in diminution of the surface available for adsorption.

H. J. E.

Catalysis by Platinum Black. G. VAVON and A. HUSSON (*Compt. rend.*, 1922, **175**, 277—279).—A platinum black catalyst which has become poisoned and inactive in the hydrogenation of a particular substance is not necessarily inactive towards another substance, and experiments were undertaken to determine the point at which absorption of hydrogen ceased with various unsaturated substances when the catalyst was progressively poisoned by the gradual addition of small quantities of carbon disulphide. This limiting point was found to vary with the nature of the substance, with the nature of the solvent, with the quality of the platinum, and with the amount of catalyst used, but is independent of the concentration of the solution. In one instance, using 5.5 grams of substance, 50 c.c. of alcohol, and 0.2 gram of platinum, the amount of carbon disulphide required to inhibit hydrogenation was 1.1 mg. for *cyclohexene*, 0.8 mg. for nitrobenzene, 0.5 mg. for cinnamic acid, and 0.4 mg. for acetophenone, so that a catalyst which was inactive towards acetophenone would still hydrogenate nitrobenzene or *cyclohexene*. The author advances a physical explanation of the phenomenon, based on the adsorption of hydrogen by the metal.

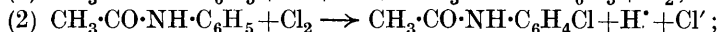
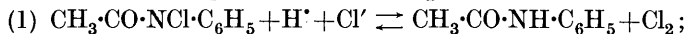
G. F. M.

Rôle of Protective Colloids in Catalysis. II. THOMAS IREDALE (T., 1922, **121**, 1536—1542).

Catalytic Addition of Hydrogen. Influence of Oxygen on the Catalyst. W. NORMANN (*Ber.*, 1922, **55**, [B], 2193—2197).—Working under conditions which are considered to exclude the presence of oxygen and with hydrogen which is free from any trace of the latter, the author has been able to effect the hardening of cotton-seed oil in the presence of nickel (prepared by the reduction of the chloride or cyanide), nickel powder, or palladised kieselguhr. It appears therefore that Willstätter's assumption of the necessity for the presence of oxygen is invalid.

H. W.

Ion Activities in Homogeneous Catalysis. Formation of *p*-Chloroacetanilide from *N*-Chloroacetanilide. HERBERT S. HARNED and HARRY SELTZ (*J. Amer. Chem. Soc.*, 1922, **44**, 1475—1484).—From theoretical considerations, it is deduced that in reactions in liquid systems catalysed by specific ions, it is the activities of such ions which determine the velocity of the reaction at any temperature when the catalysis depends on successive states of equilibria. The velocity constants of the conversion of *N*-chloroacetanilide into *p*-chloroacetanilide catalysed by hydrochloric acid have been determined at 17.65°, 25°, and 35° for concentrations of acid from 0.1*N* to 1.0*N*. This reaction according to Orton and Jones (*Brit. Assoc. Rep.*, 1910, 85) takes place thus :



reaction (1) is measurably slow, whilst reaction (2) is very rapid, so that the system approximates to a continuous series of successive equilibria and fulfils the conditions stated above. It is shown that the velocity constants at each temperature are proportional

to the product of the activities of the hydrogen and chlorine ions of the catalysing acid. The present work is the first case where homogeneous catalysis has been calculated with exactitude over a wide range of concentration and in concentrated solutions, without uncertainties arising in liquid junction potentials. The temperature coefficient has been considered and the critical increment roughly calculated and shown to vary considerably with rise of temperature. The relationship $K_T = k/\alpha_H \alpha_{Cl}$, which holds exactly for solutions of hydrochloric acid alone, fails when acid-salt mixtures are used as catalysts. J. F. S.

A Possible Reconciliation of the Atomic Models of Bohr and of Lewis and Langmuir. W. HUGHES (*Nature*, 1922, **110**, 37—38).—If it is assumed that the electron shells are fixed and the nucleus rotates on an axis, a model is obtained which, when viewed with respect to the electron shells, is precisely the same as the Lewis-Langmuir model, with its very satisfactory representation of the mechanism of chemical combination; when viewed with respect to the whole atom, it possesses all the merits of Bohr's model, yielding an accurate explanation of the reaction of atoms and molecules with radiation. Further, the existence of isotopy can be predicted with its aid, for if the nucleus of a given atom possesses more than one stable axis of rotation with respect to itself, or to its surrounding shells of electrons, or to both, and these axes are associated with different amounts of energy, it is possible for the mass of the atom to be different for the different positions of the nuclear axis, since by the theory of relativity, energy possesses mass. A. A. E.

Atomic Structure. MAURICE L. HUGGINS (*Science*, 1922, **55**, 459—460).—As an extension of Lewis's (A., 1916, ii, 310) theory of atomic structure, it is assumed that, although the number of electrons in each shell of the lighter atoms is the same as in the original theory, the fifth, sixth, seventh, and eighth electrons in the second and third shells pair with the first four, the distance between the electrons in each of these pairs, and also in each pair formed by bonding between atoms, being much less than the distance between pairs. The shells are therefore tetrahedra of pairs instead of cubes of single electrons. The electrons in each shell after the second tend to be placed opposite to the centres of the faces of the imaginary polyhedron formed by the electron groups in the underlying shell. When the nuclear charge becomes sufficiently great, the same forces which cause pairing of electrons in nitrogen result in the formation of triplets in the inner shells of the heavier atoms. As one after another of the outer electrons is drawn into an inner shell to form triplets, the remaining pairs are pushed further from the nucleus, with possible rearrangement of the kernel structure. The theory is applied in a number of instances. A. A. E.

The Quantum Mechanism in the Atom. E. T. WHITTAKER (*Proc. Roy. Soc. Edin.*, 1922, **42**, 129—142).—Ewing's model of ferromagnetic induction (*Proc. Roy. Soc. Edin.*, 1922, **42**, 30) is employed to investigate the mechanism within the atom which

compels all exchanges between kinetic energy and radiant energy to conform with the equation $U = h\nu$. In this model, a system of magnets is rigidly connected like the spokes of a wheel, having poles of the same name at the circumference and poles of a contrary sign at the centre of the circle. When an electron approaches such a model in the direction of the axis of the wheel, a rotation of the poles occurs which constitutes a magnetic current. The kinetic energy of the electron is expended in setting the magnetic structure of the atom in motion. When the velocity of the electron exceeds a critical value $2eM/\sqrt{Am}$, the magnetic structure is penetrated; M and A are quantities dependent on the atomic structure with which the electron collides. When its energy is less than this quantity, it is repelled without permanent loss of energy, the encounter being perfectly elastic. On penetrating the atom, the electron gives up $2e^2M^2/A$ of its energy and leaves the system with the remainder. This absorbed energy, which appears in the atom as a magnetic current, does not depend on the mass of the electron, but on its charge and on quantities dependent only on the atomic structure. This rotational energy is transformed into a radiant form by means of Hertzian oscillators. This view of the mechanism leads to the Planck equation $h\nu = U$. The emission of an electron already in the atom is a converse process and thus the equations may be applied to explain photo-electric phenomena. The connexion with the Bohr theory of series spectra is developed.

W. E. G.

The Quantum Mechanism in the Atom. (SIR) J. ALFRED EWING (*Proc. Roy. Soc. Edin.*, 1922, **42**, 143—146).—A discussion of the mechanism suggested by Whittaker (see preceding abstract) for the conversion of the rotational energy of the wheel atom into radiation. There are two magnetic systems in his model of the atom: a central one forming the wheel, and another around it, which may be called the ring. An electron passing through the system produces relative angular displacement of the two parts of the atom, and magnetic forces are set up which tend to restore the whole to the original configuration. Thus oscillations are set up which expend their energy in the emitted radiation.

W. E. G.

The Quantum Mechanism in the Atom. R. A. HOUSTON (*Proc. Roy. Soc. Edin.*, 1922, **42**, 221—222).—The Whittaker model is checked numerically. A calculation of the radius of the magnetic orbit gives values in satisfactory agreement with the dimensions of the hydrogen molecule. It is shown that the Planck constant comes out as the product of the unit electric charge and a unit magnetic quantity. It thus has the correct dimensions.

W. E. G.

The Importance of Whittaker's Atomic Model and of other Atomic Models. W. PEDDIE (*Proc. Roy. Soc. Edin.*, 1922, **42**, 223—224).—A general discussion of the Whittaker model pointing out the inadequacy of the simply constituted atom of the electronic type.

W. E. G.

Sizes of Atoms in Diamond Type Crystals. ROBERT N. PEASE (*J. Amer. Chem. Soc.*, 1922, **44**, 1497—1498).—On the basis of the results published in a recent paper (this vol., ii, 428), the author has recalculated the atomic radii of several elements of the rare gas type crystallising in the diamond type lattice. The following values are recorded: diamond 0.77 Å.U., silicon (S, Cl) 1.17 Å.U., germanium (Cu, Zn, Br) 1.22 Å.U., grey tin (Ag, I) 1.40 Å.U. The following interatomic distances are calculated: silicon carbide, 1.94 (1.90, 1.95); zinc sulphide, 2.39 (2.35, 2.35); cuprous chloride, 2.39 (2.38, 2.43); cuprous iodide, 2.62 (2.63, 2.78); silver iodide, 2.80 (2.83, 3.18); and cuprous bromide, 2.44 (2.52, 2.57). The values are given in Ångström units, and for comparison purposes the experimental value and the value from Bragg's atomic radii are included in brackets, the former value being placed first. J. F. S.

The Properties of Elements and Salts as Related to the Dimensions of Atoms and Ions. GEORGE L. CLARK (*Science*, 1922, **55**, 401—405).—It is shown that a considerable number of the properties of elements and salts are linearly related to the dimensions of the component atoms and ions. The relations are more general than those found by Biltz (A., 1921, ii, 487); thus it is found that if the atomic volumes of the five alkali elements are plotted on one axis (as the *X*-axis) of a three-dimensional rectangular co-ordinate system, the atomic volumes of the four halogens on the *Z*-axis, and the molecular volumes of the alkali haloids on the *Y*-axis, all the points (except some for caesium, the anomaly of which is attributed to difference in crystal-lattice form) lie approximately on a plane $z = bx + cy + d$ which passes nearly through the origin. When other properties are plotted on the *Y*-axis, in a very large number of cases the surface, whilst not a plane, is of a simple form ("doubly ruled surface"). The surfaces may commonly be expressed by the equation $z = axy + bx + cy + d$. By using this method, a number of possible new linear relationships may be predicted. Values already ascribed to the atomic and ionic radii of the halogens and alkali elements are considered, Henglein's procedure being regarded as questionable.

A. A. E.

Atomic Radii. I. MAURICE L. HUGGINS (*Physical Rev.*, 1922, **19**, 346—353).—Bragg's (A., 1920, ii, 537) "atomic spheres" and "atomic radii" may, when considered from the point of view of Lewis's theory of atomic and molecular structure (A., 1916, ii, 310), be given a definite physical meaning. The "atomic sphere" of an atom is its valency shell, and its "atomic radius" is the distance from the atomic centre to a group of electrons (usually an electron-pair) in the valency shell. It is shown that Bragg's assumption, that the distance between two adjacent atomic centres is equal to the sum of their radii, is often not valid, since in many cases the group of electrons constituting the bond does not lie on the line joining the atomic centres; that is to say, the two "atomic spheres" overlap. Eight causes of variation of the atomic radius

of an element are considered, namely: (1) some of the valency pairs may not act as bonds, (2) a valency electron-pair may be forced away from its normal position in the valency shell, (3) widely varying pulls are exerted on electron-pairs by atoms of different elements, (4) an atom of the same element in different structures may pull an electron-pair away a different distance from the nucleus of the atom to which it is linked, (5) if an atom has a different number of electron-pairs in its valency shell in two crystals, their distances from the nucleus would not be expected to be the same, (6) valency electron-pairs are pulled out from the nucleus to a different extent, according to whether they are on the centre-lines or not, (7) many atoms are capable of more than one arrangement of electrons in that part of the atom inside the valency shell, (8) the number of electrons constituting a bond may be more than two.

A. A. E.

Structure of the Ions of the Rare Earths. H. G. GRIMM (*Z. physikal. Chem.*, 1922, **101**, 403—409).—A theoretical paper in which, on the basis of Bohr's arrangement of the electrons in xenon and niton, an attempt is made to draw conclusions on the structure of the ions of the rare earths, quinquevalent tantalum, sexavalent tungsten, and octavalent osmium ions which shall be in keeping with the chemical properties of these elements. It is shown that the outside sheath of the ions of the rare earths contains in all probability the same number of electrons, namely, eight or nine. The molecular volume and basicity series of the rare earths has been used to draw conclusions on the series of ionic radii (cf. A., 1921, ii, 127).

J. F. S.

Periodic System of the Atomic Ions. H. G. GRIMM (*Z. physikal. Chem.*, 1922, **44**, 410—413).—The author has constructed a table on the basis of the structure of the ions of the elements. This divides the elements into six groups, namely, those with no electrons in the outer sheath, those with two electrons in the outer sheath, those with eight and eighteen electrons, respectively, in the outside sheath. The last three groups are composed of elements which are built up of completed sheaths, that is, sheaths occupied by the same number of electrons as in sheaths of the inactive gases. The fifth group contains elements with an incomplete outside sheath, and the sixth group contains elements with an incomplete inner sheath but a constant outside sheath. The elements of the sixth group are those of the rare earths. In the table the anions lie to the left of the inactive gases and the kations to the right. In this arrangement several elements, such as Cl^{+++} , Se^{++} , and Se^{+++} , occur in two positions.

J. F. S.

Structure of some Gaseous Molecules of which Hydrogen is a Constituent. A. O. RANKINE (*Trans. Faraday Soc.*, 1922, **17**, 719—727).—From viscosity measurements the following values have been deduced for the respective magnitudes (expressed in $\text{cm}^2 \times 10^{-15}$) of the molecular "mean collision areas" of certain gaseous compounds containing hydrogen: HCl , 0.676; HBr ,

0.763; HI, 0.926; H_2S , 0.773; NH_3 , 0.640; PH_3 , 0.911; AsH_3 , 0.985; CH_4 , 0.772. The corresponding values for the inert gases have been recalculated and found to be as follows: Ne, 0.417; Ar, 0.648; Kr, 0.757; X, 0.915. Adopting the Lewis-Langmuir view of the mechanism of combination between hydrogen atoms and other elements, and assuming, on the basis of W. L. Bragg's X-ray measurements (A., 1920, ii, 537), that the atoms towards the end of each period of the periodic table are equal in size, it is shown to be probable that as the number of hydrogen atoms in the molecule increases, their nuclei become more remote from the nucleus of the central atom. This retreat of the hydrogen nuclei is due to their mutual repulsion, and eventually leads to the failure of the formation of molecules, otherwise possible, such as BH_5 and AlH_5 . The relative dimensions of CH_4 and Kr agree to within the limit of probable experimental error. It is to be anticipated, therefore, that NH_4 and Rb, which are correspondingly related to CH_4 and Kr, respectively, would occupy nearly equal spaces. This is confirmed from crystallographic data.

J. S. G. T.

Arabic Chemistry. E. J. HOLMYARD (*Nature*, 1922, 109, 778—779).—An historical note ascribing to Maslama al-Majriti the authorship of the section on chemistry in the "Letters" of the Brethren of Purity (10th century A.D.).

A. A. E.

[**Lecture Experiment.**] **Time Reaction.** MARTIN MEYER (*J. Amer. Chem. Soc.*, 1922, 44, 1498—1500).—A time reaction of the same type as that recently described by Forbes, Estill, and Walker (this vol., ii, 271) which is suitable for a lecture experiment is described. For example, 40 c.c. of *M*-sodium thiosulphate, 20 c.c. of 1.67*M*-potassium hydroxide containing 0.67*M* of potassium sodium tartrate and 44.46 grams of antimony trioxide per litre, are mixed and 10—15 c.c. of 4*N*-hydrochloric acid added. After an induction period of thirty to sixty seconds, a white turbidity appears which changes to the characteristic orange colour of antimony trisulphide. Variations of the quantities give different induction periods.

J. F. S.

Inorganic Chemistry.

New Revision of the Density of Oxygen Gas. E. MOLES and M. CRESPI (*Anal. Fis. Quím.*, 1922, 20, 190—192; cf. Moles and González, this vol., ii, 497).—Oxygen prepared from potassium permanganate contains traces of carbon dioxide and ozone and purification by phosphoric oxide is insufficient. Determinations on oxygen from potassium permanganate from which carbon dioxide and ozone had been removed by soda-lime and mercury, respectively,

gave the value (calculated for lat. 45°) 1.42895 for the density of the gas. This is in good agreement with the value previously given (*loc. cit.*).
G. W. R.

Ozone. E. H. RIESENFELD and G. M. SCHWAB (*Ber.*, 1922, 55, [B], 2088—2099).—The main difficulty in the preparation of pure ozone and the determination of its physical constants consists in its explosiveness. The recent advances in micro-analytical methods have enabled the authors to perform the necessary experiments with such small quantities of material that explosions are avoided or are not dangerous.

Dry oxygen is ozonised in the usual manner and the product condensed in small glass bulbs with long capillaries immersed in liquid air (the apparatus is figured and fully described in the original communication). Since the condensate is always richer in ozone than the supernatant gas, the latter is pumped away after each condensation and the vessel again filled with ozonised oxygen. When in this manner a dark blue condensate (solution of oxygen in ozone) has been obtained, the subsequent condensates consist of pale blue solutions of ozone in oxygen; when the exhaustion is renewed, the oxygen evaporates and the ozone passes into the first phase. The dark blue product still contains about 30% of oxygen, but its removal can be fairly readily effected by fractionation, since the boiling points of oxygen and ozone differ by about 70° . At the temperature of liquid air, the vapour pressure of liquid ozone is practically negligible so that the glass bulbs can be evacuated completely and the capillaries sealed off without danger. Analysis of the product is effected by breaking one of the bulbs containing a known weight of substance under potassium iodide solution containing boric acid, measurement of the volume of inactive oxygen, and estimation of that of active oxygen by titration with sodium thiosulphate. Within the limits of experimental error, the volume relationship of active to inactive oxygen is 1 : 2 and the purity of the ozone is controlled further by a micro-estimation of the molecular weight by Dumas's method. The following physical constants have been determined (the methods and requisite apparatus are fully described and figured in the original); m. p. -250° , b. p. -112.3° , critical temperature -5° , $d_{-192}^{20} 1.784$. Liquid ozone is not completely miscible with liquid oxygen at all temperatures, the critical temperature of solubility lying at -158° .

Very discordant results have been obtained during investigations of the thermal production of ozone from oxygen. According to the Nernst theorem, a minimal temperature of 4000° Abs. is necessary for the production of appreciable quantities of ozone, whereas Fischer has observed considerable formation of the gas at glowing Nernst filaments at a much lower temperature. The temperature attained in the explosion of pure ozone is calculated to be about 4000° Abs., and under these conditions a distinct odour of ozone is observed. On the other hand, no trace of ozone could be perceived in explosions of mixtures of ozone and oxygen

with which a temperature of more than 2000° Abs. was obtained. A purely thermal production of ozone is not involved, therefore, in Fischer's experiments.

The explosive decomposition of ozone is very sensitive to catalytic influences, but if these are excluded the gas is found to be unexpectedly stable. According to Warburg's calculation, the half life period of pure ozone at 16° is one hundred and sixty-seven hours, whereas the authors find that under certain conditions a period of several weeks elapses before decomposition has proceeded to this extent.

Violent changes of pressure cause the explosion of ozone in all states of aggregation. An explosion when the solid or liquid material is lightly touched or on sudden solidification of the liquid has not been observed.

The authors consider that their work brings conclusive evidence against the existence of oxozone. H. W.

The Oxidising and Reducing Properties of Sulphur Dioxide. I. Mercury Chlorides. LACHLAN MACQUARIE STEWART and WILLIAM WARDLAW (T., 1922, **121**, 1481—1489).

The Physical Properties of Sulphur Trioxide. A. BERTHOUD (*Helv. Chim. Acta*, 1922, **5**, 513—532).—Doubt is thrown by the author on the existence of sulphur trioxide in the so-called α - and β -forms. The fact that the two kinds can exist together indefinitely, with other observations of a similar character, indicates that the silky crystals, the so-called β -form, are a product of hydration. The compound, if compound it be, must be, however, of a unique type, containing something like a thousand or more mols. of sulphur trioxide to one of water. A number of physical properties of sulphur trioxide were determined with the greatest care. It has m. p. $16.85^{\circ} \pm 0.02$, agreeing closely with Lichty's result, 16.79° (A., 1912, ii, 1164) and b. p. $44.52^{\circ}/760$ mm. The vapour pressure curve, as deduced from determinations at 15 points between 24° and 47.8° , is represented by $\log p = -2314/T + 10.17$. The critical pressure and temperature were determined, using a modification of Pellaton's method (cf. A., 1916, ii, 245), and the critical temperature by direct observation of the disappearance and reappearance of the meniscus. The results are, $p_c = 83.8$ atm., $t_c = 218.3^{\circ}$. The density was determined at temperatures from 17° to 55° by a pycnometer method, and from 98° to 214° by a modification of Young's method (T., 1891, **59**, 37), which gives the density of both liquid and vapour. The critical density, d_c , is 0.633. The surface tension was determined by the method of Ramsay and Shields, the results being, at 19° , 44.9° and 78.0° , respectively, $\gamma = 34.17$, 29.47, and 22.63. The molecular heat of vaporisation, calculated from the vapour tension curve, is 10,300 cal. The quotient L/T , Trouton's ratio, is surprisingly high, 32.5, the normal for liquids of similar b. p. being 21.0; the high value indicates association in the liquid form. The value of Eötvös's surface tension coefficient also indicates association of the liquid at lower temperatures, but at 78° the value is nearly

normal. The values of van der Waals's constants are : $a=0.01629$;
 $b=0.002684$. E. H. R.

Preparation of Selenium Dioxide. JULIUS MEYER (*Ber.*, 1922, **55**, [B], 2082—2084).—Selenium in quantities of 60—75 grams is heated to its melting point in a porcelain boat placed in a wide hard glass tube; a very rapid current of oxygen which has been passed through fuming nitric acid is passed over it, causing the molten selenium to burn with a brilliant blue flame and to give a sublimate of selenium dioxide the purity of which increases with increasing rate of the supply of oxygen. The product, which contains small quantities of oxides of nitrogen, is purified by being sublimed in the same tube in a current of pure oxygen. To avoid loss of material, the tube is connected with a doubly tubulated vessel of two litres capacity in which the final traces of the dioxide are deposited. The combustion of 60—70 grams of selenium can be effected in about one and a quarter hours.

The oxidation of selenium appears to be greatly affected by catalytic influence, acidic substances causing acceleration whereas alkaline materials (including glass) cause retardation. H. W.

Active Hydrogen and Nitrogen. GERALD L. WENDT (*Nature*, 1922, **109**, 749).—Newman's (this vol., ii, 279) failure to obtain a test for nitrides when sulphur, phosphorus, and iodine are treated with active nitrogen is not evidence of the absence of chemical reaction; in the cases of sulphur and phosphorus, the formation of sulphides and phosphides has been demonstrated by the author, whose experiments also show that phosphine and hydrogen sulphide are formed when phosphorus and sulphur are exposed to active hydrogen. A. A. E.

Active Hydrogen and Nitrogen. F. H. NEWMAN (*Nature*, 1922, **109**, 749; cf. Wendt, preceding abstract).—The absorption of active nitrogen by sulphur, phosphorus, and iodine probably results in chemical combination, since the absorbed gas is not liberated on heating; in the case of active hydrogen, however, absorption occurs at temperatures above 0° . This absorption may be due in part to chemical action, but other processes, such as occlusion, have to be taken into account. A. A. E.

Reaction between Cathodic Hydrogen and Nitrogen at High Pressures. J. N. PRING and E. O. RANSOME (*Trans. Faraday Soc.*, 1922, **17**, 689—694).—When hydrogen is liberated electrolytically at a cathode in contact with nitrogen, particularly at high pressures, the conditions would appear to be favourable to the synthesis of ammonia. A solution of sulphuric acid was electrolysed in the presence of nitrogen at pressures ranging from 1 to 500 atmospheres. At atmospheric pressure, the mean percentage yield of ammonia by direct union of the elements was 0.04%. At pressures from 60 to 104 atmospheres, the yield of ammonia was 0.09%. For pressures ranging from 300 to 500 atmospheres, no ammonia was synthesised. The results indicate

that no reaction occurs between nitrogen and cathodic hydrogen, the small yield of ammonia at the lower pressures being due to thermal action.

J. S. G. T.

Hydroxylamine. CARL KJELLIN (*Svensk Kem. Tidskr.*, 1921, **33**, 213—228).—In the reaction expressed by the equation: $\text{NH}_2\cdot\text{OH} + 2\text{Fe}(\text{OH})_2 + \text{H}_2\text{O} = \text{NH}_3 + 2\text{Fe}(\text{OH})_3$, the experimental results are in practically complete accord when the potassium hydroxide in the solutions does not exceed 1.75%. The reactions between hydroxylamine and stannous hydroxide and manganese hydroxide were also examined; the former yields ammonia in moderate agreement with theory, whilst in the latter case the amount of ammonia produced is negligible. The change undergone when hydroxylamine is subjected to heat in presence of aqueous potassium hydroxide appears to be expressed by the equation: $3\text{NH}_2\cdot\text{OH} = 3\text{H}_2\text{O} + \text{NH}_3 + \text{N}_2$. Compounds of the type $\text{CH}_2\text{R}\cdot\text{NH}\cdot\text{OH}$ (R=Me, Et, Pr) when hydrolysed in concentrated hydrochloric acid or potassium hydroxide, evolved up to 75% of the expected yield of ammonia. It is probable that *N*-isopropylhydroxylamine and bromine react in accordance with the scheme: $\text{CHMe}_2\cdot\text{NH}\cdot\text{OH} \rightarrow \text{CHMe}_2\cdot\text{NBr}\cdot\text{OH} \rightarrow \text{CHMe}_2\cdot\text{NO} \rightarrow \text{CMe}_2\cdot\text{NOH}$. *N*-Ethylhydroxylamine hydrochloride forms long, colourless, hygroscopic crystals, m. p. 37°.

CHEMICAL ABSTRACTS.

Crystal Structure of Phosphonium Iodide. ROSCOE G. DICKINSON (*J. Amer. Chem. Soc.*, 1922, **44**, 1489—1497).—The structure of the crystals of tetragonal phosphonium iodide has been investigated by means of X-rays, using chiefly Laue photographs. It is shown that the X-ray data are satisfactorily accounted for by a structure obtained by placing in a unit cell of the dimensions $6.34 \times 6.34 \times 4.62$ Å.U. phosphorus atoms at (000) and ($\frac{1}{2}\frac{1}{2}0$) and iodine atoms at ($0\frac{1}{2}u$) and ($\frac{1}{2}0u$) where *u* has a value very close to 0.40, and it is shown that no simpler structure is capable of accounting for the data. The close relationship between this structure and the low temperature form of ammonium chloride is demonstrated.

J. F. S.

Hypophosphorous Acid. IV. Its Reaction with Cupric Chloride. ALEC DUNCAN MITCHELL (T., 1922, **121**, 1624—1638).

The Volatilisation of Arsenic and Antimony by means of Methyl Alcohol. L. DUPARC and L. RAMADIER (*Helv. Chim. Acta*, 1922, **5**, 552—556).—By passing a current of air through a solution of arsenious or antimonious oxide in concentrated hydrochloric acid containing a suitable proportion of methyl alcohol, the whole of the arsenic or antimony can be carried over into an absorbing solution. In this way, 0.1 gram of arsenious oxide can be volatilised in one hour at 55° in 45 c.c. of methyl alcohol. In the case of antimonious oxide the vaporisation can be completely prevented by diluting the hydrochloric acid used with an equal volume of water. The method may be applicable for

separating arsenic and antimony from other metals and from each other. E. H. R.

Revision of the Atomic Weight of Boron. Analysis of Boron Trichloride. O. HÖNIGSCHMID and L. BIRCKENBACH (*Anal. Fis. Quím.*, 1922, **20**, 167—173; cf. A., 1921, ii, 646).—From determinations of the ratio $\text{BCl}_3 : 3\text{Ag}$ and $\text{BCl}_3 : 3\text{AgCl}$, following the methods used in the authors' revision of the atomic weight of bismuth (*loc. cit.*), the values of the atomic weight of boron obtained for three samples of specially purified boron trichloride were 10.840, 10.818, and 10.825, respectively. The first value is rejected and the value 10.82 is taken. It is pointed out that this value is in better accord with the theory of isotopes than the hitherto accepted value of 10.90. G. W. R.

The Action of Diamond on Carbon Monoxide. FOIX (*Bull. Soc. chim.*, 1922, [iv], **33**, 678—679).—An attempt to carry out the reaction $\text{CO}_2 + \text{C} \rightleftharpoons 2\text{CO}$ in the case of the diamond at temperatures above 1100° resulted in the deposition of amorphous carbon on the surface of diamond without the latter undergoing any change. The conclusion is drawn that the time of experiment, three hours, was insufficient for the attainment of equilibrium.

H. J. E.

The Preparation of Carbon Suboxide on a Larger Scale and the Properties of Pure Carbon Suboxide. ERWIN OTT and KARL SCHMIDT (*Ber.*, 1922, **55**, [B], 2126—2130).—Diacetyl-tartaric anhydride is heated to its boiling point in a flask the neck of which is connected to a cylinder in which an electrically heated platinum wire is suspended. The upper portion of the cylinder is connected through a series of condensing vessels to a powerful pump which, in spite of the evolution of carbon monoxide, maintains a pressure of about 11 mm. (The apparatus is fully figured and described in the original.) The decomposition of one hundred and eighty-nine grams of anhydride can be effected in six to eight hours, the yield of carbon suboxide being 41% of that theoretically possible. From this point of view the process is superior to the improved method of Stock and Stoltzenberg (A., 1917, ii, 308), which depends on the action of phosphoric oxide on malonic acid, and has the further advantage of greater cheapness. In addition, the carbon suboxide obtained in this manner can be preserved unchanged (except for a slight darkening of colour which is probably due to incompleteness in the exclusion of moisture) for long periods, whereas that prepared with the help of phosphoric oxide rapidly becomes polymerised, probably owing to the presence of traces of phosphorous oxide in the latter (cf. Manley, T., 1922, **121**, 331).

H. W.

The Crystal Structure of Quartz. MAURICE L. HUGGINS (*Physical Rev.*, 1922, **19**, 363—368).—The suggested structure of quartz, obtained by means of the Lewis theory, is in accord with Bragg's conclusions. Each silicon atom is surrounded by four pairs of electrons at tetrahedron corners, which act as bonds

connecting it to four equidistant oxygen atoms. Each oxygen atom is also surrounded by four tetrahedrally oriented electron-pairs, two of which serve as bonds connecting the oxygen to silicon atoms. The crystal is thus not composed of silica units, but is a single molecule.

A. A. E.

Solubility of Helium in Water. HAMILTON P. CADY, HOWARD M. ELSEY, and EMILY V. BERGER (*J. Amer. Chem. Soc.*, 1922, **44**, 1456—1461).—The solubility of helium has been determined at a series of temperatures lying between 2° and 30°, using material which was spectroscopically pure. The following values of the absorption coefficient are recorded: 2°, 0.00938, 10°, 0.00895, 25°, 0.00861, and 30°, 0.00817. Plotting these values shows that there is no indication of the solubility passing through a minimum as has been repeatedly stated. The values are all smaller than those of Estreicher (A., 1900, ii, 205) and Antropoff (A., 1919, ii, 511), and larger than the single determination of Ramsay (T., 1895, **67**, 697).

J. F. S.

The Preparation of Sodium Hydrogen Carbonate. ER. TOPORESCU (*Compt. rend.*, 1922, **175**, 268—270).—A study similar to that originally made at 15° (this vol., ii, 375) of the equilibrium of the four salts, sodium chloride, sodium hydrogen carbonate, ammonium chloride, and ammonium hydrogen carbonate with their saturated solutions has now been made at 35° and 50°. The geometric representation of the results obtained by means of a Le Chatelier diagram enables a calculation to be made of the theoretical yield, that is to say, the proportion of sodium chloride transformable into crystalline sodium hydrogen carbonate for a solution of any given initial composition.

G. F. M.

The Preparation of Ammonium Chloride at Low Temperatures. PAUL MONDAIN-MONVAL (*Compt. rend.*, 1922, **175**, 162—164).—The conditions governing the crystallisation of ammonium chloride at 0° from solutions containing in addition one or more of the salts sodium chloride, sodium carbonate, and ammonium carbonate, were studied in a similar manner to those previously described for 15°, and a Le Chatelier diagram is given showing the surfaces of saturation. The zone of crystallisation of sodium carbonate shows two distinct areas, one corresponding with the crystallisation of $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, and the other with a hydrate of the formula $2\text{Na}_2\text{CO}_3 \cdot 5\text{H}_2\text{O}$, the existence of which, although disputed by Wegscheider (A., 1912, ii, 156), is now confirmed.

G. F. M.

A Preliminary Attempt to Transmute Lithium. RALPH W. G. WYCKOFF (*Science*, 1922, **55**, 130—131).—Inconclusive results were obtained when lithium or its salts was bombarded with a stream of electrons, in the hope of introducing one or two electrons into the nucleus, and detecting spectroscopically the formation of helium or hydrogen.

A. A. E.

Electrolytic Preparation of Calcium Amalgam. B. S. NEUHAUSEN (*J. Amer. Chem. Soc.*, 1922, **44**, 1445—1447).—The author discusses the methods which have been adopted previously for the preparation of calcium amalgam (Smith and Bennett, A., 1909, ii, 663; 1910, ii, 500), and devises a more efficient method of preparing this material. The method consists in just covering the bottom of a crystallising dish, 25 cm. diam., with a layer of mercury which serves as cathode, and then filling the dish with a 1.75*N*-solution of calcium chloride. An anode of platinum foil (2×4 cm.) is placed in the solution parallel to the mercury surface at a distance of 4 cm., and a current of 3.5 amperes at 4.6 volts passed for thirty minutes. This arrangement prevents heating and foaming. After about thirty minutes, the generation of hydrogen sets in, but up to this point the solution remains neutral to litmus and there is no formation of a black powder which in other methods always forms and catalyses the decomposition of the amalgam. The amalgam is washed by allowing it to fall in a fine stream into two litres of distilled water. The product prepared in this way contains 0.069—0.075% of calcium, and is preserved in a bottle filled with carbon dioxide. J. F. S.

The Crystal Structures of Aragonite (CaCO_3) and Related Minerals. MAURICE L. HUGGINS (*Physical Rev.*, 1922, **19**, 354—362).—A proposed structure for aragonite is such that, as in calcite, each carbon atom is linked by double bonds to three oxygen atoms, each oxygen atom to two calcium atoms and one carbon atom, and each calcium atom to six oxygen atoms, at the corners of an irregular octahedron. The observed cleavage of aragonite is in accord with the principles that (a) cleavage tends to occur so as to leave the two new crystal surfaces electrically neutral, (b) where some bonds are weaker than others, cleavage will take place in such a way as to rupture the weaker bonds in preference to the stronger ones, (c) all bonds being equally strong, cleavage will occur between the planes connected by the fewest bonds per unit area. The structure of aragonite, and those of the isomorphous minerals strontianite, witherite, and cerussite, conform to the author's theory that the electron groups in an atomic shell tend to place themselves opposite to the faces of the imaginary polyhedron formed by the electron groups in the next underlying shell. A. A. E.

Dispersoid Chemistry of Gypsum. II. H. NEUGEBAUER (*Kolloid Z.*, 1922, **31**, 40—45).—The viscosity of suspensions of anhydrite, gypsum, burnt gypsum, dehydrated gypsum, anhydrite, and leucolith has been measured at various intervals of time after preparation, with the object of investigating the mechanism of the hydration of calcium sulphate. It is shown that in opposition to the statements of van't Hoff the preparations used in the present work could not be completely dehydrated at 115° or slightly higher. The water of crystallisation was never reduced to less than 4%. The common dihydrate lost its crystal water at 102° considerably more slowly and less completely than the other forms,

probably because of the size of the crystals. The viscosimetric investigation of the commercial "van't Hoff gypsum" gave very indefinite curves, whereas van't Hoff found extremely rapid combination with water and rapid hardening for this material. The formation of soluble anhydrite does not come into the question here. Gypsum prepared by slowly dehydrating precipitated calcium sulphate gave a normal combination curve, and the dihydrate gave curves analogous to those obtained with insufficiently dehydrated gypsum. A commercial product, anhydrite, prepared by the dehydration of natural anhydrite, exhibits, on dehydration, a behaviour analogous to that shown by "van't Hoff gypsum." Its viscosity curve is more pronounced than that of commercial gypsum obtained in the usual way, but less steep than that of precipitated gypsum. Towards the addition of alum it behaves in the same way as plaster of Paris. A further technical product, leucolith, showed no combination with water from its viscosity measurements. The behaviour in this case was analogous to that of estrich gypsum (flooring cement), the setting in these cases being due to the presence of free lime. J. F. S.

The Constitution of Strontium-Lead Alloys. E. PRWOWARSKY (*Z. Metallk.*, 1922, **14**, 300—301).—Lead and strontium form one compound, Pb_3Sr , melting at 676° and containing 12.35% Sr, and a eutectic, containing very small amounts of strontium, which melts at the same temperature as lead. Strontium is completely insoluble in solid lead. [Cf. *J. Soc. Chem. Ind.*, 1922, Sept.] A. R. P.

Barium Sulphuric Acid and Barium Selenic Acid. JULIUS MEYER and WALTER FRIEDRICH (*Z. physikal. Chem.*, 1922, **101**, 498—503).—The solubility of barium sulphate in 97.86% sulphuric acid has been determined at 25° and found to be 14.91 grams in 100 c.c. of acid. The saturated solution is shown to contain barium sulphuric acid, $\text{H}_2[\text{Ba}(\text{SO}_4)_2]$, and by electrolytic transport this compound can be accumulated in the anode compartment, where it crystallises. Dissolving barium selenate in selenic acid gives rise to a similar compound, barium selenic acid, $\text{H}_2[\text{Ba}(\text{SeO}_4)_2]$, which can similarly be crystallised by electrolytic transport. A concentrated solution of selenic acid saturated with barium selenate also deposits crystals of barium selenic acid. J. F. S.

Physical Chemistry of the Oxides of Lead. IV. Red Lead and Lead Sesquioxide. SAMUEL GLASSTONE (*T.*, 1922, **121**, 1456—1469).

Physical Chemistry of the Oxides of Lead. V. The Electromotive Behaviour of Lead Dioxide. SAMUEL GLASSTONE (*T.*, 1922, **121**, 1469—1480).

Behaviour of Sulphides of Heavy Metals in Aqueous Solutions. O. WEIGEL (*Sitzungsber. Ges. Naturw. Marburg*, 1921, No. 2, 35—50; from *Chem. Zentr.*, 1922, i, 182—183; cf. A., 1907, ii, 237).—The known solubilities of heavy metal sulphides

as experimentally determined are generally greatly in excess of the values calculated from their solubility products. The author's determinations of the solubilities of the sulphides of thallium, silver, and lead show that in each case the calculated solubility is less than that determined experimentally. From the effect of lead ions on the solubility of lead sulphide and the potential of a lead sulphide electrode, it is concluded that dissociation in aqueous solution takes place in successive stages and that most of the dissolved substance is in the form of complex ions. Removal of metallic ions by addition of sulphide ions depends on the formation of complex ions.

G. W. R.

The Blue Flame produced by Common Salt on a Coal Fire.

ARTHUR SMITHELLS (*Nature*, 1922, **109**, 745; cf. Merton, *ibid.*, 1922, **109**, 683).—A brief historical note on the recognition of the blue flame produced by common salt on a coal fire as being due to compounds of copper derived from pyrites in the coal.

A. A. E.

The Rate of Combination of Copper and Phosphorus at Various Temperatures. C. A. EDWARDS and A. J. MURPHY (*J. Inst. Metals*, Adv. Copy).—Penetration of copper rods by phosphorus vapour takes place at 640° at atmospheric pressure. The dissociation-temperature curve for alloys of copper and phosphorus containing up to 30.8% of the latter indicates the existence of the phosphides CuP and Cu_5P_2 .

CHEMICAL ABSTRACTS.

Corrosion of Copper by Salt Solutions. W. MÜLLER (*Z. Metallk.*, 1922, **14**, 286—295).—Copper is rapidly corroded by sea water, sodium chloride, and magnesium chloride, with the formation of a green, basic chloride which readily detaches itself from the metal and therefore does not form a protective coating. Weak solutions of magnesium and calcium sulphates corrode copper very slowly, the metal becoming gradually covered with a white precipitate containing bluish-green flakes of basic sulphate. [Cf. *J. Soc. Chem. Ind.*, 1922, Sept.]

A. R. P.

Critical Constants of Mercury. S. WEBER (*K. Danske Videnskab. Selskab. Math.-fys. Medd.*, 1920, **3**, No. 4; cf. A., 1921, ii, 699).—The critical pressure of mercury is 1036 atmospheres. If curves be plotted giving the density of liquid and vapour phases of mercury and hydrogen, the temperature and density being written in terms of the critical temperature and density, the two curves practically coincide. Vapour-pressure curves plotted in a similar manner also coincide, hence it is concluded that hydrogen at this low temperature is monatomic.

CHEMICAL ABSTRACTS.

Atomic Weight of Mercury from Different Sources. J. N. BRÖNSTED and G. HEVESY (*Nature*, 1922, **109**, 780; cf. this vol., ii, 149).—Measurements of the density of mercury prepared by the same method from minerals of different origin exhibit no differences exceeding the possible experimental error, which corre-

sponds with 0.0004—0.0012 in the atomic weight. It is therefore concluded, with great probability, that the isotopic composition of mercury of terrestrial origin is the same. A. A. E.

Catalytic Decomposition of certain Oxides. GUY B. TAYLOR and G. A. HULETT (*J. Amer. Chem. Soc.*, 1922, **44**, 1443—1445).—A theoretical paper in which the authors criticise the conclusions of Kendall and Fuchs (this vol., ii, 147). It is pointed out that in the system $\text{HgO}:\text{Hg}:\text{O}_2$ it is inadmissible to speak of the equilibrium pressure of oxygen at a fixed temperature without specifying the partial pressure of mercury. Further, the grounds on which Kendall and Fuchs maintain that their results are in agreement with those of Lewis (A., 1906, ii, 284) in connexion with the dissociation of silver oxide are considered to require explanation. The conclusions with regard to the decomposition of barium dioxide are also criticised, and it is pointed out that the explanation of the discrepancy between the authors' results (A., 1913, ii, 932) and those of Kendall and Fuchs does not meet the case.

J. F. S.

Catalytic Decomposition of certain Oxides. JAMES KENDALL and FRANCIS J. FUCHS (*J. Amer. Chem. Soc.*, 1922, **44**, 1447—1448).—An answer to the criticisms of Taylor and Hulett (cf. preceding abstract).

J. F. S.

Preparation of Pure Ceria-earth Compounds. R. H. MANSKE (*Can. Chem. Met.*, 1922, **6**, 83—84).—A study of the solubility curves shows that if a saturated solution of the sulphates of cerium (about 50%), lanthanum, praseodymium, and neodymium at 0° is rapidly heated to 41° , the sulphates of lanthanum and neodymium crystallise with cerium sulphate, but free from praseodymium. Separation from cerium is easy. If the saturated solution of the sulphates were heated to 65° , lanthanum would crystallise free from praseodymium and neodymium so long as cerium was present.

CHEMICAL ABSTRACTS.

The Solubility of Gases in Aluminium. J. CZOCHRALSKI (*Z. Metallk.*, 1922, **14**, 277—285).—Molten aluminium absorbs very little of the common gases below 900° , but with increasing temperature above this the amount absorbed and retained in the solid metal at ordinary temperatures increases approximately in the following order: nitrogen, carbon monoxide, air, oxygen, sulphur dioxide, carbon dioxide, illuminating gas, and hydrogen. In general, the gas is retained in the solid metal in numerous microscopic blow-holes, but very small amounts of nitrides, oxides, carbides, and sulphides are formed in atmospheres containing nitrogen, oxygen, carbon, or sulphur compounds. The technical significance of these facts is discussed with reference to the production and working of aluminium. [Cf. *J. Soc. Chem. Ind.*, 1922, Sept.]

A. R. P.

Mordants. II. Alumina. WILDER D. BANCROFT (*J. Physical Chem.*, 1922, **26**, 501—536).—A general discussion on the

hydrolysis of aluminium salts and the adsorption of aluminium sulphate and alumina by wool, silk, and cotton. It is shown that all aluminium salts are hydrolysed to some extent in aqueous solution, and the amount of hydrolysis increases with increasing temperature. The actual hydrolysis is greater with salts of weak acids, but the apparent hydrolysis may be abnormally large in sulphate solutions owing to the coagulating effect of the sulphate ions on the colloidal alumina. Different fibres adsorb alumina to different degrees, wool having a much greater adsorbing power than cotton, and silk being probably slightly inferior to wool. Owing to this difference in specific adsorption, wool decomposes aluminium salt solutions which are distinctly acid, whilst cotton is effective only in more basic solutions. The colloidal alumina is taken up and held firmly. Coagulated alumina may be adsorbed to some extent, but it easily rubs off the material. It is probable that in all cases alumina is adsorbed and not a basic salt. The phenomena may be complicated by the fact that the alumina itself will adsorb some sulphuric acid, for example, and that the wool may, and probably does, adsorb some sulphuric acid also. Since alumina is adsorbed less strongly by cotton than by wool, it is also held less strongly by cotton than by wool. If to cotton is added some substance, such as tannin, which adsorbs alumina strongly, the cotton mordanted with tannin will be able to take alumina out of solutions of aluminium salts which are not decomposed by cotton alone, and alumina is held more strongly by mordanted cotton than by cotton alone. The increase in adsorbing power shown by mercerised cotton is due to structural differences in the cotton fibre. There is no evidence of the formation of any definite compound between alumina and either wool, silk, or cotton.

J. F. S.

Preparation of Metals by Goldschmidt's Aluminothermic Method. I. TÔTARÔ FUJIBAYASHI (*J. Chem. Ind. Japan*, 1922, 25, 499—511).—Pure manganese and chromium free from carbon have been prepared by Goldschmidt's method. For the former, an intimate mixture of trimanganic tetroxide (100 parts), manganese dioxide or sesquioxide (15—20 parts), and 90% of the calculated weight of powdered aluminium was used, the yield being 85—90% of the theoretical value. The product contained 95—97% of manganese, the remainder being mainly aluminium. For the preparation of chromium, an intimate mixture of chromium sesquioxide (100 parts), calcium chromate (10—15 parts), and 90% of the calculated weight of powdered aluminium was used, the yield being 85—92% of the theoretical; the product contained 95—97% of chromium and 3—5% of aluminium.

K. K.

Reducing Action of Ferrous Hydroxide. SUSUMU MIYAMOTO (*J. Chem. Soc. Japan*, 1922, 43, 397—438).—Nitrites or nitrates can be estimated as ammonia by reduction with ferrous hydroxide in alkaline solution. In the case of the nitrite, the sample (0.1—0.3 gram) is boiled with 15 grams of ferrous sulphate and 200 c.c. of saturated alkali hydroxide solution and the evolved

ammonia is passed into sulphuric acid of known concentration as in Kjeldahl's method. Nitrates are not so easily reduced as nitrites, a reflux condenser must be attached to the boiling-flask instead of a bulb, and the boiling continued for three to three and a half hours, a current of hydrogen, nitrogen, or air being introduced into the flask to carry over ammonia. Ferrous hydroxide also reduces nitrobenzene to aniline at the ordinary temperature.

The velocity of reaction between potassium nitrite and ferrous hydroxide in alkaline solution was measured at 25°, 35°, and 45°. When the initial concentration of the nitrite is very small compared with that of the alkali hydroxide, the reaction is linear. The velocity constant increases with the concentration of the alkali hydroxide, and is expressed by the formula: $k = e^{A-B/P}(1+0.79 C_{\text{KOH}})$, where $A=20.609$ and $B=8098.2$. The velocity constant is increased 2.35 times for each elevation of 10° in temperature. The presence of potassium sulphate in the system has no effect on the reaction velocity. Attempts to measure the velocity at the boiling point, 108°, were unsuccessful, the reaction occurring too quickly.

The velocity of reaction between potassium nitrate and ferrous hydroxide in alkaline solution was measured at 108° and 112.2°, the velocity constant being approximately 7.577×10^{-3} (calc. 7.726×10^{-3} ; $C_{\text{KOH}}: 5.5394$ mol. per litre) and 2.331×10^{-2} (calc. 2.326×10^{-2} ; $C_{\text{KOH}}: 6.9541$ mol. per litre respectively).

The electric potentials of the following cells were measured at 25°, using 1*N*-, 2*N*-, 3*N*-, 4*N*-, and 5*N*-sodium hydroxide solutions:

I. Pt. platinised|NaOH, Fe(OH)₂, Fe₃O₄, x H₂O|NaOH|HgO, NaOH|Hg; II. Pt. platinised H₂|NaOH|HgO, NaOH|Hg. III. Pt. platinised|NaOH, Fe(OH)₂, Fe₃O₄, x H₂O|NaOH|NaOH|H₂, Pt. platinised. The potential of I is expressed by $E_1 = 0.8030 - 0.0015 C_{\text{NaOH}}$, that of II by $E_2 = -0.9270 - 0.00332 \log C_{\text{NaOH}}$, that of III by $E_3 = 0.1240 + 0.00332 \log C_{\text{NaOH}} - 0.0015 C_{\text{NaOH}}$. K. K.

A New Iron Salt. OTTO RÖHM (*Collegium*, 1921, No. 614, 282—284).—When a concentrated solution of ferrous sulphate is oxidised with chlorine and the excess of water allowed to evaporate, a crystalline substance having the composition FeSO₄Cl·6H₂O is obtained. This compound, which is neither a mixture nor a double salt, and does not deliquesce in damp air, may also be prepared (a) by heating 1 mol. of ferric chloride, 1 mol. of ferric sulphate, and 18 mols. of water, and (b) by heating 1 mol. of ferric chloride, 1 mol. of sulphuric acid, and 6 mols. of water, and driving off the hydrogen chloride formed. CHEMICAL ABSTRACTS.

I. The Structure of Electrolytically Deposited Nickel. II. The Influence of Superposed Alternating Current on the Deposition and Solution Potential of Nickel. V. KOHLSCHÜTTER and H. SCHÖDL (*Helv. Chim. Acta*, 1922, 5, 490—512, 593—609).—I. Continuing the work of Kohlschütter and Vuilleumier (A., 1919, ii, 9) and Stäger (A., 1920, ii, 728) on the properties of electrolytically deposited nickel, experiments have been made with the object of determining whether there is any relation between

the micro-structure of the deposits and the contraction phenomenon which has been found to depend on the deposition potential. Comparative experiments were made, using direct current and alternatively direct current with a superposed alternating current, which considerably diminishes the observed contraction of the deposit. The previous conclusion was confirmed that, when deposits showing a high contraction are formed, deposition takes place at first in a thin deposit or skin of hydrogen. The same effect can be produced by saturating the electrolyte with carbon dioxide, although to a less extent. When there is free evolution of hydrogen at the cathode, the contraction is slight; the surface of the deposit is bright and metallic, but under the microscope it has a scaly appearance. When the evolution of hydrogen is small, the deposit shows a greater contraction and it has a brown appearance. The inner structures of the different deposits are practically identical when examined microscopically. The size of the particles is from 1.4 to 2.2 μ , the larger particles generally appearing when an alternating current is used. It is concluded therefore that the contraction is purely a surface phenomenon, due to the aggregation of particles, originally deposited in a highly disperse form, into particles of larger size.

Deposits obtained with direct current were brittle, those from sulphate solutions less so than those from chloride; those obtained with alternating current were flexible. There seemed, however, to be no relation between brittleness and the contraction phenomenon. The brittleness is probably due to the presence of hydrogen in the metal.

II. The superposition of the alternating current causes a lowering of the cathode potential more or less parallel with the lessening of the contraction effect in the deposit. A number of observations, however, indicate that the relation is not so close as might appear to be the case between the structure and contraction of the deposit on the one hand and the deposition potential on the other. Since, however, the contraction takes place almost instantaneously, it is not possible to observe the structure of the metal as it is originally deposited with a high cathode potential. There is no doubt that hydrogen is the important factor influencing both the polarisation and the structure of the deposit.

E. H. R.

New Hydrate of Uranyl Nitrate. FRANK E. E. GERMANN (*J. Amer. Chem. Soc.*, 1922, **44**, 1466—1469).—The density of solutions of uranyl nitrate has been determined at 24° for compositions up to 50% and a density curve plotted which exhibits a strong curvature towards the composition axis. Cooling and heating curves have been constructed, and both show the existence of an *icositetrahydrate* of uranyl nitrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 24\text{H}_2\text{O}$. This compound forms spontaneously at -35° and exists only below -20° . The existence of five distinct fluorescence spectra due to uranyl nitrate as stated by Howes (*Physical Rev.*, 1915, **6**, 192) has been disproved. These are due to the hexahydrate, the icositetrahydrate, and various mixtures of the two depending on the concentration and rate of cooling.

J. F. S.

Complex Uranyl Hypophosphites. ARTHUR ROSENHEIM and GERT TREWENDT (*Ber.*, 1922, 55, [B], 1957—1960).—The analogy between sulphites and hypophosphites is illustrated further by the isolation of alkali uranyl hypophosphites which correspond in their composition with the alkali uranyl sulphites, $R_2[(UO_2)_2(SO_3)_3]$ and $R_2[(UO_2)_4(SO_3)_5] \cdot xH_2O$, described by Kohlschütter (*A.*, 1900, ii, 484).

Uranyl hypophosphite, $UO_2(H_2PO_2)_2$, microcrystalline, yellow prisms, is prepared by agitating solutions of one molecular proportion of uranyl nitrate and four molecular proportions of sodium hypophosphite (a microcrystalline, pale yellow *trihydrate* is also described); it is almost insoluble in water, but readily soluble in an excess of sodium hypophosphite or uranyl nitrate solution. It is transformed by a solution of sodium hypophosphite (4 molecular proportions) into the *salt*, $Na[(UO_2)_2(H_2PO_2)_5] \cdot 4.5H_2O$, slender, pale yellow needles (a *hexahydrate* is also described); the corresponding anhydrous *potassium* salt, yellow crusts, and *ammonium* salt, pale yellow leaflets, and the *dihydrated guanidinium* salt, aggregates of needles, were analysed. Uranyl hypophosphite is converted by six to eight molecular proportions of sodium hypophosphite into the *salt*, $Na[(UO_2)_2(H_2PO_2)_2] \cdot 3.5H_2O$, large, rectangular plates (the *pentahydrate* is also described). Attempts to prepare corresponding compounds with other alkali hypophosphites yielded salts of the series $R[(UO_2)_2(H_2PO_2)_5]$. The compounds from uranyl hypophosphite and ten or more molecular proportions of alkali hypophosphite could not be caused to crystallise. H. W.

The Isotopes of Tin. F. W. ASTON (*Nature*, 1922, 109, 813).—An immediate result of the application of a method for increasing the sensitivity of photographic plates towards positive rays has been the definite proof of the complex nature of tin (cf. *A.*, 1921, ii, 474). By using tin tetramethyl, eight lines corresponding approximately with atomic weights 120, 118, 116, 124, 119, 117, 122, 121 (in decreasing order of intensity) were definitely proved to be due to tin. The average atomic weight, in proportion to the intensities, agrees well with the accepted value. It is remarkable that the differences between the lines are integral to the highest accuracy, but the lines themselves compared with known lines give atomic weights always tending to be 2 or 3 parts per 1000 too light for the above whole numbers. It is strongly indicated that this divergence cannot be due to experimental error. The presence of the two faint components of xenon 128 and 130 previously suspected has now been confirmed. A. A. E.

Complex Mixed Antimony Iodobromides. A.-CH. VOURNAZOS (*Compt. rend.*, 1922, 175, 164—167).—An acid containing the complex anion $-SbI_3Br$ is obtained by the action of dry gaseous hydrogen bromide on antimony tri-iodide in a non-aqueous medium such as glacial acetic acid. It cannot be isolated in a solid state by the evaporation of the acetic acid solution, as, owing to dissociation, only a residue of the tri-iodide remains. The salts

of this acid are, however, obtained in crystalline form by triturating and finally warming equimolecular proportions of antimony triiodide and a bromide with a suitable non-aqueous medium, acetic acid, xylene, etc. The compounds form coloured crystals, which are rapidly decomposed by water or ethyl alcohol, giving antimonious oxide, hydriodic acid, and the metallic bromide. *Sodium antimoniodobromide*, SbBrI_3Na , prepared in xylene, forms small, orange-yellow crystals. *Potassium antimoniodobromide*, SbBrI_3K , is similar in colour, but the *ammonium* and *lithium* salts are reddish yellow. *Zinc antimoniodobromide*, $\text{ZnSbI}_3\text{Br}_2$, forms brown, tabular crystals, which are fairly stable and only slowly decomposed by water.

G. F. M.

Mineralogical Chemistry.

Haloos and Earth-history. A New Radioactive Element. J. JOLY (*Nature*, 1922, **109**, 517—518 and 578—579).—A description of colourless, spherical, halo-like forms, of average diameter 0.0104 mm., occurring in the Archæan black mica of Ytterby. It is suggested that they may be due to a radioactive element (for which the name “hibernium” is suggested) having an α -ray range in air of 1—1.5 cm. A. A. E.

The Crystal Structures of Marcasite (FeS_2), Arsenopyrite (FeAsS), and Loellingite (FeAs_2). MAURICE L. HUGGINS (*Physical Rev.*, 1922, **19**, 369—373).—Arsenopyrite and loellingite are assumed to have the same general arrangement as marcasite, in which the sulphur atoms are considered to be in pairs, each sulphur atom being linked, by pairs of electrons, to one sulphur and four iron atoms, and each iron atom to six sulphur atoms. A. A. E.

Minerals from near Oudjda, Morocco. J. BARTHOUX (*Compt. rend.*, 1922, **175**, 312—314).—An account is given of crystallised minerals (galena, vanadinite, pyromorphite, wulfenite, cerussite, dolomite, calcite, and aragonite) from a lead mine in dolomitic limestone at Gebel Mahser. L. J. S.

Babingtonite from Japan. MANJIRÔ WATANABÉ (*Amer. J. Sci.*, 1922, [v], **4**, 159—164).—Babingtonite occurs with hedenbergite, garnet, chalcopyrite, magnetite, etc., in a metamorphic contact in the Yakuki mine, province Iwaki. A crystallographic and optical description is given of the material. L. J. S.

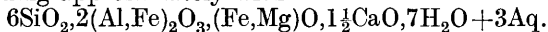
Composition of Aerinite. J. ORCEL (*Compt. rend.*, 1922, **175**, 309—311).—Aerinite from Casserras, Huesca, prov. Aragon, consists of a mixture of a blue, transparent, strongly pleochroic mineral with pyroxene, quartz, and spinel. The first is easily separated

by reason of its ready solubility in acids. Analysis of hydrochloric acid solution gave :

SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	MgO.	MnO.	CaO.	SrO.
39.26	0.49	19.80	7.13	1.35	3.52	0.03	9.08	0.20

P ₂ O ₅ .	V.	Alkalis.	H ₂ O (at 106°).	H ₂ O (at 400°).	H ₂ O (400° to 1100°).	Total.
0.07	trace	trace	5.43	11.03	2.92	100.31

corresponding approximately with



The mineral represents a new calcium-bearing type of the leptochlorites; this is supported by optical characters and its behaviour when heated. Spectroscopic analysis shows that the strontium and vanadium are present only in the hydrochloric acid extract of the mineral. The cause of the blue colour is discussed; it is regarded to be dependent on the molecular structure.

L. J. S.

Analytical Chemistry.

Nephelometry of Coloured Hydrosols. H. BECHHOLD and F. HEBLER (*Kolloid Z.*, 1922, **31**, 7—12).—In the nephelometric investigation of white turbidities it has been repeatedly shown that a strict proportionality exists between the concentration of the substance causing the turbidity and the amount of diffracted light, provided that no change occurs in the original substance. It is now shown that in the case of coloured sols and turbidities very marked deviations from this proportionality occur. Concentrated coloured sols such as colloidal indigotin and silver behave in comparison with dilute solutions as though they were less concentrated. This is shown to be due to the absorption of light by the coloured particles forming the turbidity. This action in the case of white particles is not great, but in that of coloured particles it is very strong. The disproportionality in the absorption is caused particularly by those wave-lengths which are absorbed by the turbid medium to a larger or smaller extent. This selective absorption must therefore be removed by the use of suitable light filters. The most efficient filters are shown to be isochromatic filters, that is thin layers composed of the substance under investigation. These filters may be employed either as solutions or as dry gelatin films between the source of light and the nephelometer. In this way it is possible to investigate nephelometrically coloured turbidities and coloured hydrosols in exactly the same way as colourless turbidities, and in these circumstances they show exactly the same proportionality between concentration and amount of diffracted light as white turbidities.

J. F. S.

Investigation, by Means of the Hydrogen Electrode, of the Chemical Reactions involved in Water Purification.

R. E. GREENFIELD and A. M. BUSWELL (*J. Amer. Chem. Soc.*, 1922, **44**, 1435—1442).—Titration curves have been prepared, using the hydrogen electrode, for the neutralisation of the carbonates of sodium, magnesium, and calcium with a strong acid. It is shown that the shape and position of the curve are unaffected by the metallic ion, but that the inflection point occurs at a slightly higher Sørensen value in dilute solutions than in the more concentrated solutions. Precipitation curves of the precipitation of magnesium hydroxide have been plotted, and these show that the precipitation of magnesium is complete at a Sørensen value in the neighbourhood of $P_H=10.6$. Magnesium hydroxide does not form until the value is as high as $P_H=9.0$. Precipitation curves for the precipitation of calcium as carbonate, whilst not as regular as those obtained in the case of magnesium, tend to show that the reaction is complete, sufficient carbonate being present at $P_H=9.5$. Aluminium hydroxide is shown to start precipitating in solutions as acid as $P_H=4$, and to be completely precipitated at $P_H=6.5-7.5$. At values much higher than this, resolution commenced to take place, and this was complete at a value between $P_H=10$ and $P_H=11$. The precipitation reactions were not instantaneous, but took several hours to reach completion. This was the more noticeable the more dilute the solution. J. F. S.

Sodium Sulphide as a Substitute for Hydrogen Sulphide in Qualitative Analysis. GIORGIO VORTMANN (*Boll. Sci. tecn.* **3**, No. 5; *Giorn. Chim. Ind. Appl.*, 1921, **3**, 565).—A solution in hydrochloric acid is oxidised, treated with solid sodium carbonate in slight excess, warmed with sodium hydroxide solution (boiled to remove ammonia if necessary), and precipitated with excess of a 20% solution of sodium sulphide. The precipitate (i) may contain silver, copper, bismuth, cadmium, lead, iron, cobalt, nickel, manganese, and zinc as sulphides; uranium, chromium, and rare earths as hydroxides; barium, strontium, calcium, and magnesium as carbonates; whereas the filtrate (i) may contain the sulphides of mercury, nickel, arsenic, antimony, tin, gold, platinum, molybdenum, tungsten, and vanadium. On treatment of the precipitate (i) with dilute hydrochloric acid, iron, manganese, zinc, uranium, chromium, barium, strontium, calcium, magnesium (phosphate), lithium, and rare earths pass into solution (ii), whilst silver, copper, bismuth, cadmium, lead, cobalt, and nickel remain undissolved (ii). Solution (ii) is boiled to remove hydrogen sulphide, and bromine water is then added, followed by sodium carbonate in excess. The filtrate (iii) may contain chromium, uranium, and manganese, whilst the precipitate (iii) contains iron, manganese, zinc, barium, strontium, calcium, magnesium, and lithium. After redissolution of the precipitate (iii) in hydrochloric acid, iron is precipitated with sodium acetate, manganese with ammonium hydroxide and bromine water, barium, strontium, and calcium with ammonium carbonate, the zinc in the filtrate with sodium sulphide, and finally the magnesium

and lithium. The filtrate (i) is boiled with ammonium chloride to precipitate mercury, nickel, and aluminium, whilst antimony, tin, arsenic, molybdenum, tungsten, and vanadium remaining in solution can be separated by known methods. The alkali metals are tested for in another portion of the substance.

CHEMICAL ABSTRACTS.

Titration of Acids and Bases. J. L. LIZIUS and N. EVERS (*Analyst*, 1922, **47**, 331—341).—The theory of titration and the dependence of the hydrogen-ion concentration of the end-product on the nature of the salt formed is explained. A list of newer indicators with their colour changes and the P_H range over which they are applicable is given, and four mixed indicators are suggested. A table of common titrations with the hydrogen-ion concentrations at their end-points, suitable indicators, and the colours obtained at their end-points is also given. By titrating to a definite shade of colour instead of to the colour-change of the indicator, an increase in the accuracy of titrations results, and certain titrations are made possible which are impracticable by ordinary methods.

H. C. R.

Symmetrical Diphenylguanidine as a Standard in Acidimetry and Alkalimetry. C. A. CARLTON (*J. Amer. Chem. Soc.*, 1922, **44**, 1469—1474).—The suitability of symmetrical diphenylguanidine as a standard in acidimetry and alkalimetry has been investigated. It is shown that this substance can easily be obtained in a sufficiently high state of purity for the present purpose by three recrystallisations of the crude material from toluene. The pure compound is stable in air and soluble in alcohol. It may be titrated directly in cold solutions with either an alcoholic or an aqueous solution of hydrochloric acid, using either bromophenyl-blue or methyl-red as indicator. The results obtained with this substance are comparable with those obtained with sodium carbonate or silver chloride, and diphenylguanidine is more convenient in use. Diphenylguanidine is the only basic substance, proposed as a standard, which meets all the requirements of an ideal standard.

J. F. S.

Micro-incineration. A. SCHOELLER (*Ber.*, 1922, **55**, [B], 2191—2192).—The substance under investigation is spread evenly over a thin strip of glass (5—6 mm. wide) which is placed in a horizontal hard glass tube about 10 mm. in diameter and 12 cm. long. The tube is heated very gently until all volatile matter is expelled. The residue is allowed to cool and is subsequently heated rather more strongly in a current of moist oxygen; in most cases, the carbon disappears rapidly without at any time glowing. With difficultly combustible substances it is advisable to interrupt the heating again. Too powerful ignition is to be avoided. The minutest trace of ash is readily visible under the microscope. The method is particularly suitable for the incineration of sections of plant-tissue, since the original structure is better preserved than when they are heated over a free flame.

H. W.

The Estimation of Hydrogen and its Separation from Gaseous Paraffins by means of Palladious Chloride. J. A. MULLER and A. FOIX (*Bull. Soc. chim.*, 1922, [iv], **33**, 713—717).—Hydrogen may be separated from gaseous paraffins and estimated by its reducing action on excess of palladious chloride. The precipitated palladium is dried and weighed, and hence the quantity of hydrogen is calculated. A correction should be made for the small quantity of the gas occluded in the metal; the authors state that 1 mg. of palladium represents 0.24 c.c. of hydrogen measured at 0° and 760 mm. when the reaction takes place under the prescribed conditions.
H. J. E.

Electrometric Titrations with Mercury Perchlorate. I. M. KOLTHOFF (*Z. anal. Chem.*, 1922, **61**, 332—343).—Chlorides, bromides, or iodides may be titrated with mercury perchlorate solution, the end-point of the titration being determined with accuracy by electrometric means even in very dilute solutions, but the method cannot be applied to mixtures of these salts. The method is also trustworthy in the case of thiocyanates, cyanides, ferrocyanides, formates, acetates, monochloroacetates, lactates, benzoates, and salicylates, but it cannot be used for trichloroacetates owing to the ready hydrolysis of the mercury compound, or for the salts of polybasic aliphatic acids. The mercury perchlorate solution is prepared by saturating perchloric acid with mercuric oxide.
W. P. S.

Detection of Fluorine. B. FETKENHEUER (*Wiss. Veröffentl. Siemens-Konzern*, 1922, **1**, [3], 177).—The substance is heated with sand and a few c.c. of sulphuric acid at 90° in a test-tube. On shaking the tube, the presence of fluorine is shown by the acid collecting into oily drops, which appear not to wet the surface of the glass. With 2 grams of substance, 0.01% of fluorine may be detected after heating for one minute. Insoluble fluorides such as aluminium fluoride must first be fused with sodium carbonate and sand; the fused mass is then heated as above with sulphuric acid.
A. R. P.

The Colour of Iodine Solutions at Low Temperature. JEAN PICCARD and E. HERRMANN (*Helv. Chim. Acta*, 1922, **5**, 625—626).—The brown colour formed by iodine in solvents containing oxygen has been suggested as a qualitative test for oxygen (this vol., ii, 389), in absence of other elements or groups of an unsaturated character such as tervalent nitrogen. It has been observed that very dilute solutions of iodine in hydrocarbons such as light petroleum, which are violet at the ordinary temperature, become brown at lower temperatures, in the neighbourhood of -20°. When the iodine concentration is increased beyond a certain value, about 1 mg. in 10 c.c., however, the colour change does not take place. It is shown that the brown colour is due to an impurity in the commercial light petroleum, and that it does not appear with carefully purified specimens. The phenomenon can be reproduced by addition of a small quantity of alcohol to

the pure light petroleum, or to toluene, chloroform, and other solvents.

E. H. R.

Rapid Estimation of Sulphur. LUIGI LOSANA (*Giorn. Chim. Ind. Appl.*, 1922, 4, 297—299).—The method previously described (this vol., ii, 582) gives accurate results with pyrites, copper pyrites, and other mineral sulphides, ultramarine, adulterated white lead, cement, various rocks, sulphates of copper, sodium, etc., naphtha, anthracene, coke, ichthyol, "saccharin," ebonite, and caoutchouc.

T. H. P.

Determination of Sulphur in Vulcanised Rubber. J. W. W. DYER and AMY R. WATSON (*J. Soc. Chem. Ind.*, 1922, 41, 251—252).—Methods are described for the estimation of free and combined sulphur in vulcanised rubber. These are as follows. (a) Combined sulphur. The sample (0.5—3.0 grams) is added to 30—40 c.c. of nitric acid (d 1.42) in a suitable flask and the reaction started by gentle heating; subsequently the mixture is heated to the boiling point and boiling continued until the liquid is clear. Pure powdered potassium permanganate is now added, about 0.25—0.5 gram at a time, and the heating continued between additions. The addition of permanganate is continued until finally a small black precipitate remains; this requires generally about 2 grams of permanganate. The contents of the flask are poured into a dish and evaporated to dryness, taken up with 10 c.c. of concentrated hydrochloric acid, and again evaporated to dryness. The residue is treated with water, made up to 100 c.c., and made just acid to methyl-orange at the boiling point. The sulphur is then precipitated as barium sulphate. (b) Free sulphur. To 50—60 c.c. of acetone, 0.5—1 gram of material is added and the free sulphur extracted. To the extract 0.5—1 gram of powdered permanganate is added, the mixture shaken, and kept at the ordinary temperature for thirty minutes. If the purple colour disappears a little more permanganate is added. The acetone is then distilled off on the water-bath and the brown residue heated at 100—110° for a short time. About 3—5 c.c. of hydrochloric acid (d 1.16) is added for each gram of permanganate used, and the solution heated until colourless. It is then diluted a little and filtered, the filtrate is made up to 100 c.c., and ammonia cautiously added until the solution becomes yellow and slightly turbid. It is then made just acid and precipitated while boiling with 4—5 c.c. of $N/2$ -barium chloride solution. Both methods give results which are in good agreement with those obtained by the Carius method.

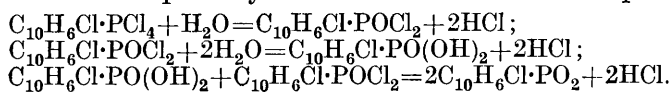
J. F. S.

Quantitative Micro-analysis of Mixtures with Special Reference to Organic Ultimate Analysis. A. BENEDETTI-PICHLER (*Z. anal. Chem.*, 1922, 61, 305—331).—The author describes the advantages of micro-chemical methods, points out the importance of obtaining representative samples in dealing with very small quantities of substances, and gives instances of the application of the methods and their limits of accuracy.

W. P. S.

Volumetric Estimation of Carbon and Hydrogen in Organic Compounds. JOSEF LINDNER (*Ber.*, 1922, 55, [B], 2025—2031).—The substance is burnt in the usual manner and the products of its combustion are passed over a substance which by its hydrolysis gives hydrogen chloride and thence into a known volume of standard barium hydroxide solution. The latter is titrated with *N*/10-hydrochloric acid in the presence of phenolphthalein; the carbon dioxide is subsequently removed after addition of an excess of hydrochloric acid and the resulting solution is again titrated with barium hydroxide. With *N*/10-solutions and burettes of 50 c.c. capacity, the analysis is conveniently performed with 20 mg. of material.

The most suitable substance for hydrolysis is chloronaphthylxy-chlorophosphine, which may contain chloronaphthyltetrachlorophosphine: it is decomposed by water in accordance with the equations:



It is prepared by passing chlorine into molten naphthylidichlorophosphine until three atomic proportions of the gas have been absorbed. It is not a well-defined individual. Hydrogen chloride is freely and quantitatively evolved when a current of moist air is passed through the molten material. It is, however, convenient to depress its melting point to some extent by a preliminary regulated treatment with moist air. The material prepared in this manner somewhat readily evolves considerable amounts of readily volatile acid products, which must be removed by protracted exposure to a current of dry air; the elimination of acid is thereby ultimately reduced to a small amount, for which a correction can be applied, but the presence of the acid has the drawback that the sharpness of the end-point in the ultimate titration is diminished.

Test analyses show that the method gives accurate results, which, however, are somewhat low for hydrogen, the source of error most probably lying in the uncertainty of the correction for the acidic products evolved spontaneously from the phosphorus compound.

H. W.

Absorption of Carbon Monoxide by Acid Cuprous Chloride Solution in the Presence of a Reducing Agent. ALFRED KROPP (*Z. angew. Chem.*, 1922, 35, 451—452).—The rate of absorption of carbon monoxide by acid cuprous chloride solution is increased by the addition of stannous chloride to the solution. The stability of the solution is improved by the use of a slight excess of stannous chloride (cf. Krauskopf and Purdy, *A.*, 1920, ii, 267).

J. S. G. T.

Comparison of Colorimetric and Electrometric Estimations of Hydrogen-ion Concentrations in Solutions containing Carbon Dioxide. GLENN E. CULLEN and A. BAIRD HASTINGS (*J. Biol. Chem.*, 1922, 52, 517—520).—Contrary to the

results obtained by Evans (A., 1921, ii, 271), the colorimetric and electrometric methods for the estimation of the hydrogen-ion concentration of solutions containing carbon dioxide yield identical results, provided precautions are taken to prevent the loss of carbon dioxide. E. S.

Estimation of Small Amounts of Potassium by the Lindo-Gladding Method. WILLIAM HAZEN (*J. Assoc. Off. Agric. Chem.*, 1922, 5, 456—460).—In the estimation of potassium by the Lindo-Gladding method, the use of 90% alcohol for washing gives better results than 80% alcohol, and when working with small amounts of potassium salts and high accuracy is desired, it is advisable to use the stronger alcohol for washing after the ammonium chloride treatment as well. The lower results obtained by using the weaker alcohol do not appear to be due to the sodium salts which may be present, as has been suggested, as equally low results are obtained in the absence of sodium salts. As, however, it takes a longer time to wash out the ammonium salts with 90% alcohol, it is preferable to use 80% alcohol for the second washing in ordinary fertiliser work, where the percentage error arising from this will not be very serious, as the samples generally contain relatively high amounts of potassium. G. F. M.

Identification of Cæsium and Rubidium. JOHN MISSENDEN (*Chem. News*, 1922, 124, 362).—The spectroscope affords the best means of distinguishing cæsium from rubidium; the former shows two bright blue lines (4557 and 4592) in the blue portion of the spectrum, whilst rubidium has two lines (4200 and 4237) in the violet and two other lines (7953 and 7810) in the red. The salts of the two metals resemble each other generally, but there is a considerable difference in the solubility of the two nitrates; 100 parts of water at 3·35° dissolve 11 parts of cæsium nitrate and 79·9 parts of rubidium nitrate. W. P. S.

Hydrotimetric Precision and Aqueous Preparation of the Standard Soap Solution. ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1922, 26, 18—21).—Clark's method as modified by Boutron and Boudet is used, but a standard soap solution of only one-tenth the strength is recommended. It is prepared by dissolving 3·5 grams of white Marseilles soap in 200 c.c. of boiling water and then making the volume up to 900 c.c. This solution is diluted, if necessary, until 24 c.c. of it corresponds exactly with 40 c.c. of a 0·025% solution of calcium chloride or of a 0·059% solution of barium nitrate. W. G.

Estimation of Calcium in Natural Phosphates. R. MEURICE (*Ann. Chim. Analyt.*, 1922, [ii], 4, 198).—The phosphate is treated with mineral acid, the silica removed, and iron and aluminium removed as phosphates. The filtrate is neutralised with ammonia, treated with 20 c.c. of 20% hydrochloric acid, and 30 c.c. of 4% ammonium oxalate. The solution is warmed and 10% ammonium acetate solution added at a rate of about 30 drops per minute. A granular precipitate of calcium oxalate

is thus obtained, and is collected, washed, and ignited as usual. Test analyses carried out on known quantities of calcium in the presence of large excess of phosphate and magnesium sulphate gave very accurate results. H. C. R.

Estimation of Magnesium and Alkalis in Minerals. L. H. BORGSTRÖM (*Hyllningsskrift tillägnad Ossian Aschan*, 1920, 118—123).—The precipitation of magnesium hydroxide is best effected with piperidine, a little of which should also be added to the washing water. Lawrence Smith's method for the separation of magnesium from alkalis in silicate analysis is the most satisfactory.

CHEMICAL ABSTRACTS.

Colorimetric Method for the Estimation of Small Amounts of Magnesium. A. P. BRIGGS (*J. Biol. Chem.*, 1922, **52**, 349—355).—The method described is similar to that of Hammett and Adams (cf. this vol., ii, 587). E. S.

Estimation of Magnesium in Blood, Plasma, and Serum. W. DENIS (*J. Biol. Chem.*, 1922, **52**, 411—415).—The method is essentially the same as that of Briggs (preceding abstract) and of Hammett and Adams (this vol., ii, 587). E. S.

Magnesium Compound of 8-Hydroxyquinoline. CARL TH. MÖRNER (*Pharm. Zentr.-h.*, 1922, **63**, 399—402; cf. Griebel, A., 1921, ii, 606).—If an aqueous solution of 8-hydroxyquinoline (sulphate) is treated with a suspension of magnesium hydroxide, the latter goes into solution and a lustrous, sulphur-yellow precipitate of the magnesium compound of 8-hydroxyquinoline is formed. The precipitate is also given by "magnesia mixture." The precipitate is microcrystalline and consists of hexagonal platelets. The reaction takes place only in alkaline solution and is sufficiently sensitive to detect 1 part of magnesium in 25,000. The precipitate contains 6.25—6.29% of magnesium and approximates to the formula $(C_9H_6ON)_2Mg \cdot 4H_2O$. The compound is also formed by the action of 8-hydroxyquinoline on magnesium ammonium phosphate. The reaction thus permits the separation of magnesium from phosphate in ammoniacal solution. Its use as a dry antiseptic is suggested. G. W. R.

Lead. I. Estimation of Minute Amounts of Lead in Biological Material. L. T. FAIRHALL (*J. Ind. Hyg.*, 1922, **4**, 9—20).—The ash is dissolved in dilute hydrochloric acid, the solution neutralised to methyl-orange with sodium hydroxide, and then slightly acidified with hydrochloric acid. Lead is precipitated as sulphide, the washed precipitate dissolved in 2—5 c.c. of concentrated nitric acid, and boiled to expel hydrogen sulphide. After neutralising with sodium hydroxide and slightly acidifying with acetic acid, an excess of potassium chromate is added, and the solution boiled. The precipitate is dissolved in hydrochloric acid, and an excess of potassium iodide is added to the solution, which is titrated with 0.005*N*-sodium thiosulphate solution. For biological materials, the method appears to be accurate to $\pm 3\%$.

CHEMICAL ABSTRACTS.

Colorimetric Estimation of Manganese in Steels, Alloys, and Ores. J. HESLINGA (*Chem. Weekblad*, 1922, 19, 302—303).—The ordinary method of oxidising to permanganate in acid solution is unsatisfactory when iron is present, because of the yellow colour of iron salts. A simple and accurate estimation may be made by employing the compound H_2MnO_3 , which in alkaline solution gives a yellowish-brown to dark brown coloration.

One hundred to 200 mg. of material are dissolved in a suitable acid, and the solution is diluted and treated with excess of powdered zinc oxide, made up to 100—200 c.c., and filtered. The zinc oxide precipitates the trivalent metals and copper completely after a few minutes' shaking at the ordinary temperature. The filtered solution is poured into a burette, and allowed to fall into a solution containing hydrogen peroxide (3%) and excess of potassium hydroxide (10%) until a suitable colour is obtained; this is matched by means of a standard manganese solution. Several titrations are carried out in succession, adding more of the unknown solution, and matching the colour by means of the standard. Addition of only 0.02 mg. of manganese is easily detected.

Lead does not interfere if excess of potassium hydroxide is employed; if nickel and/or cobalt are present, potassium cyanide is added during the titration. Accurate results are readily obtained when the manganese content is not greater than 20%. S. I. L.

Estimation of Chromium in Metals. WILLI LÖFFELBEIN (*Chem. Ztg.*, 1922, 46, 679).—Chromium is estimated in nickel bronzes and similar alloys by removing the heavy metals from a solution of the alloy with hydrogen sulphide, treating the oxidised filtrate with a slight excess of ammonia, collecting, igniting, and fusing the precipitate with sodium peroxide, acidifying the filtered solution of the melt with hydrochloric acid, adding potassium iodide, and titrating the liberated iodine with sodium thiosulphate solution. A. R. P.

Rapid Method for the Estimation of Chromium in Nickel-Chromium Steel. WILHELM HILD (*Chem. Ztg.*, 1922, 46, 702—703).—The chromium is oxidised to chromic acid in a sulphuric acid solution of the steel by means of potassium permanganate, the excess of which is destroyed with manganese sulphate. The chromic acid is then estimated by addition of an excess of standard ferrous sulphate solution and titration with permanganate or dichromate [cf. *J. Soc. Chem. Ind.*, 1922, 41, 671A.] A. R. P.

Estimation of Small Amounts of Molybdenum in Tungsten. DOROTHY HALL (*J. Amer. Chem. Soc.*, 1922, 44, 1462—1465).—Small amounts of molybdenum may be estimated in tungsten by converting the molybdenum into xanthate, extracting this with chloroform, and converting into sulphide and oxide. The method consists in dissolving 1 gram of the sample in a mixture of nitric and hydrofluoric acids and evaporating with sulphuric acid. The yellow oxides are dissolved in sodium hydroxide solution and trans-

ferred to a 200 c.c. separating funnel, acidified with sulphuric acid, and the solution diluted so that 1 c.c. contains about 0.1 mg. of molybdenum. The volume is then made up to 150 c.c., 0.5 gram of potassium xanthate and a few drops of 1 : 3-sulphuric acid are added and the mixture is shaken thoroughly. About 10 c.c. of chloroform are then added and the whole is shaken for several minutes. The highly-coloured chloroform layer settles at the bottom and is run into a second funnel for washing. The original solution is repeatedly treated with potassium xanthate, acid, and chloroform until the chloroform layer is colourless, each portion of chloroform solution being added to the first. The chloroform solution of molybdenum xanthate is washed with water several times, run into a 150 c.c. beaker, and evaporated to dryness. The residue is heated and converted into a mixture of oxide and sulphide. This is dissolved in nitric acid, evaporated with sulphuric acid, and precipitated as molybdenum sulphide by passing hydrogen sulphide into the hot molybdenum solution made alkaline with sodium hydroxide. The solution is then slowly acidified with dilute sulphuric acid and the precipitate filtered, washed with hot water, and carefully ignited to oxide. The results are easily reproducible and trustworthy, and the method is good for mixtures containing small amounts of molybdenum. J. F. S.

Rapid Analysis of Ferro-tungsten. LUIGI LOSANA and ENRICO CAROZZI (*Giorn. Chim. Ind. Appl.*, 1922, 4, 299—301).—Ferro-tungsten is readily dissolved in 50% nitric acid solution containing a little hydrofluoric acid, subsequent treatment with concentrated sulphuric acid resulting in the elimination of the hydrofluoric acid and precipitation of the tungsten as tungsten trioxide, which may be either weighed as such or estimated volumetrically (cf. *J. Soc. Chem. Ind.*, 1922, 41, 671A). T. H. P.

Electrometric Titration of Uranium with Potassium Permanganate and Potassium Dichromate. D. T. EWING and E. F. ELDRIDGE (*J. Amer. Chem. Soc.*, 1922, 44, 1484—1489).—When solutions of uranyl sulphate, reduced with zinc, are titrated electrometrically with potassium permanganate or when solutions of uranium chlorides similarly reduced are titrated with potassium dichromate, a change in the oxidation potential occurs when the tervalent uranium is all oxidised to the quadrivalent condition, and a second change occurs when the latter is all oxidised to the hexavalent condition. Thus the total amount of uranium may be calculated. A third change of potential is observed when iron is present, and this represents the point where all the ferrous iron is converted into ferric iron. The determination is carried out with apparatus of the usual type, except in the form of the titration vessel, since it is necessary to prevent the free access of air. The titration cell is a glass vessel fitted with a cover which has six holes bored in it. Through the holes pass a tube for leading in carbon dioxide, a platinum electrode, the connecting tube of a calomel cell, a stirrer fitted with a mercury seal, the tip of the burette, and the mouth of a Jones reductor. All the tubes passing

through the cover are fitted tightly. The method of procedure adopted is as follows: (a) *Estimation of uranium by permanganate.* Ten c.c. of a solution of uranium as sulphate (containing about 0.013 gram U_3O_8 per c.c.) are added to 40 c.c. of sulphuric acid solution A (2 c.c. conc. acid, 88 water) and warmed at 80–90°. Carbon dioxide is passed through the titration cell to remove the air, and the uranium solution slowly passed through the Jones reductor into the cell, the reductor being finally rinsed with 50 c.c. of sulphuric acid A. The final solution at this stage has a volume of 100 c.c., contains 2 c.c. of concentrated sulphuric acid, and is brown. The stirrer is set in motion and the permanganate slowly added. The *E.M.F.* rises slowly at first and then jumps to a steady value which represents the point at which all the tervalent uranium has been converted into the quadrivalent condition and the solution has become green. Continued addition of permanganate does not affect the *E.M.F.* noticeably until the second end-point is reached, and here the *E.M.F.* jumps rapidly. At this point, the whole of the quadrivalent uranium has been converted into the sexavalent condition. The volume of permanganate used between the first and second end-points is equal to the theoretical amount of oxidising agent required to oxidise uranium from the quadrivalent to the sexavalent condition. Hence from this quantity the total amount of uranium present, no matter what its state of oxidation provided that none of it is sexavalent, can be calculated. (b) *Estimation of uranium and iron with permanganate.* The process is carried out as above; the first and second end-points give, as before, the quantity of uranium. After the uranium has all been oxidised to the sexavalent condition, the oxidation of the ferrous iron commences and when this has been completed the third end-point is observed. Hence the volume of permanganate required to carry the *E.M.F.* from the second to the third end-point is equivalent to the amount of iron present. (c) *Estimation of uranium by dichromate.* The process is carried out exactly as in the first case, and two end-points are obtained which have the same significance as in the other cases, but the slope of the second end-point is not so clear as in the other cases. All methods yield excellent results.

J. F. S.

The Estimation of Small Quantities of Gold as Colloidal Gold by the Colorimetric Method. J. A. MULLER and A. FOIX (*Bull. Soc. chim.*, 1922, [iv], 33, 717–720).—Small quantities of gold may be rapidly and accurately estimated colorimetrically after separation from other metals, provided that the concentration of the gold is not greater than 1/40 mg. per c.c., and that the colloidal particles are of the same size in the two solutions to be compared. The latter condition is realised by precipitation in identical circumstances. The presence of vanadium leads to inaccurate results.

H. J. E.

Separation of Palladium and Platinum by means of Dimethylglyoxime. C. W. DAVIS (*U.S. Bur. Mines, Repts. Investigations*, 1922, No. 2351).—The weighed metals are dis-

solved in a little aqua regia, the solution is evaporated to dryness, the residue moistened with a drop of hydrochloric acid, diluted with cold water, and dimethylglyoxime added with constant stirring until no further precipitate is formed. After keeping for a few minutes, the voluminous precipitate is collected on a filter, well washed with cold water, and ignited, first in air and finally in hydrogen to obtain pure palladium. The method was tested with quantities of each metal ranging from 0.15 to 11 mg., and the greatest divergence in five analyses was 0.03 mg.

CHEMICAL ABSTRACTS.

A Micro-modification of Benedict's Method for the Estimation of Reducing Sugar in Urine. MILLARD SMITH (*J. Lab. Clin. Med.*, 1922, 7, 364—368).—The modification, like the original method, is applicable only to urines containing not less than 0.17% of sugar. Exactly 1.0 c.c. of Benedict's solution is run from a pipette into a special test-tube, 0.2—0.7 gram of anhydrous sodium carbonate is added, and a pebble or piece of quartz. Urine is slowly added to the mixture, maintained at the boiling point, from a Mohr pipette, graduated to read directly the percentage of sugar present.

CHEMICAL ABSTRACTS.

Critical Study of Bang's Method for the Estimation of Reducing Substances in Blood. HENRI LABBÉ, F. NEPVEUX, and MÉNÉLAS NOMIDIS (*J. Pharm. Chim.*, 1922, [vii], 26, 49—63).—Bang's micro-titrimetric method for the estimation of reducing sugars in blood, consisting in oxidising with iodic acid the cuprous oxide produced by reduction by about 100 mg. of the blood absorbed in blotting paper and clarified, and estimation of the excess of iodic acid by titration with thiosulphate in presence of an alkali iodide, gives satisfactory results provided the following points are attended to. All the reagents used must be absolutely pure. Notably the potassium chloride and uranium acetate used for preparing the clarifying solution should be specially purified, and the iodate is preferably prepared by oxidising potassium iodide with permanganate. Mercuric sulphate, or alcohol, or Patein's reagent was found to give inferior results as clarifying agents, as they all retain a quantity of sugar, and at the same time partly compensate for this by allowing a certain amount of reducing substances originating from the albumin to remain in solution. Bang's reagent exhibits these faults in a much less marked degree. The heating of the clarified blood with the iodate-copper solution should be continued for exactly four minutes, and heating by means of a current of steam generated under constant well-defined conditions in a 1500 c.c. flask containing a constant level of water is to be preferred to direct heating, as experiments showed that the method of heating had a considerable influence on the results. The errors should not on the average exceed 5% if all the above precautions are taken, and the estimation of a large number of samples to which known weights of invert-sugar had been added gave a mean of 97% of the added sugar actually found.

G. F. M.

Acetol. I. A New Test for Carbohydrates. OSKAR BAUDISCH and HARRY J. DEUEL (*J. Amer. Chem. Soc.*, 1922, **44**, 1585—1587).—The test depends on the production of acetol from carbohydrates. An aqueous solution of the carbohydrate (0.1 gram in 100 c.c.) is treated with solid sodium hydrogen carbonate (5 grams) and distilled nearly to dryness. With the carbohydrates which are more readily attacked, the solution in the distilling flask very quickly turns brown, and the distillate has a sweet odour. The residue in the flask after distillation has a strong typical caramel odour. The distillate is treated with *o*-aminobenzaldehyde (30 mg.) and enough potassium hydroxide solution to give a distinctly alkaline reaction; after addition of a piece of porous plate, it is evaporated over a free flame to about 1/3 volume, cooled, and acidified with hydrochloric acid. Then solid sodium hydrogen carbonate is added until the solution is alkaline to litmus. The presence of acetol is shown by a strong blue fluorescence, which can be seen in daylight, but more readily in light of short wave-lengths such as that yielded by the iron arc. To confirm the test, the 3-hydroxy-2-methylquinoline may be extracted by shaking the solution several times with alcohol-free ether; the ethereal solution is dried with sodium sulphate, and the solvent removed. The colourless, needle-like crystals of 3-hydroxy-2-methylquinoline which remain dissolve readily in a little alcohol, and the fluorescence shows up strongly after the addition of water to the alcoholic solution. The sensitiveness of the reaction has not been determined except for dextrose, with which quantities as small as 5 mg. give a positive result.

The test is shown by arabinose, xylose, ribose, lyxose, dextrose, fructose, mannose, galactose, glucosamine, lactose, sucrose, maltose, and dextrin, but not by acetoacetic acid, glycerol, β -hydroxybutyric acid, lactic acid, starch, or glycogen.

The formation of 3-hydroxy-2-methylquinoline when treated with *o*-aminobenzaldehyde and potassium hydroxide appears to be a specific reaction of acetol; it is not given by pure methylglyoxal, aldol, acetone, acetaldehyde, ethyl acetoacetate, crotonaldehyde, or ethyl alcohol.

H. W.

Estimation of the Cellulose Content of Wood and other Raw Materials by the Action of Chlorine and Carbon Tetrachloride. E. HEUSER and H. CASSEUS (*Papierfabr., Fest-u. Auslandheft*, 1922, 80—93; cf. *A.*, 1921, i, 708; Frank, D.R.-P. 323936).—1.2 to 1.5 Grams of material of medium fineness are shaken with 50 c.c. of a saturated solution of chlorine in carbon tetrachloride for one to two hours, and the fibre is collected on a filter and washed successively with carbon tetrachloride, alcohol, and water. The lignin chloride is then dissolved out with a 2% solution of sodium sulphite, the residue washed with water, dried, and weighed. The product, which contains 3—3.5% of pentosan and 0.04—0.05% of ash, has a copper number of 0.8—0.91 as compared with 3.14—3.23 by the older method. The yield of pure cellulose was 56%.

CHEMICAL ABSTRACTS.

Estimation of α -, β -, and γ -Cellulose. OPFERMANN (*Paper*, 1921, 28, 19—25).—The cellulose content of the pulp is estimated as follows: 10 grams of pulp are covered with 50 c.c. of mercurising liquid (17—18% sodium hydroxide) and allowed to stand for thirty minutes. The fibre mass is then rubbed with 50 c.c. of water, filtered on a Buchner funnel with a fine cotton filter, and carefully sucked dry. The residue is washed with cold water until the wash-water no longer has an alkaline reaction; this usually requires ten to twelve washings, 50 c.c. of water being used each time. Finally, the α -cellulose is washed with hot dilute acetic acid, then with hot water (six to eight times), dried, and weighed. β -Cellulose is estimated by adding concentrated acetic acid to the alkaline filtrate until a marked acid reaction is produced, when β -cellulose separates in a finely divided state, and the colour of the brown filtrate becomes considerably lighter. To assist coagulation, the precipitate is heated on the water-bath at 100° until it settles. It is filtered on a fine cloth filter, washed six to eight times with hot water, transferred to a porcelain dish, dried, and weighed. γ -Cellulose is estimated by difference.

CHEMICAL ABSTRACTS.

Determination of the Iodine Value of Aliphatic and Aromatic Unsaturated Compounds. D. HOLDE (*Chem. Umschau*, 1922, 29, 253—254; cf. this vol., ii, 533).—Attention is directed to the different behaviour of the Hanus reagent with simple aliphatic oils such as sesame oil and mineral oils containing unsaturated cyclic structures. In the first case, even with varying excess of iodine, constant values are obtained, whilst in the second case variable values far above the theoretical are obtained with more or less considerable excess of the reagent. This is due to the rupture of bridge structures, and in certain circumstances the behaviour of an oil with excess of the Hanus reagent can be utilised to determine whether cyclic unsaturated compounds are present.

G. F. M.

The Sulphuric Acid Test for Liver Oils. J. C. DRUMMOND and A. F. WATSON (*Analyst*, 1922, 47, 341—348).—The substance present in liver oils which is responsible for the well-known purple coloration with sulphuric acid was found in the following species: Man, horse, ox, pig, cat, monkey, rabbit, guinea pig, chicken, duck, pigeon, rat, mouse, frog, shark, cod, haddock, ling, coal fish, dog fish, sprat, and skate. The substance appears to be a normal constituent of the liver, and is not derived from the bile or from products of autolysis or putrefaction. Evidence is presented to show that it is probably derived from the food, although an examination of the stages in the food of the cod did not reveal its ultimate origin with certainty. The chemical nature of the substance has not been ascertained. It forms a low proportion of the unsaponifiable fraction, is not cholesterol, and probably not a member of the lipochrome pigments. It is thermo-stable in the absence of air or oxygen, but is rapidly destroyed by oxidation. The few properties of the substance which are known, as

well as the available data regarding its distribution in natural products, show certain resemblances to the unidentified dietary unit known as vitamin-A; and, without assuming the identity of the two factors, it is suggested that the association may be of some significance. The colour test cannot be regarded as specific for liver fats, although they usually give the most intense reactions. The body fat and fat from other organs of animals, especially if they have been fed on liver oils, may give the reaction.

H. C. R.

Chemical and Physiological Investigation of the Fats and Lipoids of the Blood. II. The Kumagawa-Suto Method of Estimation of Lipoids. P. LEMELAND (*Bull. Soc. Chim. biol.*, 1922, 4, 300—321; cf. A., 1921, i, 633).—In the Kumagawa-Suto method, errors occur which are due to oxidation of the unsaturated acids during the heating and drying processes, and to loss of volatile constituents of the total unsaponifiable matter. The author promises to describe a new technique for the estimation.

E. S.

Estimation of Small Quantities of Furfuraldehyde Colorimetrically. PAUL FLEURY and GABRIEL POIROT (*J. Pharm. Chim.*, 1922, [vii], 26, 87—96).—Small quantities of furfuraldehyde may be estimated colorimetrically with an accuracy of about $\pm 1\%$ by means of the blue coloration which is formed in acidic medium with orcinol in a suitable solvent, preferably acetic acid, and is intensified by the presence of traces of iron. The reagents required are hydrochloric acid (*d* 1.19) containing 20 mg. of iron as ferric chloride per litre; glacial acetic acid containing 1 gram of orcinol in 1600 c.c., and a standard solution of furfuraldehyde containing 1 gram in 10 litres of 1% acetic acid. One c.c. of the standard solution or of the solution to be estimated is mixed with 4 c.c. of the acetic acid-orcinol solution and 5 c.c. of the hydrochloric acid, and warmed for one minute in a water-bath. After keeping for thirty minutes, the maximum coloration is developed, and comparison is made with the standard in a Duboscq colorimeter. The reaction has a sensibility of about 4 mg. of furfuraldehyde per litre.

G. F. M.

New Analytical Applications of Nessler's Reagent. Characterisation of Ketones; Estimation of Aldehydes. J. BOUGAULT and R. GROS (*J. Pharm. Chim.*, 1922, 26, 5—11).—Certain ketones, such as acetone, methyl ethyl ketone, cyclohexanone, trimethylcyclohexenone, acetophenone, and *p*-methoxyacetophenone, give with Nessler's reagent in the cold a yellowish-white precipitate which dissolves in acid or on the addition of potassium cyanide with liberation of the ketone. This reaction may be used for the detection of acetone in urine, by suspending a small capsule, containing 10 c.c. of Nessler's reagent, over 200 c.c. of urine, previously acidified, the whole being covered by a bell-jar. The time required for the formation of a precipitate varies inversely as the concentration of the acetone in the urine.

Certain aldehydes react quantitatively with Nessler's reagent according to the equation $R \cdot CHO + H_2O + 2I = 2HI + R \cdot CO_2H$, the iodine coming from the mercuric iodide. To a known volume of the aldehyde solution, corresponding with 0.01–0.05 gram of the aldehyde, is added an excess (about 30 c.c.) of Nessler's solution, and 10 c.c. of sodium hydroxide solution. The mixture is well shaken, and after some time is neutralised with hydrochloric acid. A known volume of standard iodine solution is added, and then the excess of iodine is titrated back with standard thiosulphate solution. It is necessary to make a control estimation on the sodium hydroxide. Accurate results were obtained with formaldehyde, furfuraldehyde, benzaldehyde, and piperonaldehyde, but the method is not satisfactory for vanillin or acetaldehyde.

W. G.

The U.S.P. Test for Acetone in Alcohol. J. W. E. HARRISSON (*J. Amer. Pharm. Assoc.*, 1922, **11**, 16).—Some zinc salts and antimony compounds interfere with the test, which depends on the development of a violet colour in presence of sodium hydroxide and sodium nitroprusside. The best test consists in the addition of 1 c.c. of potassium hydroxide solution to 5 c.c. of the ethyl alcohol, followed by a solution of iodine in potassium iodide until coloration occurs; heat must not be used. A precipitate is obtained immediately if 0.25% of acetone is present.

CHEMICAL ABSTRACTS.

Analysis of Camphor Preparations. MAURICE FRANÇOIS and ÉMILE LUCE (*J. Pharm. Chim.*, 1922, [vii], **25**, 500–507).—Tincture of camphor (French Codex) contains 10 grams of camphor dissolved in 90 grams of 90% alcohol, and should have $\alpha +6.5^\circ$ in a 200 mm. tube. The optical rotation varies somewhat with the strength of the alcohol, but, provided that the alcoholic concentration is correct, a lower rotation than that mentioned will indicate a deficiency in the camphor content or that artificial (inactive) camphor is present. The optical rotation of camphor decreases slightly with increase of temperature and in alcoholic solution the value decreases considerably for a decrease in the alcoholic concentration. For instance, in absolute alcohol camphor has $\alpha_D +43.0^\circ$, and in 90% alcohol $\alpha +39.66^\circ$. To ascertain whether a low value for the optical rotation of a sample of tincture of camphor is due to deficiency in camphor or to the presence of artificial camphor, 50 c.c. of the sample are evaporated under a bell-jar over sulphuric acid, the crystalline residue is dried for a further forty-eight hours over sulphuric acid, and its optical rotation then determined in alcoholic solution; natural camphor has $\alpha_D +43^\circ$. The alcoholic strength of tincture of camphor may be ascertained from the specific gravity, allowance being made for the fact that each 1% of camphor present increases the specific gravity by 0.00116.

W. P. S.

Estimation of Cyanogen. HIDEKICHI YANAGISAWA (*J. Pharm. Soc. Japan*, 1922, 369–377).—The method is based on

the conversion of cyanogen into ammonia. A cyanogen compound is heated with dilute sulphuric acid in a sealed tube at 200° during four hours; after cooling, the product is transferred to a Kjeldahl flask, and after making alkaline with sodium hydroxide, the ammonia is distilled into $N/4$ -sulphuric acid; the excess is titrated with $N/4$ -ammonia as usual. K. K.

Comparison of Methods for the Estimation of Urea. J. CARRA (*Biochim. therapia sper.*, 1921, 8, 225).—A comparison of various methods for the estimation of urea shows that a gravimetric method based on the formation of a compound of 1 mol. of carbamide and 2 mols. of xanthidrol is extremely exact. The urease method is also excellent. CHEMICAL ABSTRACTS.

Influence of Sodium Fluoride on the Estimation of Urea by the Xanthidrol Method. M. POLONOVSKI and C. AUGUSTE (*Compt. rend. Soc. Biol.*, 1922, 86, 1027—1028; from *Physiol. Abstr.*, 1922, 7, 214).—The presence of sodium fluoride renders the results obtained by this method too high. This is probably due to the liberation by the acetic acid of hydrofluoric acid. The error may be avoided by the removal of the fluoride by calcium acetate. W. O. K.

Microchemical Detection of Tryptophan in the Plant. FRITZ KRETZ (*Biochem. Z.*, 1922, 130, 86—98).—Tryptophan can be detected in plant-tissues by Fürth's modification of Voisenet's reaction, if the tissues be preserved in a silica gel by soaking in sodium silicate and subsequent addition of concentrated hydrochloric acid. Tryptophan is found in moulds and richly in the embryonic tissues of higher plants and in all other parts containing protein. H. K.

Uric Acid. I. Examination of the Variables in the Folin and Wu Uric Acid Method. II. A Modification of the Folin and Wu Uric Acid Method. GEORGE W. PUCHER (*J. Biol. Chem.*, 1922, 52, 317—327, 329—334).—Using Folin and Wu's method (*A.*, 1919, ii, 308) for the estimation of uric acid in blood, only 75% of added uric acid was recovered. When, however, the solution was heated before filtering the coagulated proteins, a recovery of 93% was obtained. E. S.

Rapid Estimation of Uric Acid in Urine. E. VAILLANT (*Ann. Chim. Analyt.*, 1922, [ii], 4, 178—180).—The liquid is titrated with a standard iodine solution made by dissolving 3.78 grams of re-sublimed iodine and 15 grams of potassium iodide in a little water and diluting to 1 litre. Two c.c. of this solution oxidise 0.005 gram of uric acid (to alloxan and urea). The analysis is carried out by measuring into a small tube 2 c.c. of iodine solution and 1 c.c. of carbon disulphide and allowing the urine to fall a drop at a time from a burette, shaking the tube after each addition, until the carbon disulphide becomes first pale rose and then colourless. The uric acid content per litre of urine is then calculated by dividing the number of c.c. used into 5. Sugar and small amounts of albumin do not interfere; larger amounts of albumin should be

removed by heating to coagulate and then filtering. If the urine is alkaline, a few drops of acetic acid are added; if it contains crystals of uric acid, it is warmed until they dissolve and the analysis is conducted at 25–30°.

A. R. P.

Direct Estimation of Uric Acid in Urine. STANLEY R. BENEDICT and ELIZABETH FRANKE (*J. Biol. Chem.*, 1922, **52**, 387–391).—The same reagents are employed as in the method for blood (this vol., ii, 405). To 10 c.c. of the diluted urine (containing 0.15 to 0.30 mg. of uric acid) are added 5 c.c. of the sodium cyanide solution and 1 c.c. of the arsenophosphotungstic acid reagent. After five minutes, the mixture is diluted to 50 c.c. and the colour compared with a standard containing 0.2 mg. of uric acid similarly diluted to 50 c.c. Owing to the larger amount of uric acid present in urine than in blood, it is unnecessary to heat the solution. Of the other constituents of urine, albumin appears to be the only one which interferes with the reaction. This may be removed, if present, by coagulation by heat in the presence of a drop of acetic acid.

E. S.

Rapid Estimation of Quinine Salts. S. G. LIVERSEDGE and F. W. ANDREWS (*Pharm. J.*, 1922, **109**, 92–94).—Quinine in quinine salts is rapidly estimated by dissolving the alkaloidal salt in 20 c.c. of *N*/5-sulphuric acid, a known excess of *N*/2-sodium hydroxide is then added and the liberated quinine extracted with ether saturated with water, and subsequently the excess of alkali titrated with *N*/5-sulphuric acid, using phenolphthalein as indicator. The amount of acid originally combined with quinine is thus determined, whence the percentage of quinine or quinine salt is obtained by calculation. If boric acid is present, hæmatoxylin is used as indicator.

G. F. M.

Estimation of Small Quantities of Atropine in Blood-serum. H. C. VAN DER HEYDE (*J. Lab. Clin. Med.*, 1922, **7**, 280–287).—Atropine was estimated in 1 c.c. of serum in maximum concentrations of 0.5%. Proteins are first precipitated with absolute alcohol, the precipitate being washed several times with absolute alcohol, and the alcoholic filtrates evaporated to dryness. The residue is treated with a small quantity of water and the solution filtered from fats on a microfilter. The dilution is then determined in which Mayer's reagent (potassium mercury iodide) will just give a precipitate, and compared with control solutions of known dilution.

CHEMICAL ABSTRACTS.

Method for the Separation of Strychnine from Quinine. NORMAN EVERS (*Pharm. J.*, 1922, **109**, 90–91).—A practically quantitative separation of strychnine from quinine is achieved by taking advantage of the fact that chloroform extracts strychnine hydrochloride from strongly acid aqueous solutions, but does not remove quinine hydrochloride under similar conditions. The solution of the mixed alkaloids is acidified with hydrochloric acid to make it about 2*N*, and is extracted with five successive quantities of 50 c.c. each of chloroform. The chloroform extracts are united,

concentrated to 50 c.c., shaken with dilute aqueous ammonia, and evaporated to dryness. The residue is almost pure strychnine, and the quinine is extracted from the residual acid solution with chloroform after rendering alkaline in the usual way. G. F. M.

Detection of Thymine in the Presence of Sugar. HARRY J. DEUEL and OSKAR BAUDISCH (*J. Amer. Chem. Soc.*, 1922, **44**, 1581—1584).—A modification of the method, described recently by Johnson and Baudisch (this vol., ii, 238) for the detection of thymine, is given which makes it applicable in the presence of sugar. For this purpose, the thymine is precipitated as the mercury salt by the addition of saturated mercuric chloride solution (10 c.c.) and sufficient sodium hydroxide solution to make the mixture distinctly alkaline. The precipitate is separated by means of a centrifuge, and, after pouring off the supernatant liquid, it is thoroughly mixed with about 100 c.c. of distilled water and again centrifuged. It is then suspended in water (100 c.c.) and decomposed with hydrogen sulphide; the precipitated mercuric sulphide is filtered and excess of hydrogen sulphide is removed by boiling the filtrate. The remaining liquid is cooled and made up to 100 c.c. Oxidation of the thymine is effected by treating the solution with sodium hydrogen carbonate and ferrous sulphate in the presence of air and the test is completed as described previously. Thymine in quantities of 10—15 mg. may readily be detected in the daylight, whilst as small a quantity as 1 mg. may be detected by the use of the iron arc light. H. W.

Recognition of Proteins and Derivatives by Colour Reactions. M. A. RAKUSIN (*Biochem. Z.*, 1922, **130**, 268—281).—The author has examined a large number of animal and vegetable proteins, ferments, and toxins in respect of their behaviour towards eight colour reagents, namely, biuret, Millon's, xanthoprotein, Liebermann's, Adamkewitsch's, Molisch's, Pettenkofer's, and Ostromysslenski's, and the behaviour towards the sulphur reaction of Vohl and Rakusin. Each protein corresponds with a definite complex of reactions. H. K.

Estimation of Small Amounts of Albumin in Urine. G. GÉRARD (*Bull. sci. pharmacol.*, 1921, **28**, 466—467; from *Physiol. Abstr.*, 1922, **7**, 158—159).—Ten c.c. of urine are placed in each of two test-tubes. One is warmed and a few drops of trichloroacetic acid are added, giving the usual turbidity when albumin is present. To the other there is added drop by drop official spirit of peppermint. The tube and contents are shaken after each drop is added, and the turbidity of the two tubes is compared. When the opacity of both is alike, the test is completed. The author has found that 1 drop of the alcohol used is equivalent to 0.04 c.c. of albumin. No results are given. W. O. K.

The Differential Precipitation of the Proteins of Colostrum and a Method for the Estimation of the Proteins in Colostrum. PAUL E. HOWE (*J. Biol. Chem.*, 1922, **52**, 51—68).—When cow's colostrum is precipitated by addition of successive small quantities of sodium sulphate, a precipitation curve is

obtained which shows three "critical zones" at which increases in the concentration of sodium sulphate cause only small increases in the amount of protein precipitated. These zones occur at concentrations of 13.5—14.5, 17.4—18.4, and 21—22% of sodium sulphate. Up to concentrations of 13.5% euglobulin is precipitated, between 14.5 and 17.4% a mixture of caseinogen and ψ -globulin I is obtained, whilst the precipitate produced between 18.4 and 21% is termed ψ -globulin II. After removal of euglobulin, caseinogen may be precipitated separately by addition of either acetic acid or alum. Total precipitation, including albumin, is effected by means of trichloroacetic acid. By combining these precipitations with Kjeldahl estimations on the filtrate before and after precipitation, a method for the estimation of the proteins of colostrum and of milk is developed (cf. Woodman, A., 1921, i, 625).
E. S.

Estimation of Globulins in Blood-serum. R. R. HENLEY (*J. Biol. Chem.*, 1922, **52**, 367—375).—Two methods are described. In the first, the globulins are precipitated by saturation with magnesium sulphate and the non-globulin nitrogen is estimated in the filtrate. The difference between this and the total nitrogen gives the globulin nitrogen. In the second method, the globulins are precipitated by half saturation with ammonium sulphate, filtered, dissolved in salt solution, and again precipitated. The precipitate is once more dissolved in salt solution and the globulins are finally precipitated by boiling, one or two drops of 10% acetic acid being added if necessary. The precipitate is then filtered on to a tared, hardened filter-paper, washed, dried at 100°, and weighed. The results obtained by both methods vary slightly according to the dilution employed, but are otherwise in agreement with those obtained by Cullen and Van Slyke's method (A., 1920, ii, 398).
E. S.

New Method for the Detection of Bile Pigments. AL. IONESCU and C. POP (*Bul. Soc. Chim. Romania*, 1922, **4**, 20—26).—The following method is recommended as a quick and satisfactory means of detecting bile pigments in urine. To 10 c.c. of the urine are added 2 c.c. of a 0.5% solution of albumin and a few drops of 10% acetic acid. The mixture is boiled and filtered. The precipitate is washed with water and to it on the filter-paper is added one drop of a mixture of 4 c.c. of 6% potassium dichromate and 1 c.c. of 20% sulphuric acid. If the urine contains bile pigments the yellow precipitate turns a green or bluish-green colour. The depth of the colour depends on the amount of pigment present. The reaction is characteristic and very sensitive and is not given by other normal or abnormal urinary pigments.
W. G.

Estimation of Bilirubin in Human Serum. The Ehrlich-Pröscher Reaction. J. S. THANNHAUSER and E. ANDERSEN (*Deut. Arch. klin. Med.*, 1921, **137**, 179—186; from *Chem. Zentr.*, 1922, ii, 425).—The colorimetric method of Hijmans van den Bergh, in which, after precipitation of protein from serum by means of ethyl alcohol, bilirubin is directly combined with diazobenzene-

sulphonic acid, is considered to be inexact owing to precipitation of a portion of the bilirubin by ethyl alcohol and also owing to the coloration obtained differing from that of the test solution. The latter difficulty can be avoided by the presence of excess of mineral acid. Directions are given for the estimation of bilirubin in different sera. G. W. R.

Estimation of Trypsin. A Modification of Gross's Method. SOTARO KAI (*J. Biol. Chem.*, 1922, 52, 133—136).—The relative strengths of trypsin are estimated by measuring the time taken by equal amounts of each to digest 25 c.c. of a casein solution, the time of digestion being inversely proportional to the concentration of trypsin. The end-point of digestion is determined by adding a sodium hydroxide-acetic acid solution to test portions withdrawn from time to time, no precipitate being produced when digestion is complete. By arbitrarily choosing one preparation as standard, the concentrations of others may be expressed in terms of this. E. S.

Acidosis. XVIII. Estimation of the Hydrogen Carbonate Concentration of the Blood and Plasma. DONALD D. VAN SLYKE (*J. Biol. Chem.*, 1922, 52, 495—499).—Two methods are described. In the first, total carbon dioxide is estimated by Van Slyke and Stadie's method (this vol., ii, 78) and P_H either electrometrically or colorimetrically by Cullen's method (following abstract). The hydrogen carbonate concentration is then calculated from the equation $[B\text{HCO}_3] = [\text{CO}_2]/(1 + 10^{P_{K'} - P_H})$, which is derived from $[\text{H}'] = K' \cdot [\text{H}_2\text{CO}_3]/[B\text{HCO}_3]$, $P_{K'}$ being the negative logarithm of K' . The second is a titration method. One c.c. of plasma is treated with 5 c.c. of 0.01*N*-hydrochloric acid and shaken in a 100 c.c. round flask to remove carbon dioxide. It is then brought back to the original alkalinity by the addition of 0.01*N*-sodium hydroxide, phenol-red being used as indicator and 1 c.c. of the original plasma as standard. Sodium chloride solution (0.9%) is used for the preparation of the standard acid and alkali, and also for the dilution, where necessary, of the plasma. Special precautions must be observed to prevent loss of carbon dioxide from the standard. E. S.

Acidosis. XIX. Colorimetric Estimation of the Hydrogen-ion Concentration of Blood Plasma. GLENN E. CULLEN (*J. Biol. Chem.*, 1922, 52, 501—515).—The hydrogen-ion concentration of diluted plasma or serum is estimated colorimetrically at 20° by comparison with Sørensen's phosphate standards, using phenol-red as indicator, and is then converted into that for undiluted plasma at 38° by use of an empirical factor. The latter has been determined by direct comparison of colorimetric with electrometric estimations, and has been found to be constant for plasma of the same species. It is different, however, for plasma of different species and also for plasma and serum of the same species. The success of the method depends on the use of a technique, which is described in the original, to prevent the loss of carbon dioxide during both the preparation of the plasma and the estimation. E. S.

General and Physical Chemistry.

The Reflexion of X-Rays by Crystals. R. DARDORD (*J. Phys. Radium*, 1922, [vi], **3**, 218—220).—When X-rays are reflected from a cylindrical crystalline surface, such as may be obtained by bending a sheet of mica, the analogy between the reflexion of X-rays and light becomes closer; the only difference is that the reflexion of the former is selective. An image of a rectilinear source of X-rays may be obtained from a cylindrical surface and received on a photographic plate. The theory of the formation of the image is discussed and this verified experimentally. W. E. G.

Errors arising in the Measurement of Unsymmetrical Spectrum Lines. T. R. MERTON and D. N. HARRISON (*Proc. Roy. Soc.*, 1922, [A], **101**, 431—434).—One of the most serious sources of error in the measurement of the spectrum lines by juxtaposition of an arc spectrum is the drift of the spectrum across the plate due to either mechanical displacement or changes in the temperature of prism or grating. The methods frequently employed to reduce these errors are not satisfactory for unsymmetrical lines. It is shown that the position of the maximum of an unsymmetrical line in the case of a uniform drift lies at the intersection of the intensity distribution curves at the beginning and the end of the exposure, and hence in the comparison with symmetrical lines, errors amounting to a large fraction of the displacement may easily occur. For this reason, the spectra of gases at low pressures, in which the lines are known to be symmetrical, are to be preferred as standards of wave-length. W. E. G.

Atomic Hydrogen and the Balmer Series Spectrum. R. W. WOOD (*Phil. Mag.*, 1922, [vi], **44**, 538—546).—From the investigation of the hydrogen spectrum developed by an electric discharge in long vacuum tubes containing hydrogen (A., 1921, ii, 665), it is concluded that the secondary spectrum is emitted by the hydrogen molecules, the Balmer series by the atoms. The latter series has been extended to the 20th line by abolishing the secondary spectrum and the faint continuous background of illumination and employing a sufficiently long exposure. It appears extremely probable that the part played by water vapour in enhancing the development of the Balmer series consists in supplying a "poison" (oxygen) to the catalysing wall of the discharge tube, thus permitting a high concentration of atomic hydrogen in the tube under the action of a heavy discharge. With a feeble discharge, the secondary spectrum predominates, as atomic hydrogen is not formed sufficiently fast to overtake the catalysing power of the tube wall. The whiteness of the discharge when the discharge tube is immersed in liquid air, observed by Merton, is due to the increased catalysing power of the wall at low temperatures. The catalysis theory is

likewise applicable to explain the characteristic spectrum developed when air or nitrogen is admitted to the discharge tube containing hydrogen, and the more complete development of the Balmer series in the solar corona and probably in nebulae. The wave-lengths of the components of the doublet H_γ were found to be 4340.494 and 4340.435 Å. J. S. G. T.

The Emission Spectrum of Monatomic Iodine Vapour. ST. LANDAU-ZIEMECKI (*Phil. Mag.*, 1922, [vi], **44**, 651—656).—The band spectrum of iodine vapour at low temperatures showed distinct maxima at $\lambda\lambda$ 422, 404, 395, 387, 380, 373, 368, 363, 340, 325, 323, 320, 319, 312, 310, 306, 304, 302, and 299 $\mu\mu$. The band spectrum became gradually fainter and the line spectrum developed as the temperature was raised. At 960—1000°, corresponding with almost complete dissociation of the iodine molecules, the band spectrum disappeared entirely and was replaced by the line spectrum, due to atomic iodine vapour, and consisting of wave-lengths 4868, 4769, 4680, 4324, 4132, 4100, 3384, 3281, 3081, 2879, 2593, 2583, and 2566 Å. Of these, λ 3281 Å. is certainly new. It is concluded that the band spectrum originates in the molecule, and the line spectrum in the atom. J. S. G. T.

The Spectrum of Helium in the Extreme Ultra-violet. THEODORE LYMAN (*Nature*, 1922, **110**, 278—279; cf. Fricke and Lyman, A., 1921, ii, 362).—When an improved apparatus is used, the line at 584.4 is of very great strength, and is accompanied by three new lines at 537.1, 522.3, and 515.7, of which the intensities decrease with the wave-length in a manner strongly suggesting a series relation. The spacing of these lines on the frequency scale is identical with that of the first four lines in the singlet principal series. The line at 584 is therefore regarded as the first member of a principal series, $oS-mP$. The wave-lengths of the new lines, however, are not in complete agreement with the accepted values of the resonance and ionisation potentials. A. A. E.

Some Spectrum Lines of Neutral Helium derived theoretically. LUDWIK SILBERSTEIN (*Nature*, 1922, **110**, 247—248).—Owing to the prohibitive nature of the general problem of three or more bodies, Bohr's quantum theory can account only for those spectrum lines which form a series of the simple Balmerian type, that is (apart from X-ray spectra of the higher atoms), only those of atomic hydrogen and ionised helium. An attempt is therefore made to obtain a special solution to the problem in the case of neutral helium, the spectrum of which, containing some 105 lines, has not been accounted for theoretically. Assumption that the nucleus and the two electrons are always collinear with each other, the latter describing two equal and oppositely situated ellipses round the former, is evidently erroneous, since the corresponding formula does not cover a single observed line of helium. On the other hand, assumption that the mutual perturbation of the two electrons is negligible yields a spectrum formula which covers about forty lines of the spectrum of neutral helium, and will

probably be found to cover fifty more lines. It therefore appears that the electrons within the atom do not repel each other even with a small fraction of the force usually attributed to them. Lithium appears to yield similar, although less striking results. It is concluded that the field of force of a bound electron is entirely engaged by the nucleus, at least in the case of helium and probably lithium, but possibly also in that of the higher atoms. A. A. E.

Spectrum Lines of Neutral Helium. W. M. HICKS (*Nature*, 1922, **110**, 309).—The constitution of the secondary spectrum of hydrogen may be examined by a method similar to that used by Silberstein (preceding abstract) for helium. Practically the whole of this spectrum depends on the sequence of the Balmer series. If $f(m)$ denote the m th sequent, the wave-length of any line is of the form $\Sigma k_m f(m)$, where the k_m are positive or negative integers. The spectrum is a kind of linkage spectrum in which the usual links are replaced by the separations between the successive lines of the primary, namely, 5331.57, 2467.75, etc. In Silberstein's theory, as in all orbital theories, the two electrons are considered to be moving independently, and each to pass between two of its corresponding paths; if, however, the combined change of energy is radiated, these two events must be simultaneous. A. A. E.

Ionisation in the Solar Atmosphere. HENRY NORRIS RUSSELL (*Astrophys. J.*, 1922, **55**, 354–359).—Barium is much more highly ionised in the sun than sodium, although their ionisation potentials are the same. The absorption of photospheric radiation by atoms in the solar atmosphere tends to increase the degree of ionisation, both directly, by shifting an electron into a position from which its removal is easier, and indirectly, when enhanced lines are absorbed, by getting the ionised atoms into states in which they are probably less likely to combine with electrons. The case of lithium, however, is anomalous. Barium lines and enhanced rubidium lines in the solar spectrum are tabulated. The ionisation potential of manganese (7.6 volts) agrees well with the value predicted from the behaviour of its lines in the solar spectrum.

A. A. E.

The Spectrum of Glucinum and its Noteworthy Relation to the Spectrum of Aluminium. L. C. GLASER (*Ann. Physik*, 1922, [iv], **68**, 73–88).—Employing the arc or spark between electrodes of glucinum, the author has investigated the spectrum of the metal in the visible and ultra-violet regions. The line spectrum observed confirms, with certain limitations, the previous measurements of Rowland and Tatrall. In the region $\lambda\lambda$ 5500–4900 Å., no lines, apart from those constituting part of the band spectrum, attributable with certainty to glucinum, were observed. The line spectrum observed was constituted of $\lambda\lambda$ 4607?, 4600?, 4572, 4486.7?, 4277.8?, 4263.6?, 4216.0, 4079.0, 3994.0, 3936.0, 3909.3, 3891.0. A more accurate measurement of the strongest line, λ 4572, gave the result 4572.73 ± 0.0098 Å., in terms of the normal international iron spectrum. Attention is directed to

certain analogous physical features characterising the production of the band spectra of glucinum and aluminium. The wave-lengths of the constituent bands in the spectra of both elements are tabulated, and it is remarked that there is considerable agreement between the respective first differences of wave-lengths of successive lines in corresponding bands in the two spectra. Deslandre's rule is true only as a first approximation. Attention is also directed to the approximate constancy of certain numerical values calculated from the wave numbers of the heads of the bands $\lambda\lambda$ 4708 and 4842 in the case of the glucinum and aluminium spectrum, respectively. It is concluded that the atomic structures of glucinum and aluminium, so far as the emission of their band spectra is concerned, are the same.

J. S. G. T.

The Band Spectra of Cadmium. ERIK HULTHÉN and ERNST BENGTSOON (*Compt. rend.*, 1922, **175**, 423—426).—Two systems of bands have been measured at $\lambda=4500$ and $\lambda=4300$ and their structures studied. The results show that the bands of the elements zinc, cadmium, and mercury can be embodied in the same expressions, and the constants of the series in the bands of cadmium are given.

W. G.

A Continuous Spectrum from Mercury Vapour. C. D. CHILD (*Astrophys. J.*, 1922, **55**, 329—344; cf. A., 1921, ii, 3).—A continuous spectrum identical with the fluorescence spectrum is emitted in addition to the ordinary line spectrum when (a) the temperature of the vapour is above 120° and below $300\text{--}400^\circ$, depending on the pressure, (b) the pressure is above 1 mm., (c) the current density is low, (d) very little air or other contaminating gas is present. Ionisation of the vapour is not, however, necessary. It is suggested that the carriers of the spectrum are molecules consisting of two or more atoms, which emit the fluorescence spectrum as a result of excitation by ultra-violet radiation λ 2536 emitted by atoms struck by electrons with energies corresponding with at least 4.9 volts. The ionisation potential for mercury appears to vary with the temperature, reaching a minimum at about 140° . Above 120° , mercury vapour reacts with air to form a dark compound; the reaction is associated with the appearance of the continuous spectrum. A continuous spectrum of sodium, much fainter than the line spectrum, has also been observed.

A. A. E.

The Lanthanum Violet Bands and the Associated Lines. JUNZŌ ÔKUBO (*Sci. Rep. Tohoku Imp. Univ.*, 1922, **11**, 95—104).—The edges of the bands in the violet and green regions of the lanthanum spectrum consist of closed doublets, and the edges of these are determined accurately in order to seek a relation between the band and line spectra. The best conditions for observing the bands and diffused lines are obtained when the temperature of the arc is low, or by using lanthanum as the negative electrode with a moderate current; under these conditions, the sharp lines are comparatively faint. It was found that one pair of double

lines exists nearly midway between the corresponding heads of each series of bands, and another between the heads of successive series so that the bands are not independent of each other. By the introduction of the quantum theory, the conclusion is drawn that the lanthanum violet bands are emitted as a consequence of the molecular rotation when line emission takes place in the atom, thus accounting for the double structure of the bands.

W. E. G.

The Arc Spectra of Gallium and Indium. H. S. UHLER and J. W. TANCH (*Astrophys. J.*, 1922, **55**, 291—301).—By the use of a concave grating with 590 lines per mm. and a radius of curvature of 640 cm., accurate determinations were made of the wave-lengths for air and the vacuum wave numbers of twenty-three gallium lines and thirty-four indium lines, λ 4511 to λ 2170. All the gallium lines and twenty-eight of the indium lines were found to belong to the two subordinate series, for each of which from five to eight terms were identified. Four indium lines, previously supposed to be single, were resolved. An attempt to obtain the absorption spectrum of indium vapour gave only the two strongest lines, λ 4511 and λ 4102.

A. A. E.

Optical Experiment Demonstrating the Bragg Method of Crystal Analysis. BILFRIED QUARDER (*Physikal. Z.*, 1922, **23**, 350—352).—An optical analogue to the distribution of intensities in the various orders of X-ray spectra reflected from the 1, 1, 1, planes of sodium chloride or the 1, 0, 0 planes of zinc sulphide is afforded by the use of a photographic grating consisting of equally spaced, alternately thick and thin lines. By reducing the grating aperture, broadening of the lines occurs, a result analogous to the broadening of the lines in the X-ray spectrum, occurring on powdering the diffracting crystals, as observed by Debye and Scherrer (A., 1917, ii, 437).

J. S. G. T.

Spectra of X-Rays and the Theory of Atomic Structure. IV and V. D. COSTER (*Phil. Mag.*, 1922, [vi], **44**, 546—573).—In continuation of previous work (A., 1922, ii, 491), the author has investigated the *L*-series of the characteristic X-ray spectra of the rare elements from lanthanum (atomic number 57) to lutecium (atomic number 71). In general, the lines for these elements are much sharper than those for elements of lower atomic number, and most of the stronger lines are accompanied by fairly intense satellites. Measurements have been made of a great number of lines which may be arranged in a simple diagram and are conveniently referred to as diagram lines, a number of non-diagram lines, and some absorption discontinuities. The measured frequencies of the diagram lines are in agreement with results to be anticipated from Bohr's theory of the successive development of the shells of electrons in the various atoms. Most of the non-diagram lines lie on the short wave-length side of an intense diagram line, and the difference of frequency between the two lines is approximately proportional to the atomic number of the element.

A theoretical discussion is given of the origin of the non-diagram lines and of the fine structure of the absorption discontinuities. In criticism of the views of Wentzel (this vol., ii, 249) in this connexion, experimental results have been obtained showing that the assumption of the successive ionisation of the inner shells of the atom is untenable, and that part of the non-diagram lines are emitted by atoms which have lost more than one electron at the same time by the impact of a single high-speed β -particle. An explanation is given of the origin of some non-diagram lines lying on the long wave-length side of diagram lines, and it is suggested that these lines should appear both in the emission and in the absorption spectra.

J. S. G. T.

Analysis of the Electronic Structure of the Elements.

A. DAUVILLIER (*J. Phys. Radium*, 1922, [vi], 3, 221—251).—The author has investigated the *L*-series of lines in the characteristic X-ray spectra of uranium, gold, platinum, iridium, osmium, tungsten, and antimony, and the *K*-lines in the spectra of copper and molybdenum (cf. A., 1921, ii, 669; this vol., ii, 43, 101, 559). The numbers of observed lines have been at least doubled, and owing to the correction of certain errors, it is shown that Sommerfeld's theory is applicable to the calculation of the frequencies of these lines. The results have been applied to determine the energy levels of the atoms of most of the elements and afford a complete qualitative explanation of their absorption spectra; they have likewise been correlated with the ionisation potentials of certain gases and metallic vapours, by the application of the quantum hypothesis. The numbers of electrons in the various corpuscular layers of the respective elements have been calculated, and it is shown that the number n of such electrons is related to the quantum number τ characterising the layer by the equation $n=2\tau^2$. A theory is advanced to account for the complex structures of the *K* and *L* series of lines in the X-ray spectra of the light elements, and these spectra are, by the aid of the theory, correlated with the corresponding spectra of the elements in the visible region. The variation of atomic volume and chemical valency of the elements, as shown by the periodic table, is also at least partly explained by the theory developed.

J. S. G. T.

The Absorption Spectrum of Potassium Vapour.

SNEHAMOY DATTA (*Proc. Roy. Soc.*, 1922, [A], 101, 539—547).—The principal series lines in the absorption spectrum of potassium vapour have been measured up to $m=42$ (compared with $m=24$ previously). Satisfactory agreement is shown between the measured frequencies and those calculated by the series formula $p_1(m)=35008.480-109736.1/(m+1.29667-0.06154/m)^2$, except for $m=3$ and $m=39$ to 42. The value for $m=3$ is abnormal, and the latter values receive a possible explanation along the lines of Sommerfeld's assumption of the occurrence of collisions between the electrons emitted from the atom and other electrons or atoms. The first seven members of the principal series have been resolved, compared with five previously. New absorption lines, first

appearing at 20 mm. pressure, and apparently not corresponding with known lines in the emission spectrum, were found at higher pressures. The combination lines $1s-2d$ and $1s-3d$ were found to be absorbed, the first as a pair, confirming the presence of a satellite to the lines of the diffuse series. The appearance of these absorption lines contradicts the selection principle. J. S. G. T.

Absorption of Potassium Vapour in the Associated Series.

A. L. NARAYANA and D. GUNNAIYA (*Nature*, 1922, **110**, 250).—Traces of absorption occur at about 1100° . In the diffuse series, distinct traces of absorption have been detected; the bands 5780, 5340, 5300, and 5100 apparently correspond with 5782, 5340, 5323, and 5100 of ($2p-m.d$). A. A. E.

Absorption of Light by Sodium and Potassium Vapours.

GEORGE R. HARRISON (*Proc. Nat. Acad. Sci.*, 1922, **8**, 260—263).—Vapour density alone determines the development of the continuous absorption spectrum of sodium vapour. No visible effect is attributable to hydrogen present in pressures up to 400 mm. of mercury. Absorption begins at the last resolved line of the principal series. No definite break in the continuous absorption spectrum was observed, but the absorption decreases rapidly with decreasing wave-length, the region λ 2200 Å. being one of the most transparent regions studied. With unsaturated sodium vapour, the band spectrum is much weaker than the line and continuous spectra. It is suggested that the bands are due to loose molecular aggregates. Fluorescence, which was marked in saturated vapour, disappeared on superheating the vapour. The continuous absorption spectrum of potassium vapour resembled that of sodium. J. S. G. T.

The Absorption and Fluorescence Spectra of Benzene.

VICTOR HENRI (*J. Phys. Radium*, 1922, [vi], **3**, 181—211).—The ultra-violet spectrum of benzene has been studied over pressures ranging from 0.01 to 65 mm. At the low pressures the absorption bands are resolved into a series of narrow bands, about 0.15 Å. apart, which fuse very readily on passing a certain limited pressure. They are distributed in eight groups, of which only five are visible at 0.01 mm. More than 350 bands have been counted.

The application of Bohr's theory to the study of these band spectra permits of their classification into four series, each band being given by an equation of the form $1/\lambda = A - B + na - (pb + p^2b') + \alpha(m^2 - q^2)$, in which A , B , a , b , b' , and α are constants and n , p , m , and q whole numbers. The intensities of the heads of the bands are greatest for $p=0$ and diminish rapidly as p increases, which is in agreement with the theory. The coefficients deduced from the results of the ultra-violet absorption are available for the calculation of the infra-red absorption spectra of benzene. The terms A and B are due to electronic movements and do not enter into the frequency of the infra-red absorption bands, for which a simple formula is deduced, $1/\lambda = an - bp$; the agreement between the calculated and experimental values is very satisfactory. The moment of inertia of the benzene molecule ($I = 1.45 \times 10^{-38}$) is

derived from the value of the constant α and compared with that calculable from the crystal models of benzene derivatives deduced by Bragg.

The ultra-violet spectra of liquid benzene and its solutions correspond closely with the spectra of the vapour, except for a slight shift towards longer wave-lengths. On dilution, the specific effect of the solvent becomes more marked, the bands widen and move towards the red; this effect, which is analogous to the Stark effect, may be due to the action of an intense electric field of the solvent molecules. The displacement does not bear any relation to the dielectric constant of the solvent. The fluorescent spectrum of liquid benzene consists of six bands, which are excited by monochromatic light of wave-lengths lying within the benzene absorption bands *D*, *E*, *F*, *G*, and *H*; lines which correspond with the *A* and *B* absorption bands do not excite any fluorescence. The molecules absorbing the monochromatic light do not return to their original state on the emission of the fluorescent light, and the fluorescent bands lie towards the red with respect to the absorption bands. When the vapour of benzene is subjected to a high frequency discharge, a new absorption band appears ($\lambda=2750\cdot5$ Å.).

W. E. G.

The Ultra-violet Absorption Spectra of Dihydric Phenols.

F. W. KLINGSTEDT (*Compt. rend.*, 1922, **175**, 365—367).—The quantitative study of the absorption spectra of dihydric phenols in hexane solution has given new results. Diagrams of the normal spectra of phenol, resorcinol, catechol, and quinol are given. These show that *m*- and *o*-derivatives yield results similar to those obtained with phenol, whilst the *p*-compound possesses a series of eight distinct bands in place of three exhibited by the other substances. This is a general result, as shown by the spectra of other benzene derivatives. The spectra are considerably modified by the solvents used, especially by alcohol; the authors consider that, as alcohol has been used for much work on absorption spectra, the observations should be repeated with hexane solutions.

H. J. E.

Phosphorescent Zinc Sulphide containing Copper.

B. GUDDEN and R. POHL (*Ann. Physik*, 1922, [iv], **68**, 154—156).—Wilde has recently investigated the variation of the dielectric constant of phosphorescent zinc sulphide containing copper due to illumination, a phenomenon previously studied by the authors and by Molthan. Briefly, the results indicate that the increase in the value of the dielectric constant due to illumination is a maximum at about 140° . The effect is small at high temperatures. Temporary fluctuations of the effect at all temperatures, and for all exciting wave-lengths, is correlated with the luminosity of the phosphorescent substance. Regarding the phenomenon as originating in certain centres of excitation surrounding the relatively few copper atoms present, it follows that the effect must decrease with increasing temperature, and increase to a limiting value with decrease of temperature. The occurrence of the experimentally determined maximum at 140° is explained by assuming that the mobility of the electrons

within the excited centres diminishes as the temperature is reduced, an assumption which is in accord with other experimental results. The failure to detect the effect in other varieties of these phosphorescent substances is regarded as a matter of accuracy of measurement.

J. S. G. T.

Fluorescence, Photochemical Action, and Einstein's Law. FRITZ WEIGERT (*Z. Physik*, 1922, **10**, 349—351).—A theoretical paper in which the author criticises Perrin's theory of fluorescence (cf. A., 1918, ii, 418; 1919, ii, 177). The part played by oxygen in the photochemical change of most fluorescent substances demonstrates the independence of the fluorescence and the sensitivity to light. For example, an oxygen-free solution of fluorescein is stable to light. The photochemical reaction velocity decreases with increasing partial pressure of oxygen, whereas the brightness of the fluorescence is unaffected. The experiments of Wood and Pringsheim are to be explained along these lines. Einstein's law cannot be applied to these photochemical processes, since under the most favourable conditions 200 energy quanta are necessary for the absorption of one molecule of oxygen by the fluorescent substance.

W. E. G.

Ionisation of Potassium Vapour by Light. R. C. WILLIAMSON (*Proc. Nat. Acad. Sci.*, 1922, **8**, 255—260).—By employing a jet of hot potassium vapour, directed into a cool vacuum chamber and traversed by a pencil of light derived from a mercury arc in quartz, evidence has been obtained of the ionisation of potassium vapour by light. The limiting long wave-length (λ 2856 Å.) of the exciting radiation can be calculated from the ionising potential V by the quantum relation $Ve = h\nu$. Below this limit, the ionising power of the radiation increases continuously as the wave-length decreases.

J. S. G. T.

Rise of γ -Ray Activity of Radium Emanation. F. P. SLATER (*Phil. Mag.*, 1922, [vi], **44**, 300—304; cf. this vol., ii, 13).—Curves are given showing the rise of γ -ray activity from pure radium emanation when enclosed by lead and aluminium of varying thicknesses. The fraction of the ionisation due to radium-*B* when in radioactive equilibrium with radium-*C* has been deduced by trial for thicknesses of lead up to 20 mm. The data have been utilised in deducing the absorption coefficients of the heterogeneous γ -radiation from radium-*B*.

W. E. G.

The Distribution of Radioactive Substances in Solutions. HILARY LACHS and MATHILDE WERTENSTEIN (*Physikal. Z.*, 1922, **23**, 318—322).—In alkaline or neutral solutions of polonium, radium-*D*, radium-*E*, and radium, allowed to remain for a period of hours, the radioactivity exhibited at various depths increases as the depth increases. In acid solutions, the radioactivity is very approximately uniformly distributed throughout the solution. No conclusive results were obtained with solutions of radium-*A*, -*B*, and -*C*. The effects are attributed to the presence of minute particles, derived from the air or the vessel, in the solutions, the

radioactive material being adsorbed by these particles. The results are applied to explain the low values obtained by Paneth for the diffusion coefficient of polonium in neutral and alkaline solution, and of thorium-*B* in alkaline solution. J. S. G. T.

The Disintegration of Elements by α -Particles. (SIR) E. RUTHERFORD and J. CHADWICK (*Phil. Mag.*, 1922, [vi], **44**, 417—432).—The nature of the particles ejected from various elements by bombardment with swiftly moving α -particles (cf. A., 1921, ii, 293), has been investigated by determining the deflexion of the particles in a magnetic field. The results show that the particles ejected from aluminium, phosphorus, and fluorine consist of positively charged hydrogen nuclei. The same is also probably true of boron and sodium. The ranges of the particles ejected, in the forward and backward directions, from nitrogen, aluminium, boron, fluorine, sodium, and phosphorus have been more accurately determined. In all cases, hydrogen particles were ejected in all directions, and the maximum range in the backward direction was less than in the forward direction. The maximum ranges, in cms. of air, of the ejected particles, in the forward and backward directions, respectively, were found to be: boron, 58 and 38; nitrogen, 40 and 18; fluorine, 65 and 48; sodium, 58 and 36; aluminium, 90 and 67; and phosphorus, 65 and 49. Only in the case of nitrogen was the maximum range of the ejected particles in the backward direction much less than that of free hydrogen particles. No particles of range greater than 30 cm. of air, in the forward direction, were ejected from either lithium or glucinum, and there was no evidence of the ejection of long range particles from magnesium, silicon, or chlorine. Of the series of elements from hydrogen to potassium hitherto examined, the active elements (those from which hydrogen nuclei are ejected) are odd-numbered in the order of atomic number in the regular sequence 5, 7, 9, 11, 13, 15. The atomic masses of the active elements are expressed by $4n+a$, where n is a whole number, and $a=3$ for all except nitrogen, for which $a=2$. With the exception of boron, which has two isotopes, the active elements are pure elements. The results indicate that neither lithium nor chlorine has any lightly bound satellites in its nuclear structure. The hydrogen satellite of nitrogen is relatively close to the main nucleus. The nuclei of even light elements are very complex systems, and it is difficult to advance any simple rule to account for the wide difference in structure of successive elements.

J. S. G. T.

Temperature Coefficient of Electromotive Force of Galvanic Cells and the Entropy of Reactions. ROSCOE H. GERKE (*J. Amer. Chem. Soc.*, 1922, **44**, 1684—1704).—The *E.M.F.* of a number of electrolytic cells has been determined at a number of temperatures and the following values of the *E.M.F.* of the cell at 25° and the temperature coefficient are recorded: $\text{Ag}|\text{AgCl}|\text{HCl}(N)|\text{AgCl}|\text{Cl}_2$ (1 atm.), $E=1.1362$ volts, $\Delta E/\Delta T=-0.000595$ volts/degree; $\text{Hg}|\text{HgCl}|\text{HCl}(N)|\text{Cl}_2$ (1 atm.), $E=1.0904$ volts, $\Delta E/\Delta T=-0.000945$; $\text{Ag}|\text{AgCl}|\text{KCl}(N)|\text{HgCl}|\text{Hg}$, $E=0.0455$,

$\Delta E/\Delta T = 0.000338$; $\text{Ag}|\text{AgCl}|\text{HCl}(N)|\text{HgCl}|\text{Hg}$, $E = 0.0455$, $\Delta E/\Delta T = 0.000337$; $\text{Pb}(\text{cryst.})|\text{Pb}(\text{OAc})_2(2N)|\text{Pb}(\text{Hg})$, $E = 0.0057$, $\Delta E/\Delta T = 0.000021$; $\text{Pb}(\text{stick})|\text{Pb}(\text{OAc})_2|\text{Pb}(\text{Hg})$, $E = 0.0057$, $\Delta E/\Delta T = 0.000015$; $\text{Pb}(\text{Hg})|\text{PbCl}_2|\text{HCl}(N) + \text{PbCl}_2|\text{AgCl}|\text{Ag}$, $E = 0.4843$, $\Delta E/\Delta T = 0.000202$; $\text{Pb}(\text{Hg})|\text{PbCl}_2|\text{HCl}(N) + \text{PbCl}_2|\text{HgCl}|\text{Hg}$, $E = 0.5299$, $\Delta E/\Delta T = 0.000129$; $\text{Ti}(\text{stick})|\text{Ti}(\text{OH})|\text{Ti}(\text{Hg})$, $E = 0.0027$, $\Delta E/\Delta T = 0.000020$; $\text{Ti}(\text{Hg})|\text{TiCl}|\text{NaCl}(N) + \text{HCl}(0.001N)|\text{TiCl} + \text{AgCl}|\text{Ag}$, $E = 0.7766$, $\Delta E/\Delta T = -0.0000794$; $\text{Pb}(\text{Hg})|\text{PbI}_2|\text{Pb}(\text{ClO}_4)_2(0.218M) + \text{HClO}_4|\text{PbI}_2|\text{I}_2$, $E = 0.8936$, $\Delta E/\Delta T = -0.000042$; $\text{Pb}(\text{Hg})|\text{PbI}_2|\text{KI}(N)|\text{PbI}_2 + \text{AgI}|\text{Ag}$, $E = 0.2078$, $\Delta E/\Delta T = -0.000189$; and $\text{Pb}(\text{Hg})|\text{PbI}_2|\text{KI}(0.1N)|\text{AgI}|\text{Ag}$, $E = 0.2135$, $\Delta E/\Delta T = -0.000173$. The free energy, ΔF_{298} , the entropy change, ΔS_{298} , and the change of heat content, ΔH_{298} , have been calculated from the *E.M.F.* measurements and the temperature coefficients of a number of reactions. The following are recorded: $\text{Ag} + \text{HgCl} = \text{AgCl} + \text{Hg}$; $\Delta F = -1050$ Cal., $\Delta S = 7.80$ Cal./degree, $\Delta H = 1275$ Cal.; $\text{Pb}(\text{cryst.}) = \text{Pb}(\text{Hg})$, $\Delta F = -263$, $\Delta S = 0.97$, $\Delta H = 26$; $\text{Pb}(\text{stick}) = \text{Pb}(\text{Hg})$, $\Delta F = -263$, $\Delta S = 0.69$, $\Delta H = -57$; $\text{Pb}(\text{solid}) = \text{Pb}(\text{Hg})$, $\Delta F = -263$, $\Delta S = 0.74$; $\Delta H = -42.4$; $\text{Pb}(\text{solid}) + 2\text{AgCl} = \text{PbCl}_2 + 2\text{Ag}$, $\Delta F = -22612$, $\Delta S = -8.58$, $\Delta H = -25170$; $\text{Pb}(\text{solid}) + 2\text{HgCl} = \text{PbCl}_2 + 2\text{Hg}$, $\Delta F = -24717$, $\Delta S = 6.70$, $\Delta H = -22720$; $\text{Ti}(\text{cryst.}) + \text{AgCl} = \text{TiCl} + \text{Ag}$, $\Delta F = -17975$, $\Delta S = -1.08$, $\Delta H = -18296$; $\text{Pb}(\text{solid}) + \text{I}_2 = \text{PbI}_2$, $\Delta F = -41501$, $\Delta S = -1.20$, $\Delta H = -41859$; $\text{Pb}(\text{solid}) + 2\text{AgI} = \text{PbI}_2 + 2\text{Ag}$, $\Delta F = -9852$, $\Delta S = -7.98$, $\Delta H = -12231$; $\text{Hg} + \frac{1}{2}\text{Cl}_2 = \text{HgCl}$, $\Delta S = -21.80$; and $\text{Ag} + \frac{1}{2}\text{Cl}_2 = \text{AgCl}$, $\Delta S = -13.73$. The third law of thermodynamics has been submitted to a most rigorous test and discrepancies found earlier by Lewis and Latimer (this vol., ii, 471) have been reduced tenfold. Assuming the validity of the third law, the entropies of chlorine and iodine have been calculated and the following values recorded: $\frac{1}{2}\text{Cl}_2$, $S_{298} = 27.1$; $\frac{1}{2}\text{I}_2$, $S_{298} = 13.5$.
J. F. S.

Electric Kataphoresis of Metallic Protein Compounds obtained by Treatment with Powdered Metals. A. BENEDICENTI and S. REBELLO-ALVES (*Arch. intern. pharmacodynamie*, 1922, **26**, 297—316).—In shaking a solution of egg-albumin or of blood-serum with powdered metals the metals become attached to the proteins and the properties of the latter change. They become coloured, their reactions are altered, they are not coagulated by heat, and resist putrefaction. The “fixation” of the metals is independent of the reaction of the protein solution and of its gas and salt content. The metals in this combination lose their ionic properties and are not dialysable. Metals vary in their power to combine with proteins: cobalt, copper, and iron combine to a greater extent than do aluminium and lead. Powdered oxides of the metals do not combine with proteins. By passage of an electric current through an alkaline solution of the metallic protein compound, the protein particles become negatively charged and move towards the positive electrode, carrying with them the fixed metal. In an acid solution the protein particles become negatively charged, move to the cathode and a part of the metal is deposited

on the electrode. At the chemically neutral (? isoelectric) point a protein coagulum forms, which gradually changes into a membrane upon which the fixed metal deposits. Boiling or heating a metallic protein solution to 50–60° changes profoundly its electrophoretic properties. It is suggested that the thermolability of sera, the fixation of metals by certain organs and their elimination, etc. depend on the formation of metastable protein compounds and on changes in the chemical equilibria of these compounds.

CHEMICAL ABSTRACTS.

Kataphoresis of Water in Organic Liquids. A. GYEMANT (*Z. physikal. Chem.*, 1922, **104**, 74–88).—The kataphoresis of drops of water and aqueous solutions of acids, bases, salts, and dyes in aniline, guaiacol, and benzonitrile has been measured by a microscopic process. In the case of guaiacol (less in aniline and still less in benzonitrile), it is found that water and aqueous solutions of inorganic electrolytes do not migrate at all or at best only very slowly, whilst solutions of salts which furnish organic ions possess a considerable kataphoric velocity. The sense of the direction is exactly that which would be expected from the kataphoresis of the same organic liquids in the corresponding aqueous solutions. In the case of organic kations, the water drops are negatively charged towards the organic medium and with organic anions positively charged. Some cases have been found which point to the assumption that only a portion of the total potential (ϵ), the so-called ζ -potential, is determinative of the kataphoresis. Thus, for example, it is found that drops of aqueous solutions of hydrochloric acid and aluminium chloride in benzonitrile are positively charged, although when benzonitrile emulsifies in the solutions it is positively charged; this phenomenon finds its explanation in the ζ -potential. The smaller velocity of migration of drops of aqueous solutions of electrolytes cannot be directly explained by the assumption that in these cases the ζ -potential in the organic liquid is much smaller. Probably it is to be explained by the inorganic ions being much less solvated in organic liquids than the organic ions. The Helmholtz formula for the velocity of kataphoresis cannot be directly applied to a water emulsion in organic liquids.

J. F. S.

Thermo-compression and Thermo-addition. MAURICE DELEUVER (*Bull. Assoc. Chim. Sucr.*, 1922, **39**, 477–480).—A theoretical paper in which the conditions under which the equations, moist vapour+moist vapour=superheated vapour, and superheated vapour+superheated vapour=moist vapour, are true are discussed.

J. F. S.

Determination of Specific Heats at Low Temperatures. FRANZ SIMON (*Ann. Physik*, 1922, [iv], **68**, 241–280).—The accuracy of determination of specific heats of substances at low temperatures devised by Nernst and Schweser (A., 1914, ii, 336), has been considerably increased by using a larger calorimeter designed so that the amount of liquid hydrogen employed is not

unnecessarily increased. Determinations have been made and the values tabulated of the respective specific heats of quartz glass, cristobalite, "Lindemann" glass, mercury, ammonium chloride, dextrose, cuprous iodide, glycerol, and keton-resin ("Ketonharz," D.R.-P. 309224), at temperatures ranging from 15° Abs. to the ordinary temperature. The T^3 law, expressing the value of the molecular heat divided by the number of atoms in the molecule, by the relation $c_p = 6.94 \times 10^{-6} T^3$, where T is the absolute temperature, is very closely obeyed by ammonium chloride, for temperatures between 20° and 32° Abs. Anomalous values of the specific heat of ammonium salts are due to a transformation occurring within a certain range of temperature—from about 140° Abs. to 243° Abs. in the case of ammonium chloride. The sudden drop in the value of the atomic heat of glycerol when the temperature is reduced just below 180° Abs. is correlated with the softening of the substance at this temperature. In the case of cuprous iodide, values of the free energy calculated by means of Nernst's theorem are in agreement with experimentally determined values. The values of the energy liberated by the combustion of dextrose at various temperatures are tabulated. The value of A , the free energy of the reaction in Nernst's relation, is 704,500 cal. at 290° and 706,700 at 310° T . It is shown that the value of the specific heat of complex bodies at different temperatures can be represented by the Nernst interpolation formula consisting of the sum of the Debye and Einstein functions. The number of the latter functions is small compared with the number of the former. The general characteristics of the variation with temperature of the atomic heats of complex bodies is discussed from the point of view of atomic vibrations, and it is shown why, in many cases, Berthelot's principle affords a close approximation to the energy relations involved.

J. S. G. T.

A New Physico-chemical Law. HAWKSWORTH COLLINS (*Chem. News*, 1922, 125, 81—83, 97—98).—From tables of the atomic weight and specific gravity of the elements, and the specific gravity and heat of formation of a number of molecules, the relative volumes of the elements in combination and the heat of formation of the elements when combining to form molecules are deduced. The values calculated never differ more than 1% from the observed values. It is also shown that the heat of formation of each element is proportional to the product of the atomic weight and the change of volume. By change of volume is meant the difference between the volume of the element in the solid state at 15° and the volume of the element in combination with others at 15°.

J. F. S.

Heat of Crystallisation of Quartz. RAMES CHANDRA RAY (*Proc. Roy. Soc.*, 1922, [A], 101, 509—516).—The heat of crystallisation of quartz has been determined by measuring the respective heats of solution of silver sand and silica glass in hydrofluoric acid. The following values were obtained for the specific heat of aqueous hydrofluoric acid solutions containing the respective percentages by weight of hydrofluoric acid: 10%, 0.908; 20%,

0.838; 30%, 0.756; 34.6%, 0.724. The mean values of the heats of solution in hydrofluoric acid per gram-molecule of silicon dioxide were found to be: silica glass, 37.24 Cal.; silver sand, 30.29 Cal. The heat of crystallisation of quartz, represented by the difference, is therefore 6.95 Cal. per gram-molecule. This value agrees with that calculated from Tschernobaef and Wologdine's results, but is much higher than those obtained by Mulert (2.21) (A., 1912, ii, 626) and Wietzel (2.32), (A., 1921, ii, 504). The discrepancy is attributed to the effect of prolonged grinding in reducing part of the substance to the vitreous condition. The calculated value of the heat of crystallisation at 900° is 6.50 Cal. per gram-molecule. At 1300–1400°, the value is not much different from that at ordinary temperature. J. S. G. T.

Separation of Liquid Mixtures by Centrifuging. ROBERT S. MULLIKEN (*J. Amer. Chem. Soc.*, 1922, **44**, 1729–1730).—In an earlier paper (this vol., ii, 492) the author showed thermodynamically that the same separation of isotopes should be obtainable by centrifuging a liquid as a gaseous mixture, at a given speed. The same result was stated to be true for ideal solutions in general. The latter statement is now shown to be incorrect. The result depends not only on the ideality of the solutions, but also on equality of the vapour pressures and of the atomic or molecular volumes of the constituents. These conditions are fulfilled in few cases except that of a mixture of isotopes. J. F. S.

Viscosity and Molecular Dimensions of Sulphur Dioxide. C. J. SMITH (*Phil. Mag.*, 1922, [vi], **44**, 508–511).—By Rankine's method, the author has determined the viscosity of sulphur dioxide to be 1.253×10^{-4} C.G.S. units at 18.0°, and 1.630×10^{-4} at 100.0°. The value of Sutherland's constant calculated therefrom is 416, and the corresponding value of the viscosity at 0°, extrapolated by Sutherland's formula, is 1.168×10^{-4} C.G.S. units. The value of the mean collision area, calculated from the results by Chapman's formula, is 0.94×10^{-15} sq. cm. with a possible error of 2 or 3%. J. S. G. T.

Viscosity and Molecular Dimensions of Gaseous Carbon Oxsulphide. C. J. SMITH (*Phil. Mag.*, 1922, [vi], **44**, 289–292).—The viscosities of carbon oxsulphide have been determined at 15° and 100° by the method described by Rankine and Smith (cf. A., 1921, ii, 694, 696; this vol., ii, 549). The values obtained were $\eta_{15} = 1.200 \times 10^{-4}$ C.G.S. units, and $\eta_{100} = 1.554 \times 10^{-4}$ C.G.S. units; and by extrapolation from Sutherland's formula $\eta_0 = 1.135 \times 10^{-4}$ C.G.S. units. The mean area which the molecule presents in mutual collision is $\text{\AA} = 1.06 \times 10^{-15} \text{ cm.}^2$. W. E. G.

Measurement of the Pressure of "Surface Fluids": Oleic Acid. A. MARCELIN (*Compt. rend.*, 1922, **175**, 346–348).—In order to measure the pressure exerted by thin layers of liquid resting on the surface of a second liquid, the author has

constructed a "surface manometer" which is sensitive and capable of rapid measurement. In the case studied, the addition of successive small quantities of oleic acid to the surface of water contained in a vessel results in a corresponding increase of pressure until a limiting value is reached, at which point a portion of the acid is floating as a drop of oil on the surface. This "surface saturation pressure" is comparable with the maximum tension of saturated vapour; it characterises the equilibrium between the "surface fluid"—a two-dimensional phase—and the same substance in a three-dimensional phase. At the equilibrium point, pressure on the surface liquid results in condensation into drops, and conversely. A further series of experiments was made in which the quantity of oleic acid was insufficient to cover the entire surface of the water. By surface compression, the pressure which is initially zero increases slowly at first, then more rapidly tending towards the saturation limit, and on allowing the surface liquid to expand, its pressure decreases in the inverse sense. If curves are drawn representing these pressures as functions of the surfaces, the second curve falls below the first; the two meet asymptotically, and the whole is of the same type as the curves of magnetic hysteresis. It is also shown that there is no limit to the extension of the surface liquid; this apparently corresponds with the limitless expansion of a gas.

H. J. E.

The Properties and Molecular Structure of Thin Films.
III. Expanded Films. N. K. ADAM (*Proc. Roy. Soc.*, 1922, [A], 101, 516—531).—In continuation of previous work, the author has investigated the effect of temperature on thin films of fatty acids spread on surfaces of distilled water, a phosphate solution, a dilute solution of hydrochloric acid, and of sodium hydroxide. At a certain temperature, dependent both on the nature of the substance in the film and on the composition of the solution, the films expand along the surface. The phenomena observed are discussed at length and the attempt is made to correlate the behaviour of such expanded films with that of a gas, the barriers on the surface over which the film is expanded representing the walls of the containing vessel in the case of the gas. The "gas" equation for the expanded films is of the Van der Waals's type, the b term, however, representing twice and not four times the area of the molecules, and the v term being replaced by the area of the film. It is shown that expanded films are one molecule thick, and that the molecules are probably arranged vertically, that is, they do not lie flat on the surface. It is shown that the steady increase in the expansion temperature with length of chain constituting the compound probably arises owing to the lateral attraction of chains lying side by side. The bearing of this result on the crystal structure of fatty acids and their esters is discussed. There appears to be no *a priori* reason for the view that lateral adhesion between the molecules prevents the films dissolving. Conclusions previously reached (this vol., i, 424) regarding the structure of *cis*- and *trans*-acids are now considered to be incorrect.

J. S. G. T.

Electric Endosmose. ALVIN STRICKLER and J. HOWARD MATHEWS (*J. Amer. Chem. Soc.*, 1922, **44**, 1647—1662).—The rate and direction of the endosmotic flow of acetone, amyl alcohol, nitrobenzene, pyridine, benzaldehyde, *n*-butyl alcohol, furfuraldehyde, isopropyl alcohol, and *o*-nitrotoluene have been determined, using a modified form of Briggs's apparatus (A., 1917, ii, 236; 1918, ii, 214). The influence of the addition of acids, bases, and salts on the endosmosis has also been investigated. An adsorption orientation hypothesis has been suggested to explain the establishment of the original charge at the surface of contact of the membrane and solvent. This states that the molecules of the solvent, on adsorption, are orientated on the membrane surface producing a charge by their polarity. If dissociated molecules are present, they affect the membrane charge by specific adsorption of the ions produced. This does not eliminate adsorption, but suggests a more comprehensive view of the mechanism for the establishment of the original charge. The experiments show that the permeability of the membrane is an important factor in determining endosmotic flow, and that it is possible to use and duplicate membranes of filter-paper when using organic solvents. The rate of endosmosis is not quite a linear function of the voltage applied when this is varied over a wide range. Briggs's results (*loc. cit.*) as to temperature effects with water have been confirmed with non-aqueous solvents. The valency rule does not hold with the non-aqueous solvents investigated, and the order of adsorption of ions and their relative adsorption varies with the solvent employed. The concentration curve exhibits a maximum with non-aqueous solvents and the flow at low concentrations is in the same direction as that of the pure solvent. The addition of water to non-aqueous solutions changes the endosmosis in the direction it would manifest in pure water, the first additions showing the greatest effect. The direction of endosmosis is not determined by the dielectric constant ratio, although this is probably a measure of the magnitude of flow. The Hofmeister series is not consistent when considering endosmotic effects in non-aqueous solvents.

J. F. S.

Dependence of the Adsorption by Charcoal on the Quantity of Charcoal and the Nature of the Adsorption Isothermal. A. FODOR and B. SCHÖNFELD (*Kolloid Z.*, 1922, **31**, 75—80).—The adsorption of acetic, lactic, and tartaric acids by various amounts of animal charcoal from solutions of various concentration has been determined. It is shown that with sufficiently dilute solutions of these substances and with a sufficient quantity of adsorbent the index $1/n$ of the adsorption equation approaches and reaches unity in the same way as was previously shown to be the case for amino-acids, polypeptides, and some carbohydrates (A., 1921, ii, 21). In sufficiently dilute solutions the value of n is very sensitive to changes in the amount of charcoal employed in the sense stated above. In less dilute solutions the value of n is practically independent of the amount of charcoal used. The

$(c_0 - c) - w$ curves, where w is the amount of adsorbent and $(c_0 - c)$ the quantity adsorbed, are parabolic and convex to the w axis and are steeper the greater the initial concentration, c_0 , and the smaller w is. The $c - w$ curves are also parabolic but concave to the w axis, the concavity being greater the larger c_0 and the smaller w . From this behaviour it is concluded that the expression $dc/dw = nc/w$ is correct, and interprets the adsorption equation $x = k'(c_0 - x)^{1/n}$ or $x^n = k(c_0 - x)$. In keeping with this interpretation of the index n , the rôle of this quantity in catalytic and fermentation processes is discussed.

J. F. S.

The Adsorption of Ions. JNANENDRA NATH MUKHERJEE (*Phil. Mag.*, 1922, [vi], 44, 321—346).—A critical résumé of the literature on the adsorption of ions in which the author applies his theory of the origin of the charge of a colloidal particle and its neutralisation by electrolytes (cf. this vol., ii, 198). The characteristic form of the adsorption isotherm, obtained when the ions are multivalent or complex, is explained on the basis of the greater chemical activity of the complex anions over that of the simple kations. It is assumed that the electrostatic attraction of the surface on the kation is less than the chemical affinity acting on the anion. With increasing concentration of electrolytes, the charge on the surface will decrease until a balance is reached between the chemical adsorption of the anion and the electrical adsorption of the kation. The second maximum is due to a balance between the electrical adsorption of the kation and anion. A theory of the action of acids and alkalis on the surface is developed for (1) an inert surface, and (2) a chemically active surface: preferential adsorption of one ion. The maximum charge due to acids gives a measure of the hydration of the surface. The conception of the chemical adsorption of the anion is applied to ionic equilibria on the surface of colloids and to the interchange of kations in the soil.

W. E. G.

The Connexion between Hydrolysis and Adsorption. W. MOELLER (*Z. Leder- u. Gerb.-Chem.*, 1922, 1, 160—165, 183—188; cf. *ibid.*, 1921, 1, 47; *Collegium*, 1920, 109, 152, 209, 267).—An investigation of the swelling and hydrolysis of gelatin in hydrochloric, acetic, lactic, and butyric acids yielded results similar to those with hide powder. Hydrolysis products with organic acids are adsorbed by the intact gelatin. With mineral acids hydrolysis, and with organic acids adsorption predominates.

CHEMICAL ABSTRACTS.

Free Energy of Gaseous Molecules with any [possible] Partition of Velocities. MAX PLANCK (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1922, 63—70).—A theoretical paper in which the question is raised and discussed as to whether or no the free energy of a mixture of similar gaseous molecules is made up additively of the free energies of the individual groups of velocities, when the partition of velocities is anything possible and the internal energy is in accord with the temperature. It is shown that the

above question must be answered in the affirmative. It is also shown that in the diffusion of two molecular systems similar in all respects except that of velocity, the reduction of the free energy is independent of the difference in the velocities. Further, in connexion with the foregoing, it is shown how this case explains the so-called Gibbs paradox, despite the fact that the velocity is a continually changing quantity. J. F. S.

Diffusion and Intertraction. C. G. SCHONEBOOM (*Proc. Roy. Soc.*, 1922, [A], **101**, 531—539).—The phenomenon of “pseudopodial” intertraction was originally observed by Wright, when blood-serum was run slowly on to an aqueous solution containing from 5 to 8% of common salt. The upper fluid is carried down into the lower, and the lower rises into the upper. The phenomenon may be observed with all inorganic and organic compounds soluble in water, provided the difference in specific gravity of the two solutions is not too great and the solutions do not react chemically. Surface tension alone is concerned in the production of the phenomenon, size of molecule and water of hydration exerting no influence. Distinction is drawn between the processes of “pseudopodial” intertraction and “simple” intertraction, a process intermediate between the former and the process of diffusion. J. S. G. T.

Preparation and Use of Collodion Osmometers. WILLIAM BROWN (*Ann. Bot.*, 1922, **36**, 433—439).—Details are given for the preparation and use of collodion thimbles for osmotic experiments. They are adapted for comparative rather than for absolute measurements. G. W. R.

Ionic Properties and Chemical Facts. IV. Lattice Energy and the Work of Ionisation of Inorganic Compounds. H. G. GRIMM (*Z. physikal. Chem.*, 1922, **102**, 113—140; cf. this vol., ii, 127, 483, 635).—A theoretical paper in which the author has collected and calculated the necessary data for comparing the regularities of the heat of formation of inorganic substances, and for showing the connexion between the heat of formation with the ionic properties, charge, radius, and structure. The lattice energy and work of ionisation have been calculated or approximated for about one hundred inorganic substances from the newer experimental data and where this is not available the differences of the lattice energy have been measured and the variation thus determined. J. F. S.

Ionic Properties and Chemical Facts. V. Connexion between Heat of Formation, Lattice Energy, and the Ionic Properties. H. G. GRIMM (*Z. physikal. Chem.*, 1922, **102**, 141—168; cf. preceding abstract).—The connexion between the heat of formation, lattice energy, ionic radius, ionic structure, and ionic charge has been investigated. It is shown that, in opposition to the heat of formation, the lattice energy of solid substances and the work of ionisation of gaseous substances, so far as these are known, are definitely related to the ionic properties, charge, structure, and radius. The lattice energy and work of ionisation

decrease with increasing radius both with anions and cations when the ions compared have the same number of exterior electrons. The characteristic gradation of the ionic radii is in general reproduced in the gradation of the lattice energy. The difference between the lattice energies of compounds of two outwardly similarly constructed cations or anions with a common anion or cation with the same exterior sheath, decreases with increasing radius of the common ion. Compounds which contain cations with eighteen exterior electrons have considerably greater lattice energies than compounds with the corresponding cation of the same period which have only eight electrons. The haloids of cations with eighteen or twenty exterior electrons show a much smaller dependence of the lattice energy on the halogen-ion radius than the haloids of cations with eight exterior electrons. In all cases investigated the series $U_{H^+} > U_{Li^+} > U_{Na^+}$ is true, where H^+ has 0, Li^+ has 2 and Na^+ has 8 exterior electrons. The empirical relationship $(U_{(SiX'_2)} - U_{(SiX''_2)})|4 > (U_{(AlX'_3)} - U_{(AlX''_3)})|3 > (U_{(NaX')} - U_{(NaX'')})$ is shown to be true, where U represents the work of ionisation of the substance in the brackets and X' and X'' are halogens. A similar expression is also true for boron and lithium haloids. These relationships can be deduced when heteropolar linkings are assumed for all the substances concerned. The haloids of carbon and the halogen-substituted hydrocarbons do not follow a relationship corresponding with that followed by ions containing the helium sheath. This indicates, as also do preliminary and approximate calculations on the models of BH_3 and CH_4 , that the carbon compounds concerned do not possess a polar linking. Making use of Born's cycle, many of the known regularities of the heat of formation of solid substances and of dissolved substances as well as the exceptions to the regularities can be investigated. The gradation of the heat of formation by the variation of a single ion of the compound can be attributed to the variation of three thermochemical quantities which depend on the ionic properties in the simplest manner. The periodicity of the heat of formation of oxides and chlorides can, in the neighbourhood of the maxima and minima, be explained by similar analysis.

J. F. S.

Effect of Sucrose on the Activities of the Chloride- and Hydrogen-ions. J. W. CORRAN and W. C. MCC. LEWIS (*J. Amer. Chem. Soc.*, 1922, **44**, 1673—1684).—The effect of the addition of sucrose on the activity of the chloride-ion in 0.1*N*- and 0.5*N*-solutions of potassium chloride solutions has been investigated by means of the cell $Ag|AgCl|KCl(c_1)||KCl(c_2)+Sucrose|AgCl|Ag$. It has been found that the increase in activity could be accounted for by simply taking account of the decrease in the total water present in the solutions; that is, the potassium- and chloride-ions are soluble in the water of hydration of the sucrose. The effect of sucrose on the activity of the hydrogen-ion in 0.1*N*-hydrochloric acid has also been investigated, making use of the assumption of MacInnes (*A.*, 1919, ii, 385) of the independent activity of the chloride-ion in solutions of chlorides of the same concentration.

It is shown by means of a comparison between the hydrogen-ion activities obtained in the present experiments, and the values obtained with a hydrogen electrode, that the hydrogen electrode measures the hydrogen-ion activity and not the geometric mean of the activities of the hydrogen-ion and the accompanying anion.

J. F. S.

Ionisation Constant of Hypochlorous Acid: Evidence for Amphoteric Ionisation. WILLIAM A. NOYES and THOMAS A. WILSON (*J. Amer. Chem. Soc.*, 1922, **44**, 1630—1637).—The electrical conductivity of dilute solutions of hypochlorous acid and mixtures of nitric acid and hypochlorous acid at 25° was measured, using a flowing electrolyte, with the object of testing the view of Stieglitz (A., 1902, ii, 66) that hypochlorous acid is an amphoteric electrolyte. The results show that the value k_a is 6.70×10^{-10} , the value of k_b for hypochlorous acid is too small to be determined by the change in the conductivity of 0.0001*N*-nitric acid when hypochlorous acid is added to it. When a current of air is passed through a solution of hypochlorous acid, chlorine monoxide and not the acid escapes. This indicates the presence of positive chlorine-ions in such a solution and confirms the amphoteric ionisation of the acid; $\text{HClO} \rightleftharpoons \text{H}^+ + \text{ClO}'$; $\text{HClO} \rightleftharpoons \text{Cl}' + \text{OH}'$. If the Lewis-Langmuir hypothesis is accepted, it requires an interpretation consistent with these facts.

J. F. S.

State of Aggregation and Liquid Crystals. O. LEHMANN (*Z. physikal. Chem.*, 1922, **102**, 91—101).—In a recently published work ("Die Aggregatzustände") Tammann has questioned the existence of liquid crystals because they do not fall into the scheme of states of aggregation. The author, therefore, has repeated the evidence on which the existence of the liquid crystal state of aggregation is based.

J. F. S.

Glass Suspensions produced by Rubbing Glass Walls with Glass Rods. ROBERT FRICKE (*Kolloid Z.*, 1922, **31**, 80—81).—Moderately concentrated glass suspensions may be prepared by rubbing the sides of a test-tube with a glass rod. These suspensions are alkaline to phenolphthalein and have a normality of the order 1/1000 which increases on keeping the suspension. They generally settle completely in twenty-four hours, but the settling is more rapid if electrolytes are added. The particles are negatively charged and wander to the anode on the application of an electric current. Examined in the ultramicroscope, the particles are seen to have diameters varying between 20μ and 0.5μ .

J. F. S.

A New Apparatus: The Nephelectrometer. I. NEWTON KUGELMASS (*Compt. rend.*, 1922, **175**, 343—345).—Changes in the degree of aggregation of a colloidal solution may be observed quantitatively by measuring variations in the degree of transparency. This is effected by allowing light of weak intensity from a constant source to fall on a sensitive thermopile after traversing a vessel containing the solution. The apparatus is

standardised by taking a series of readings after filling the vessel with distilled water. The author has used the apparatus in order to observe the coagulation of fibrinogen and the results obtained are expressed numerically.

H. J. E.

Nephelometric Effect of Colloidal Systems of Different Size of Particles. H. BECHHOLD and F. HEBLER (*Kolloid Z.*, 1922, **31**, 70—74).—The connexion between the turbidity and size of the suspended particles has been examined nephelometrically in the case of suspensions of barium sulphate in various mixtures of ethyl alcohol and glycerol. The degree of dispersion of the suspensions varied from $2.5\ \mu$ to $4\ \mu\mu$. The results show that for suspensions containing the same amount of barium sulphate but of varying degrees of dispersion, the turbidity increases from $2.5\ \mu$ downwards. The maximum turbidity is reached with particles of about $800\ \mu\mu$ for white light, that is, in the region of the extreme red. Further reduction of the size of the particles caused the turbidity to decrease strongly. It is in this region that Rayleigh's law holds. By the term turbidity is to be understood the effect, observed with the nephelometer, which is brought about by the diffraction of the light by the disperse phase. A method is described whereby the diameter of submicrons and amicrons may be determined if a comparison turbidity of a substance with particles of known diameter is available.

J. F. S.

Turbidity Standard. H. BECHHOLD and F. HEBLER (*Kolloid Z.*, 1922, **31**, 132—137).—The authors have prepared an easily reproducible and fairly stable standard turbidity and a sol suitable for use as a standard in work on turbidities and suspensions. They characterise as standard turbidity one which contains 1/1000 mol. of barium sulphate; this is prepared by mixing 1/500 mol. of hydroxylamine sulphate dissolved in glycerol with an equal volume of 1/500 mol. barium chloride also dissolved in glycerol. The precipitate is chiefly made up of particles $2.5\ \mu$ in diameter. The standard sol is characterised as a turbidity which contains 1/200 mol. of barium sulphate; this is prepared by mixing barium chloride and magnesium sulphate dissolved in a mixture of glycerol (6.5) and *isobutyl* alcohol (1.5). This is three times as turbid as the standard turbidity and can be made of the same turbidity by mixing with glycerol containing 15% of *isobutyl* alcohol. The standard sol consists of primary particles of not more than $90\ \mu\mu$ diameter. The standard sol is stable and constant for at least six months, whilst the standard turbidity is not trustworthy after eight days.

J. F. S.

Theory of the Mechanical Synthesis of Colloids. F. SEKERA (*Kolloid Z.*, 1922, **31**, 137—147).—The theory of the production of colloids in Plauson's colloid mill is briefly as follows. The mechanical grinding process bursts the active molecular compounds in the interior of the solid substance and produces particles of colloidal dimensions. From the surface of these particles the residual valencies tend to cause an aggregation of the small particles, so that secondary to the dispersion an aggregation process

is taking place. To retard or prevent the aggregation, the residual valencies are saturated by the addition of an electrolyte which produces salt complexes and charges the particles. J. F. S.

Dielectric Constants of Colloidal Solutions. J. ERRERA (*Kolloid Z.*, 1922, **31**, 59—64).—A method for measuring the dielectric constants of colloidal solutions, based on the Nernst condenser method is described and has been used to measure the dielectric constant of vanadium pentoxide sols. It is shown that a solution containing 14 per thousand has a dielectric constant of 400 in comparison with that of water of 81. This high value is not obtained with the freshly prepared sol, but appears only after long preservation. Thus a freshly prepared sol gave a value 74.7 which in seventeen days had risen to 94.8. The value given above was for a sol which had been kept for five years. The dielectric constant shows a characteristic dilution curve and a definite dependence on the temperature, current density, and the potential amplitude. The dielectric constant obtained is doubtless connected with the well-known double refraction of this sol.

J. F. S.

An Experimental Test of Smoluchowski's Theory of the Kinetics of the Process of Coagulation. JÑANENDRA NATH MUKHERJEE and B. CONSTANTINE PAPAConstantinou (*Phil. Mag.*, 1922, [vi], **44**, 305—320).—According to the theory of Smoluchowski (cf. A., 1917, ii, 297), the successive stages in the coalescence of a colloidal solution are always the same and depend only on the time, and thus any property of the sol that varies continuously can be utilised to fix a definite stage in the coalescence. If his equations hold, all curves showing variations in the physical properties of the colloidal solution should be similar. Previous experimental work in which ultramicroscopical measurements have been made has yielded inconclusive data, possibly owing to difficulties inherent in the methods of measurement. The authors have tested the views of Smoluchowski by measurements of the changes in colour of gold sols on the addition of an electrolyte (cf. T., 1920, **117**, 1563). Since the absorption coefficient in the red region varies continuously with the coagulation, the attainment of a definite value of the absorption coefficient for a fixed wave length ($683\text{ }\mu\mu$) is taken as representing a definite stage in the coalescence. Experimental values of the absorption coefficients for the addition of several concentrations of potassium chloride, potassium nitrate, and barium chloride have been previously given (*loc. cit.*), and it is shown that the ratios of the times required to reach the same absorption coefficient are independent of the time or the stage of coalescence. The data thus supply the best evidence so far recorded in favour of the theory of Smoluchowski; T in his equations is a constant in the case of the gold sols within the limits of coagulation studied. The percentage of successful collisions between the colloidal particles increases rapidly with increase in concentration of electrolyte and varies markedly with changes in temperature.

W. E. G.

Colloidal Solutions of Carbon in Water. P. C. L. THORNE (*Kolloid Z.*, 1922, **31**, 119—132).—The author briefly summarises the literature on the formation of colloidal solutions of carbon and discusses the results obtained. An account is given of the preparation of colloidal solutions of carbon by the dispersion of charcoal anodes in the electrolysis of solutions of ammonia, sodium hydroxide, and dilute acids; similar experiments were carried out with graphite electrodes. A stable carbon sol may be prepared by the electrolysis of a solution of ammonia for six hours between two carbon electrodes with an anode current density of 0.6—1.2 amperes/cm.² and a voltage of 220. On filtering, the solution had a concentration 0.145*N* of ammonia and gave a residue of 0.034 gram per 100 c.c. This residue was insoluble in water, but redissolved in a dilute solution of ammonia; the excess of ammonia may be removed by boiling and the sol is then more stable than one which has been dialysed and still contains 0.039*N* ammonia. The ammonia-free sol is deep black in layers greater than 1 cm. thick and in thinner layers brown, and is made up of particles of about the same size as those of metallic sols. The influence of electrolytes on the sol has been investigated and the number of millimols. necessary to coagulate 1000 c.c. of the dialysed sol found to be: hydrochloric acid, 60; sodium hydroxide, 290; ammonium hydroxide, >9000; sodium chloride, 450; barium chloride, 0.5; and aluminium chloride, 0.3. These quantities are very similar to those required to coagulate a platinum sol. Similar experiments have been carried out with graphite sols and results of the same kind obtained. The most marked difference between the carbon sols and the graphite sols is that of colour, the former being brown and the latter black. An analysis of the dried sol shows that it is not a pure carbon sol which has been dealt with, but a mixture, the composition being C, 66.61%; H, 1.99%; O, 15.25%, insoluble and incombustible residue (probably silica), 16.15%.

J. F. S.

Electrical Properties of Silicic Acid Sols. OTTO LÖSENBECK (*Koll. Chem. Beihefte*, 1922, **16**, 27—46).—A number of experiments are described on the influence of silicic acid sols on the electrical conductivity of solutions of hydrochloric acid, and on the kataphoresis of the sol both pure and in the presence of hydrochloric acid of various concentrations. It is shown that the electrical conductivity of hydrochloric acid solutions of concentrations up to 0.01*N* is considerably reduced by the presence of silicic acid sol. This reduction does not take place instantaneously, but the amount of decrease increases with time according to a function of e , that is, the decrease is at first rapid and then continuously slower until it becomes asymptotic and a limiting value is approached. From the measurements of the migration velocity of the silicic acid particles under a known potential fall, the contact potential has been calculated by means of Smoluchowski's theory. It is shown that the particles of a pure silicic acid sol are negatively charged and that the charge is steadily reduced by the addition

of hydrochloric acid until the isoelectric point is reached. With further addition of acid the sign of the charge changes and the charge increases until the positive value is greater than the original negative value. The silicic acid particles are shown not to be uniform. The contact potential of the particles determined in different concentrations of the same preparation shows that this quantity is dependent on the concentration of the sol, in the sense that the isoelectric point of different sols lies at greater concentrations of hydrochloric acid the greater the concentration of the sol. The observed results are explained by the assumption that the silicic acid particles are saturated with hydrochloric acid, like a sponge, and that this is taken up slowly. The hydrogen-ions are expelled from these sponges with a definite tension, so that the contact potential between particle and solution may be approximately represented by the Nernst formula. J. F. S.

Colour of Photochlorides and Colloidal Silver. II. KARL SCHAUM and THEODOR MARX (*Kolloid Z.*, 1922, **31**, 64—70; cf. A., 1921, ii, 506).—In a previous paper (*loc. cit.*) the authors describe the presence of faintly illuminating red particles in silver sols of medium dispersion; these particles do not conform to Mie's theory. The authors now show that the red particles do not exist and the red colour observed was due to a contrast with the many green particles present. A method of determining the true colours of the colloidal particles in the presence of other particles is described. Previous attempts to reverse the order of colours obtained in photographic intensification by reduction failed, but it is now shown that a complete reversal may be obtained as follows. A blue silver sol is mixed with an equal volume of 10% gelatin solution and allowed to solidify, then a concentrated solution of ammonium hydroxide, potassium cyanide, or sodium thiosulphate is poured on to it and allowed to diffuse. After several days the following range of colours is observed, commencing at the top of the tube: colourless, yellow, orange, red, reddish-violet, bluish-violet, and blue. The action of electrolytes in definite amounts on silver sols is to produce definite colours. Thus in the case of magnesium sulphate and silver sols, 2 c.c. of the sol when treated with the following quantities of *N*/20-magnesium sulphate gives the colours indicated: 0 c.c., yellow; 0.10 c.c., orange; 0.20 c.c., red; 0.25 c.c., purple; 0.30 c.c., reddish-violet; 0.50 c.c., bluish-violet; and 1.50 c.c., blue. Similar changes were also obtained with ammonium chloride, sodium chloride, and potassium sulphate. J. F. S.

Behaviour of Carey Lea's Silver Sol towards Electrolytes and Hydrophilic Colloids. H. FREUNDLICH and E. LOENING (*Koll. Chem. Beihefte*, 1922, **16**, 1—26).—Carey Lea's silver sol behaves as an entirely hydrophobic sol, and since its particles are negatively charged the valency of the kations and the adsorbability are of most importance in its coagulation. The dependence of the coagulation value on the concentration of silver micellæ is bound up with the valency of the kations. The coagulum has a quite

different appearance when it is produced by univalent kations from that produced by bi- and ter-valent kations. Hydrophilic colloids such as saponin and gum arabic exert a protective action at all concentrations. This action increases strongly with the concentration of the hydrophilic colloid in the coagulation by trivalent kations, less strongly with bivalent kations, and weakly with univalent kations. This is explained by the fact that with the trivalent kations much smaller concentrations are necessary, so that the displacing action of the protective colloid is made more noticeable. Other hydrophilic colloids such as gelatin and caseinogen in smaller concentrations coagulate the silver sol, but above a definite concentration exert a protective action; this concentration increases with the concentration of the silver micellæ in the sol. The coagulation with small concentrations is, in the main, similar to the coagulation of acid gold sols by hydrophilic sols investigated by Gann (A., 1917, ii, 21). In neither case need complete coagulation occur, and an increase in the sensitiveness is brought about, that is, the metallic sol which contains small quantities of the hydrophilic colloid, is more sensitive toward electrolytes than the pure sol. Coagulation and increase in the sensitiveness by means of hydrophilic colloids are due to the fact that the sols of the hydrophilic colloids contain ions. In the case of the negative metallic sols, the colloid kations are operative and coagulate in the same manner as other kations. The silver sol is not discharged in solutions of colloids such as gelatin and caseinogen which are concentrated enough to exert a protective action, but here it is negatively charged. This is explained by the assumption that the amphoteric ions of gelatin lie with their positive ends toward the silver particles and the negative ends toward the interior of the solution. The above explanations are in keeping with the facts, that gelatin behaves in a protective but non-coagulating manner toward an alkaline gold sol, because even in alkaline solutions it contains too few colloidal kations; on the other hand, clupein sulphate, a protamine salt, which contains definite colloidal kations, coagulates an alkaline gold sol strongly. J. F. S.

Influence of Temperature on the Coagulation of Colloidal Gold. H. LACHS and STEPHANIE GOLDBERG (*Kolloid Z.*, 1922, **31**, 116—119).—The time required for the coagulation of gold sols prepared in various ways by a constant amount of sodium chloride has been determined at temperatures up to 70°, and in this way the influence of temperature on the rate of coagulation ascertained. The results show that the influence of temperature corresponds with that demanded by Smoluchowski's hypothesis, namely, that the coagulation time is inversely proportional to the absolute temperature. The sensitiveness, toward temperature changes, of the coagulation of colloidal gold is very much smaller than that of chemical reactions. J. F. S.

The Kinetics of the Coagulation of Proteins by Heat. HEINRICH LÜERS and MAX LANDAUER (*Z. angew. Chem.*, 1922, **35**, 469—471).—The velocity of coagulation of the plant albumin,

leucosin, was determined by the direct weighing of the coagulum produced at intervals during the reaction. The change of hydrogen-ion concentration during the reaction was very slight. It was concluded that the coagulation occurs in two stages; a chemical denaturation process followed by a colloidal phenomenon of coagulation, which is a flocculation of the denatured protein particles. The denaturation of the leucosin particles was shown to be a chemical reaction of the first order. The temperature coefficient of the denaturation in a medium of p_{H} 6.09 and at temperatures between 52.90° and 57.05° was 1.47 per 1°. A. G. P.

Is the Gelatin-Gum Arabic Coagulation a Chemical or a Colloid-chemical Process? F. W. TIEBACKX (*Kolloid Z.*, 1922, **31**, 102—103).—A discussion of the coagulation of gelatin-gum arabic mixtures by acids, alkalis, and salts, from which it is shown that the coagulation is a mixed process which can be regarded as in part of a chemical nature and in part of a colloid-chemical nature. J. F. S.

Influence of Substituents on Various Chemical Reactions. SVEN BODFORSS (*Z. physikal. Chem.*, 1922, **102**, 40—53).—It has been shown previously (A., 1918, i, 229) that a number of substituted aromatic aldehydes react with bromoacetophenone in the presence of sodium ethoxide according to the equation: $\text{Ph}\cdot\text{CHO} + \text{CO}\cdot\text{Ph}\cdot\text{CH}_2\text{Br} \rightarrow \text{CO}\cdot\text{Ph}\cdot\underset{\text{O}}{\underset{\text{O}}{\text{CH}}}\cdot\text{CH}\cdot\text{C}_6\text{H}_5$, whilst others do

not react in this way. The aldehydes which react all contain a negative substituent and those which do not may be brought to react by substituting such a negative group in them. It is now shown that the acids produced from the aldehydes which react are stronger than those produced from the aldehydes which do not react. The relationship between the reactivity of the aldehydes and the strength of the corresponding acid has been investigated. The strength of a number of substituted benzoic acids has been determined from conductivity measurements and the dissociation constant compared with the values for other acids found in the literature. The following newly determined values of K at 25° are recorded: 3-nitroanisic acid, 1.9×10^{-4} ; 3-bromoanisic acid, 7.2×10^{-5} ; cumic acid, 5.2×10^{-5} ; piperonylic acid, 4.5×10^{-5} . A further series of experiments has been carried out to ascertain the relationship between the maximum work of a given type of reaction and the nature of the substituting group. The reaction chosen is represented by the equation $\text{H} + \text{AgBz}(\text{solid}) = \text{HBz}(\text{solid}) + \text{Ag}$ and the maximal work of this reaction has been calculated from *E.M.F.* measurements of cells of the type $\text{Ag}|\text{AgBz}, \text{HBz}(\text{solid})||\text{HBz}(\text{solid})|\text{H}_2$ and $\text{Ag}|\text{AgBz}(\text{solid})||\text{HBz}(\text{solid})|\text{Quinhydrone}|\text{Pt.}$ at 25° (cf. Biilmann, A., 1921, ii, 372). The following values of the *E.M.F.* (π), the maximum work (A cal.), and the dissociation constant, respectively, are recorded: 5-nitrosalicylic acid, 0.066, 1520, 8.9×10^{-3} ; salicylic acid, 0.087, 2010, 1.0×10^{-3} ; *m*-nitrobenzoic acid, 0.109, 2510, 3.5×10^{-4} ; 3-nitroanisic acid, 0.135, 3110, 1.9×10^{-4} ; anisic acid, 0.144, 3320,

3.2×10^{-5} ; *m*-nitrocinnamic acid, 0.145, 3340, 8.3×10^{-5} ; *o*-chlorobenzoic acid, 0.147, 3390, 1.3×10^{-3} ; benzoic acid, 0.154, 3550, 6.7×10^{-5} ; *p*-nitrobenzoic acid, 0.160, 3690, 4.0×10^{-4} ; 3-bromoanisic acid, 0.163, 3760, 7.2×10^{-5} ; and piperonylic acid, 0.165, 3800, 4.2×10^{-5} . The above results show that generally the maximum work decreases with increasing dissociation constant. The cases where this relationship is not strict are probably to be explained either by the formation of hydrates by the silver salts or by the formation of acid silver salts. J. F. S.

Equilibrium in Heterogeneous Systems. JA. K. SYRKIN (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1921, **4**, 161—165).—Investigation of the reaction $\text{CaSO}_4 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{Na}_2\text{SO}_4$ with concentrations ranging from 0.01 to 0.002 gram-mol. per litre and thus corresponding with widely varying degrees of dissociation of the component salts, shows that the reaction does not conform to the law of equilibrium, the "constants" of the reaction exhibiting wide divergences. The reaction is reversible, the reversibility, that is, the proportion of non-reacting molecules, amounting to 58% at the ordinary temperature and at low concentrations. At 7°, scarcely any action occurs. The value of the reversibility at 38° is similar to that at 18°, probably owing to the solubility of calcium sulphate being at a maximum at 38°. The reversibility is a function of the concentration and increases with dilution, the more rapidly at low temperatures.

Thus, with reactions involving the formation of a new phase, the laws of equilibrium are incomparably more complex than with homogeneous reactions. At present, the dependence of the reversibility on the concentration is expressible only by an empirical relation of the form $Z = 1 + ac + bc^2$ T. H. P.

The Equilibria in Aqueous Solutions of the Alkali Metal Bisulphites. EDWARD CHARLES CYRIL BALY and ROBERT ARTHUR BAILEY (*T.*, 1922, **121**, 1813—1821).

Equilibria and Reaction Velocities. W. F. BRANDSMA (*Chem. Weekblad*, 1922, **19**, 318—322).—The treatment of reaction velocities based on molecular collisions of substances in the gaseous state or in dilute solution becomes difficult when the course of a reaction is not expressed by a simple equation, and experimental results do not agree with theory. The conditions leading to equilibrium may be regarded from two points of view, the first dealing with the forces involved, that is, the energy units, and the second with space factors, that is, with entropy units. The factors deduced from the first vary inversely with the absolute temperatures, and so determine the temperature coefficients; the entropy factors are independent of temperature.

This division is of great importance in organic reactions, since the theoretical treatment can take due account of both energy and space factors. S. I. L.

Theory of the Velocity of Chemical Reactions. J. N. BRÖNSTED (*Z. physikal. Chem.*, 1922, **102**, 169—207).—A theoretical

paper in which the laws of the velocity of chemical reactions are considered. It is shown that chemical reactions between neutral molecules, or between neutral molecules and ions, are normal, that is, they follow very closely the law of mass action and are insensitive or only slightly sensitive to the addition of a neutral salt. Reactions between ions are abnormal, that is, the velocity constant is to a high degree dependent on the concentration of the reacting ions and on the concentration of an added neutral salt. For thermodynamical reasons, the concentrations or osmotic partial pressures in the ordinary kinetic reaction equations are to be replaced by the activities, and the equations are then true when the activities alone are changed. The reaction determinative of the velocity in a chemical change consists of the formation of an unstable critical complex in the sense put forward by Marcellin (A., 1915, ii, 328). The electrical charge of the complex is the sum of the charges of the reacting molecular species. The regularities and exceptions mentioned above are to be explained by the assumption that the velocity is inversely proportional to the activity coefficient of the critical complex, and that this is influenced by changes in the salt concentration in the same way as the ordinary ions. The data concerning the activity coefficients necessary for calculating the anomalies in the velocity are most easily obtained from solubility determinations of sparingly soluble salts in solvents containing dissimilar ions. The dependence of the activity coefficient on the concentration, obtained in this way, for the ions of various types makes it possible to calculate the extent of the neutral salt action, that is, the kinetic anomalies for the various types of reactions. On the basis of the foregoing, the following theoretical result is obtained. In reactions between ions of the same sign the salt action is positive, that is, the velocity is increased by an increasing salt concentration. In reactions where the reacting ions have opposite signs, the salt action is negative, that is, the reaction is retarded by increasing salt concentration. These theoretical results have been applied to a large number of chemical reactions in solution and for the greater number found to be confirmed, in some cases quantitatively. The kinetic and static anomalies may be removed by employing a concentrated solution of an indifferent salt as solvent.

J. F. S.

Velocity of Decomposition of Crystalline Substances.

A. SIEVERTS (*Z. physikal. Chem.*, 1922, **102**, 89—90).—An answer to Hinshelwood and Bowen (this vol., ii, 628; see also this vol., ii, 360; A., 1920, ii, 743; 1921, ii, 443).

J. F. S.

Mechanism of the Reduction of Permanganate and its Physico-chemical Foundation. III. Reaction between Manganate and Formic Acid. JOSEF HOLLUTA (*Z. physikal. Chem.*, 1922, **102**, 32—39; cf. this vol., ii, 448, 628).—The velocity of the reaction between sodium manganate and sodium formate has been determined at temperatures varying between 27.4° and 22.6°, with constant concentrations of manganate and hydroxyl-ion and also with varying concentrations of all constituents. The results show

that the reaction as measured is of the second order, and is to be represented by the equation $\text{MnO}_4'' + \text{HCO}_2' + 2\text{H}_2\text{O} = \text{Mn}(\text{OH})_4 + \text{CO}_3'' + \text{OH}'$. Intermediate stages therefore do not need to be taken into account in the mechanism of this reaction. J. F. S.

Dependence of the Velocity of Alkaline Hydrolysis of Esters on the Constitution of the Alcohol. I. L. SMITH and HUGO OLSSON (*Z. physikal. Chem.*, 1922, **102**, 26—31).—The alkaline hydrolysis of propyl acetate and isopropyl acetate by 0.1145N-sodium hydroxide has been determined at 20°. The reaction constants are found to be 4.23 and 1.263, respectively, giving as the ratio between the propyl and isopropyl esters the value 3.4, a value which is very near the value (3.2) found by Menshutkin for the ratio of the rates of formation of the two esters.

J. F. S.

Catalysts and Chemical Equilibrium. J. F. DURAND (*Bull. Soc. chim.*, 1922, [iv], **31**, 759—762).—The conclusions drawn by Clarens (this vol., ii, 436) with regard to the effect of catalysts on the equilibrium of a system are criticised.

H. J. E.

Catalytic Formation of Water Vapour from Hydrogen and Oxygen in the Presence of Copper and Copper Oxide. ROBERT N. PEASE and HUGH S. TAYLOR (*J. Amer. Chem. Soc.*, 1922, **44**, 1637—1647; cf. this vol., ii, 148).—The catalytic combination of hydrogen and oxygen in the presence of metallic copper (produced by the reduction of copper oxide in hydrogen at 150—200°) has been investigated over the temperature range 100—200°, using gaseous mixtures containing up to 5% of oxygen. The results show that combination is practically complete at 200°, and is just measurable at 100°. In nearly all cases, copper oxide is formed simultaneously with water. After the oxygen is shut off and pure hydrogen alone passed over the catalyst, the oxide so formed is reduced at a greater rate than that of the formation of water while the oxygen is passing. Between 130° and 100°, the rate of oxidation of the copper and the rate of reduction of the oxide so formed, as well as the catalytic activity, suffer a marked reduction. At 130°, with oxygen equivalent to 10 milligrams of water passing in five minutes, the rate of formation of water passes through a maximum to a steady minimum value. The above results are satisfactorily explained by assuming that the combination takes place mainly as a result of the alternate oxidation and reduction of the catalyst, the reduction reaction being complicated by the known inhibitory influence of free oxygen on that reaction. J. F. S.

Catalysis of Hydrogen Peroxide by Finely Divided Platinum. The Influence of Inhibitors. EDWARD BRADFORD MAXTED (*T.*, 1922, **121**, 1760—1765).

Bohr and Langmuir Atoms. (SIR) OLIVER LODGE (*Nature*, 1922, **110**, 341).—In view of the difficulty of explaining molecular combination in terms of electrical attraction between revolving electrons composing the peripheral parts of an atom (in accordance with

the demands of spectroscopic observations) rather than in terms of a static arrangement (more suited to the facts of chemical combination), it is considered that the idea of electrical attraction between the atoms as the major chemical force should give place to that of the interlacement of the magnetic fields which inevitably accompany rapidly revolving electric charges. A. A. E.

The Neuburger Nuclear Model. F. PABLO VALERAS (*Physikal. Z.*, 1922, **23**, 304—305).—The relative merits of the Neuburger (cf. this vol., ii, 208, 365) and Meitner (cf. *ibid.*, ii, 15) models are discussed and an objection is raised to the latter model since it cannot be applied to the nuclei of boron¹⁰, boron¹¹, nitrogen, or fluorine. The Neuburger model is unsatisfactory, since it requires the existence of *isohelium* nuclei. The author proposes a new model in which the nuclear formulæ are given by $F_k = n\alpha + pH^+ + v\beta$ which takes account of all known atoms. W. E. G.

The Neuburger Nuclear Model. LISE MEITNER (*Physikal. Z.*, 1922, **23**, 305).—A reply to Pablo Valeras (preceding abstract), pointing out that the new model is not in agreement with radioactive phenomena. W. E. G.

The Neuburger Nuclear Model. MAXIMILIAN CAMILLO NEUBURGER (*Physikal. Z.*, 1922, **23**, 305—307).—A reply to F. Pablo Valeras (cf. preceding abstracts). The assumption of the existence of the *isohelium* nucleus is useful in explaining the structure of Gl⁹ which cannot be expressed by the new model. A schematic representation is given of the structure and genesis of some of the lighter atoms. W. E. G.

The Stability of Atom Nuclei, the Separation of Isotopes, and the Whole Number Rule. WILLIAM D. HARKINS (*J. Franklin Inst.*, 1922, **194**, 165—211; cf. A., 1915, ii, 543, 544, 814; 1920, ii, 479, 541).—The author has pointed out that of the first twenty-seven elements except hydrogen the atomic weights are very close to whole numbers on the basis of O=16, and those of which the atomic weights are multiples of 4 are much closer to whole numbers than the others. The simple explanation is that all the elements are intra-atomic compounds of hydrogen and that whilst in molecular compounds the latter has the atomic weight 1.0078, in these much closer combinations it has the atomic weight 1.000. Those atoms of which the atomic weights are divisible by 4 are regarded as being built up of α -particles which are known to be the nuclei of helium atoms. A system of notation denoting the electronic structure of the atoms has been introduced; for example, "Oxygen=16" is written $p_{16}e_{16}$ as a compound of 16 positive and 16 negative electrons. This is further elaborated to show the number of α -particles (a) present in the nucleus, and negative electrons in the nucleus are differentiated from those in the planetary system. The nuclei of elements of even atomic number can be represented as built up in this way of α -particles alone or with "cementing" negative electrons, usually two in

number. Those of odd number cannot be so represented but need the introduction usually of a "proton-electron" group, p_3e_2 .

From a consideration of the composition of meteorites, the earth's crust, and the radioactive series, the conclusion is drawn that the elements of even atomic number are much more stable than those which are odd. The atomic numbers of the five undiscovered elements are all odd. The stability is attributed to the great stability of the α -particle in the nucleus. The special relativity theory is used to explain the loss in weight of the four hydrogen atoms (4×1.0078) which form the helium atom (4.000), and the energy freed by this loss is shown to be 6.708×10^{11} cal. per gram-atom of helium formed. This theory is also applied to the calculation of weight losses in radioactive disintegrations, and it is shown that an experimental determination of the loss of mass of radiothorium over a period of three years would be a check on the validity of the theory.

A. C.

Model of the Ionised Hydrogen Molecule. W. PAULI, jun. (*Ann. Physik*, 1922, [iv], **68**, 177—240).—A mathematical investigation of the conditions determining the stability of a model representing the motion of an electron under the influence of two positively charged nuclei, at rest and in equilibrium, a structure illustrating the ionised hydrogen molecule H_2^+ met with in positive rays. The analysis is based on an application of the quantum theory, and the extension of Bohr's correspondence principle to impacts between atoms or molecules and free electrons. Various orbits are investigated. Of quantised orbits symmetrical with regard to the medium plane bisecting at right angles the line joining the nuclei, that of minimum energy is characterised by three quantum numbers, 0, 1, 1, and fills up in a uniform manner the space contained within an ellipsoid of revolution. The possibility of the existence of a stable unsymmetrical quantised orbit remains for the present open. Consideration of the value of the ionisation potential of the hydrogen molecule indicates that the structure of the ionised hydrogen molecule is essentially meta-stable, and it is concluded that its real normal representation consists of an electron moving in a circular orbit in the medium plane between the nuclei, and characterised by conditions of stability and energy similar to those of the earlier Bohr model of the helium atom. Preliminary remarks are made concerning the application of the theory to the band emission spectrum of the ionised hydrogen molecule.

J. S. G. T.

The Mathematics of the Dicyclic Colour Theory, and a New Theory of the Structure of the Nitrogen Atom. JAMES MOIR (T., 1922, **121**, 1808—1813).

The Distribution of Electrons around the Nucleus in the Sodium and Chlorine Atoms. W. LAWRENCE BRAGG, R. W. JAMES, and C. H. BOSANQUET (*Phil. Mag.*, 1922, **44**, 433—449).—The distribution of electrons in the atoms of sodium and chlorine has been determined by measuring, by the method of X-ray analysis, the reflecting power per unit volume of the units constitut-

ing a crystal of sodium chloride. The experimental results indicate that the sodium atom comprises seven electrons arranged on a shell of radius 0.29 \AA . and three electrons on a shell of radius 0.76 \AA . The chlorine atom comprises ten electrons arranged on a shell of radius 0.25 \AA ., five electrons on a shell of radius 0.86 \AA ., and three electrons on a shell of radius 1.46 \AA . Alternatively, the results are interpreted by continuous curves in which the electron density is plotted as ordinate against the corresponding distance of the electron from the centre of the atoms as abscissa. Considerable agreement is found between the experimentally determined values of the distribution factor F and those calculated for an atom of the type proposed by Bohr and comprising two electrons describing circular one-quantum orbits of radius 0.05 \AA ., four electrons describing two quantum circular orbits of radius 0.34 \AA ., and four electrons describing two-quantum elliptical orbits of semi-major axis 0.42 \AA . The principal source of error in the conclusions arises owing to lack of information as to the part played by "extinction" in affecting the intensity of X-ray spectra. The results indicate that there cannot be, either in the sodium or chlorine atom, an outer shell of eight electrons. Eight electrons revolving in circular orbits of the same radius are equally inadmissible. J. S. G. T.

The Molecular Structure of Carbon Oxysulphide and Carbon Disulphide. A. O. RANKINE (*Phil. Mag.*, 1922, [vi], 44, 292—300).—The mean collision areas of molecules of carbon oxysulphide and carbon disulphide are calculated from certain assumptions based on the Lewis-Langmuir theory of valency (cf. A., 1921, ii, 192, 584). The electronic configuration in carbon oxysulphide is the same as that of an arrangement of argon and neon atoms in the sequence neon-neon-argon, and that of carbon disulphide corresponds with the sequence of inert atoms argon-neon-argon. The radii of the outer electron shells of atoms possessing the electronic configurations of neon and argon are 0.65 \AA . and 1.03 \AA ., respectively, and the radii of the collision spheres of argon and neon atoms are 1.15 \AA . and 1.44 \AA ., respectively. For the purpose of intermolecular encounters, the molecules consist of overlapping spheres the centres of which are separated by 1.30 \AA . for neon-neon and 1.68 \AA . for the argon-neon combination, and of which the radii are the collision radii of argon and neon atoms. The mean collision area of carbon oxysulphide should lie between the limits $1.00 \times 10^{-15} \text{ cm}^2$ and $1.09 \times 10^{-15} \text{ cm}^2$ and of carbon disulphide between the limits $1.23 \times 10^{-15} \text{ cm}^2$ and $1.37 \times 10^{-15} \text{ cm}^2$. In the former case, the agreement between the results of this examination and the value obtained by Smith (cf. this vol., ii, 686) is striking. In the latter case, comparison is not yet possible. W. E. G.

Valency Theories of Organic Chemistry. F. HENRICH (*Jahrb. Radioaktiv. Elektronik.*, 1922, 19, 1—38).—An historical account of the theory of valency leading up to a discussion of the modern views of Kossel, Hinsberg, J. Stark, Pauli, and Vorländer on the valency of organic compounds. W. E. G.

The Electron Theory of Valency as Applied to Organic Compounds. JULIUS STIEGLITZ (*J. Amer. Chem. Soc.*, 1922, **44**, 1833—1834).—An addendum to a previous communication (this vol., ii, 560).

The rupture of the union of two carbon atoms by oxidation, involving the loss of two electrons by one of the atoms or jointly by both, takes place with particular ease when two neighbouring carbonyl groups are present in the molecule. In this case, there are no exposed valencies, but the structure is undoubtedly highly polar. Thus oxalic acid may be formulated, $\text{H}^+ - \text{O}^+ \begin{array}{c} \text{C} \\ \text{+} \end{array} \begin{array}{c} \text{C} \\ \text{+} \end{array} - \text{O}^+ \text{H}$,
 $\begin{array}{c} \text{+} \\ \text{O} \end{array} \begin{array}{c} \text{+} \\ \text{O} \end{array}$

and the high polarity of the field surrounding the carbon atoms evidently loosens the union between the two and exposes the electrons held by them somewhat in the same manner, but not to the same extent, as in the case of actual ionisation in a similar field. Similar considerations are applied to cyanogen and to dicarbonyl derivatives in general.

H. W.

Lecture-room Demonstration of Atomic Models. LOUIS V. KING (*Phil. Mag.*, 1922, [vi], 44, 395—400).—Atomic models are described in which a number of steel spheres or soft iron rods are arranged in a strong alternating magnetic field. A simple form of the model consists of a coil of copper wire carrying alternating current over which is placed a large watch glass. Steel bearing-balls are used as magnetic elements. Since the spheres repel each other with a force varying as the inverse fourth power of the distance and the attraction to the centre varies as the distance, symmetrical stable groupings of the spheres are formed. When two coils are employed, mercury is used as a floating surface for the steel balls. The system of spheres may be set in oscillation by external magnets, giving a good illustration of the internal vibrations in the atom. The motion of molecules of a gas or the Brownian movement may be illustrated by employing short cylinders of iron or steel wire, which undergo violent movements if the field is suddenly applied. An experimental model illustrating the Rutherford atom may be constructed with two coils. Lengths of steel wire placed axially to the coils are used to make up the nucleus. Arrangements suitable for the demonstration of hydrogen or helium atoms are described.

W. E. G.

Technical Sedimentation Analysis. I. FRIEDRICH-VINCENZ VON HAHN and DOROTHEA VON HAHN (*Kolloid Z.*, 1922, **31**, 96—101).—The authors describe an apparatus, which is a slight modification of Ostwald and Hahn's two-limbed coagulation measurer, by means of which a rapid and accurate knowledge of the size of particles of commercial powders may be obtained. This apparatus has been employed to determine the relative size of the particles of a number of commercial preparations of soot and lamp-black. As a control of the results obtained with this apparatus, the older methods of differentiation have also been used, and it is shown that exactly similar results are obtained by all methods.

but that the new method is handier, more rapid, and more accurate (cf. this vol., ii, 205).

J. F. S.

Gas Generator with Washing Apparatus. ROBERT MÜLLER, KOMANDIT-GESELLSCHAFT (D.R.-P. 346325; from *Chem. Zentr.*, 1922, ii, 978).—The apparatus consists of a conical flask fitted with a stopper which contains the essential features of the device. This consists of a tube, furnished with a funnel at the upper end and terminating in a trap at the lower end, through which the liquid used in generating the gas is introduced. The gas after generation passes through a washing apparatus of annular cross section fixed concentrically with the upper part of the tube.

G. W. R.

Inorganic Chemistry.

Solubility of Sulphur in certain Organic Liquids. R. DELAPLACE (*J. Pharm. Chim.*, 1922, [vii], **26**, 139—140).—The solubility of sulphur in chloroform, carbon tetrachloride, benzene, toluene, and ether was determined at various temperatures ranging from 13° to 24°. The divergence of the results from those obtained by earlier workers is attributed in some cases to the slowness of saturation, twelve hours' continuous agitation being necessary to obtain saturated solutions in toluene and benzene, for example. From the results, which are given in tabular form, the following figures for the weights of sulphur dissolved in 100 grams of solvent, are abstracted: in chloroform at 15°, 0.874 gram; in carbon tetrachloride at 15.5°, 0.645 gram; in toluene at 20°, 1.857 grams; in benzene at 15°, 1.582 grams; in anhydrous ether at 13°, 0.188 gram.
G. F. M.

Autoreduction of Sulphurous Acid. GEORGE MACDONALD BENNETT (*T.*, 1922, **121**, 1794—1795).

Some Properties of Selenium Oxychloride. II. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1922, **44**, 1664—1667; cf. A., 1921, ii, 256).—Selenium oxychloride is extremely hygroscopic and the very greatest precautions must be taken in preparing the anhydrous material. The presence of small quantities of water increases the electrical conductivity enormously, and its reactivity towards carbonates is largely dependent on the amount of water present. The best qualitative test for the presence of water in selenium oxychloride makes use of cobalt carbonate. When cobalt carbonate which has been dried at 200° for three hours is sealed up with anhydrous selenium oxychloride, no action of any description occurs, but if the merest trace of water is present the oxychloride becomes blue and if the tube is sealed a pressure of carbon dioxide is set up. The dry carbonates of calcium, strontium, copper, nickel, cobalt, and ferrous iron are unattacked by anhydrous

selenium oxychloride, whilst the dry carbonates of barium, lithium, and magnesium slowly evolve carbon dioxide and that of zinc much more rapidly. The fused carbonates of sodium and potassium react readily with anhydrous selenium oxychloride with the development of a large amount of heat. Sulphur dioxide is without action on boiling anhydrous selenium oxychloride, but in the presence of water selenium is precipitated. Dry hydrogen sulphide in contact with selenium oxychloride produces a reddish-brown colour, after which hydrogen chloride is evolved and yellow selenium sulphide produced. At the same time, heat is developed which dissociates the sulphide into sulphur and red selenium. Liquid hydrogen disulphide reacts vigorously with selenium oxychloride in the cold, producing the same products as hydrogen sulphide. Carbon monoxide has no action on selenium oxychloride. Iodic acid, iodine pentoxide, and potassium iodate with selenium oxychloride give at first chlorine and then iodine chloride. Periodic acid with the oxychloride evolves chlorine and, when warmed, iodine chloride. Potassium bromate with selenium oxychloride in the cold gives chlorine followed rapidly by a mixture of bromine and chlorine. Selenium oxychloride warmed with potassium persulphate evolves chlorine, but in the presence of sulphuric acid the evolution occurs in the cold and with effervescence. Telluric and selenic acids evolve chlorine when gently warmed with the oxychloride. The metals tungsten, tantalum, and titanium are only slightly attacked by selenium oxychloride after long treatment at high temperatures. Phosphorus reacts with selenium oxychloride at low temperatures to form phosphoric oxide, selenium monochloride, and selenium tetrachloride. Selenium oxychloride dissolves readily in carbon tetrachloride, but after a time reaction takes place with the formation of selenium tetrachloride and carbonyl chloride. Gliadin, zein, glutenin, elastin, and albumin are readily attacked and dissolved by selenium oxychloride.

J. F. S.

Selenium Oxybromide. VICTOR LENHER (*J. Amer. Chem. Soc.*, 1922, **44**, 1668—1673).—Selenium oxybromide is best prepared by adding to pure sublimed selenium dioxide the calculated amount of fused selenium in a flask fitted with a rubber stopper through which passes a dropping funnel and a safety tube filled with fused calcium bromide. The flask is cooled to 0° and the amount of bromine necessary to convert the metal into tetrabromide cautiously added in small quantities. The mixture is then warmed until the whole of the oxide has dissolved to form the oxybromide. Selenium oxybromide is a reddish-yellow solid, m. p. $41.5\text{--}41.7^{\circ}$, b. p. $217^{\circ}/740$ mm. with considerable decomposition, d^{20}_4 3.38. The product decomposes so readily on heating, that it cannot be purified by distillation even under reduced pressure. It has an electrical conductivity at $40\text{--}50^{\circ}$ of 6×10^{-5} ohms $^{-1}$. Water converts it slowly into selenious and hydrochloric acids. It dissolves in carbon disulphide, chloroform, benzene, toluene, and xylene, and the fused material is miscible in all proportions with these solvents. Carbon tetrachloride dissolves it readily, but the

fused material dissolves only to the extent of 6%, and on heating the solution for several days carbonyl chloride is evolved and selenium tetrabromide formed. Selenium oxybromide is a very active chemical reagent. Sulphur reacts readily with it in the cold with the evolution of sulphur dioxide; selenium dissolves in it to form the monobromide. Yellow phosphorus explodes with the solid, whilst red phosphorus takes fire with the solid and burns. Iodine dissolves in large quantities in selenium oxybromide, whilst chlorine displaces bromine. Silicon and carbon are not attacked. Sodium reacts explosively with the oxybromide, producing the bromide and selenium monobromide, whilst potassium reacts even more violently. Mercury, arsenic, antimony, tin, bismuth, iron, calcium, copper, lead, silver, molybdenum, thallium, gold, platinum, and zinc are all attacked, forming the metallic bromide and selenium monobromide. Zinc dust burns in the oxybromide; aluminium and magnesium are only slightly corroded after heating for a week at 100° in the oxybromide. Cadmium, chromium, nickel, cobalt, tungsten, and tantalum are not attacked when heated for ten days at 100°. The oxides of mercury, silver, calcium, and sodium react energetically with selenium oxybromide, those of arsenic, tin, and tellurium less energetically, and those of columbium, tantalum, vanadium, thorium, titanium, zirconium, and uranium are unattacked after heating for several days at 100°. With most carbonates, the anhydrous oxybromide reacts only sluggishly even on heating, but in the presence of moisture the reaction is vigorous. The commoner sulphides react with the oxybromide with the development of heat, forming metallic bromides and selenium monobromide. Potassium chlorate liberates bromine from the oxybromide, but potassium perchlorate, permanganate, dichromate, and chromium trioxide are without action on it. When dry air is bubbled through the oxybromide at 60°, bromine is set free, due to a primary dissociation into the dioxide and tetrabromide followed by a secondary dissociation of the tetrabromide into bromine and the monobromide. Sulphur dioxide and carbon monoxide are without action on the oxybromide, and hydrogen sulphide causes a slight decomposition.

J. F. S.

Production of Colourless Glass in Tank Furnaces with Particular Reference to the Use of Selenium. I. A. COUSEN and W. E. S. TURNER (*J. Soc. Glass Technology*, 1922, **6**, 168—181).—Numerous small melts at 1380° and 1440° showed that not more than 0.09% of iron oxide in a glass could be effectively decolorised by selenium or sodium selenite. The greater corrosive action of the salt-cake on the pot and its action on the selenium at high temperatures rendered more decoloriser necessary for batches containing this ingredient than for those with soda ash alone. Experiments showed the distinct formation of sodium selenite from selenium when dropped on to fused sodium sulphate. In a batch containing only soda ash and no salt-cake, sodium selenite was much more effective than selenium in decolorising. Reheating the glasses only changed the tint of those which had been

over-decoloured, and then only when heated between 525° and 550°. A. C.

Limits for the Propagation of Flame at Various Temperatures in Mixtures of Ammonia with Air and Oxygen. ALBERT GREVILLE WHITE (T., 1922, 121, 1688—1695).

Acetone in Commercial Ammonia. J. BOUGAULT and R. GROS (*J. Pharm. Chim.*, 1922, 26, 170—171).—In many cases in which ammonia is used as a reagent in the presence of iodine, the formation of small quantities of iodoform is observed. An explanation of this fact was put forward by Guérin (A., 1909, i, 126), but this is set aside by the authors, who show that iodoform results from the presence of acetone. The quantity of acetone was found to vary from 0.01—0.5 gram per litre in the different samples examined, and it has been found in so-called "pure ammonia for analysis" in addition to the commercial product. It is pointed out that the use of ammonia in testing for acetone in physiological products is liable to give misleading results.

H. J. E.

Viscous Properties and Molecular Dimensions of Silicane.

A. O. RANKINE and C. J. SMITH (*Proc. Physical Soc.*, 1922, 34, 181—186).—The authors have determined experimentally the viscosity of gaseous silicon hydride at 15° and 100°, and on the assumption that Sutherland's law holds for this gas over the whole temperature range concerned the viscosity at 0° has been extrapolated. The data have been used to calculate the mean collision area presented by the silicon hydride molecule in the gaseous state. The experimental method employed was the same as that previously described (A., 1921, ii, 694). The following numerical data are recorded: viscosity in C.G.S. units $\times 10^{-4}$, 0°, 1.078; 15°, 1.134; 100°, 1.436; Sutherland's constant, (c), 229; mean collision area of the molecule, (A), 0.989×10^{-14} cm.². Using these data, an attempt is made to determine the structure of the silicon hydride molecule in relation to those of other gaseous hydrides the molecules of which have equal numbers of extra-nuclear electrons. J. F. S.

Effect of Magnesia on the Resistance of Glass to Corroding Agents and a Comparison of the Durability of Lime and Magnesia Glasses. VIOLET DIMBLEBY, CONSTANCE M. M. MUIRHEAD, and W. E. S. TURNER (*J. Soc. Glass Technology*, 1922, 6, 101—107).—Magnesia glasses appear to possess a slight advantage over lime glasses as regards corrosion by water; they show no advantage in the case of hydrochloric acid, and are decidedly inferior as regards their resistance towards alkaline solutions.

W. P. S.

Crystal Structure of Potassium. L. W. MCKEEHAN (*Proc. Nat. Acad. Sci.*, 1922, 8, 254—255).—Determination by the X-ray method of the crystalline structure of potassium cooled to -150° in a current of air shows that the atoms of the metal are arranged in a body-centred cubic lattice with $a = 5.20 \times 10^{-8}$ cm. The

corresponding value of the density is 0.92 gram/cm.³ compared with the commonly accepted value of 0.862 gram/cm.³. The difference is probably partly attributable to the imperfect crystallisation of samples previously examined. The observed crystalline structure does not persist as the temperature rises to about 20°.

J. S. G. T.

Symmetry and Crystal Structure of Sodium Hydrogen Acetate. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1922, [v], 4, 193—198).—Cubes (d 1.402) having the composition $\text{NaH}(\text{C}_2\text{H}_3\text{O}_2)_2$ were obtained by the long digestion of fused sodium acetate, glacial acetic acid, and acetic anhydride. The X-ray analysis (reflexion spectra and Laue photographs) gives a unit cube of edge 15.98 Å.U. containing twenty-four chemical molecules. The space group is probably T_h^7 .

L. J. S.

Symmetry and Crystal Structure of Zinc Bromate Hexahydrate. RALPH W. G. WYCKOFF (*Amer. J. Sci.*, 1922, [v], 4, 188—192).—Good crystals having the composition $\text{Zn}(\text{BrO}_3)_2 \cdot 6\text{H}_2\text{O}$, mostly octahedral in habit, are formed by the slow cooling, or slow evaporation, of solutions. Reflexion X-ray photographs were obtained from the octahedral face, and Laue photographs through both octahedral and cube faces. These show an absence of planes of symmetry. From the various alternative arrangements, the space group T_h^6 is selected. The unit cube contains four chemical molecules and has length of edge 10.31 Å.U.

L. J. S.

Chemical Method of Separating the Isotopes of Lead. THOMAS DILLON, ROSALIND CLARKE, and VICTOR M. HINCHY (*Sci. Proc. Royal Dublin Soc.*, 1922, 17, 53—57).—The authors have attempted to effect a separation of the isotopes of lead by means of the Grignard reaction. Lead chloride prepared from some residues recovered from the manufacture of mesothorium was treated with lead tetraethyl and the reaction represented by the equation $2\text{PbCl}_2 + 4\text{MgRX} = \text{R}_4\text{Pb} + 2\text{MgCl}_2 + 2\text{MgX}_2 + \text{Pb}$ carried out. The lead tetraethyl and metallic lead remaining constitute two fractions which are used separately in a repetition of the process. The process was carried out twice and the atomic weight of the lead in the tetraethyl from one and the lead residue in the other process was then determined by the method employed by Soddy and Hyman (T., 1914, 105, 1402). The relative values 207.1 and 207.4 were obtained, thus indicating that the above reaction furnishes a possible method of separating isotopes and that the chemical properties of isotopes although similar are not identical.

J. F. S.

The Mass-spectrum of Iron. F. W. ASTON (*Nature*, 1922, 110, 312—313).—The mass spectrum of iron, examined as iron pentacarbonyl mixed with carbon dioxide, is characterised by a strong line at 55.94 ± 0.05 , and possibly a very faint line at 54.

A. A. E.

The Constitutional Diagram of the Iron-Carbon System based on Recent Investigations. KÔTARÔ HONDA (*Sci. Rep. Tohoku Imp. Univ.*, 1921, **11**, 119—129).—In a previous communication with Murakami (cf. A., 1921, ii, 699), it is shown that the graphitisation of iron always takes place after solidification of the fusion, the formation of graphite being due to the catalytic action of carbon monoxide on the solid cementite, just below the eutectic point, 1130° to 1100° . This being the case, the graphite lines on the usual double iron-carbon diagrams must be omitted. The shape of the solidus curve is frequently given incorrectly; according to the principles of thermodynamics, this curve, like the liquidus curve, should be bent upwards. In a discussion of the allotropic transformations of the various forms of iron, it is concluded that the α — β transformation is not a sudden change of phase, but a progressive change beginning from the lowest temperatures and ending at about 790° , the amount of change being dependent on the temperature. The magnetisation of iron is not accompanied by changes in the atomic configuration as in the case of allotropic change, but is a consequence of a gradual alteration in the energy of the atoms with rise in temperature. This transformation is represented by a dotted line passing through 790° for pure iron and 775° at 4% of carbon. Similarly, the cementite transformation is progressive and extends from the lowest temperature up to 215° . The break in the heating curve of cast iron observed by Ruer (A., 1921, ii, 198) is not evidence of the existence of a graphite eutectoid. W. E. G.

Crystal Structure of Iron and Steel. II. ARNE WESTGREN and GÖSTA PHRAGMÉN (*Z. physikal. Chem.*, 1922, **102**, 1—25; cf. this vol., ii, 152).—Röntgen photographs of iron wire at 800° , 1100° , and 1425° , obtained by the Debye and Scheerer method, show that iron within the so-called β and δ regions similarly to α -iron has a space-centred cubic lattice, whilst iron in the γ -iron region has a face-centred cubic lattice. The characteristic fact is therefore that the transition which occurs at 900° (A_3) is reversed at 1400° (A_4). The γ -iron lattice of austenite steel is extended by the dissolved carbon. It is found that a steel containing 1.98% of carbon possesses a larger iron lattice when it is quenched at 1100° than at 1000° , also that the α -iron lattice in martensite appears to be somewhat extended by the carbon. The homogeneous lattice region within the α -iron in martensite is shown to be extremely small. A steel containing 0.80% of carbon which has been quenched at 760° is shown to be practically amorphous. Debye photographs of cementite and spiegeleisen crystals are identical. By means of Laue photographs and an investigation of the interferences of a spiegeleisen crystal rotating in a Debye camera, it is shown that cementite belongs to the rhombic system and has an axial ratio 0.670 : 0.755 : 1. The dimensions of the elementary parallelepiped are 4.53, 5.11, and 6.77 Å.U., respectively. The unit crystal contains four molecules of Fe_3C , from which it follows that the specific gravity of cementite is 7.62. J. F. S.

The System Chromium Trioxide-Sulphur Trioxide-Water. LIONEL FELIX GILBERT, HAROLD BUCKLEY, and IRVINE MASSON (T., 1922, **121**, 1934—1938).

Rôle of Chromates in Electrolysis for Chlorate. A. V. PAMFILOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1921, **4**, 113—117).—Chromate plays a triple part in the electrolytic production of chlorate in an acid solution. (1) It acts as a "buffer" salt, regulating automatically the kinetic acidity of the liquid. (2) It forms a film on the cathode and thus prevents reduction of the hypochlorite formed as an intermediate product, and (3) this film protects the cathode from disintegration and hence allows the platinum electrodes to be replaced by those of metals more readily accessible, such as copper. These effects of chromate are specific and are not exhibited by any other compound. T. H. P.

The Adsorption of Uranium-X and its Isotope, Thorium, by Basic Ferric Acetate. ANDREW CHARLES BROWN (T., 1922, **121**, 1736—1743).

Zirconium Ferrocyanide and Ferricyanide. F. P. VENABLE and E. O. MOEHLMANN (*J. Amer. Chem. Soc.*, 1922, **44**, 1705—1707).—When solutions of potassium ferrocyanide are added to solutions of zirconyl salts, white precipitates are obtained which are unstable in the air and of varying composition. The precipitates are basic zirconium ferrocyanides and the composition depends on the extent to which the hydrolysis has proceeded. Thus, a freshly prepared solution of zirconyl chloride gives a substance of the formula $\text{ZrO}(\text{OH})_2 \cdot 2(\text{ZrO})_2\text{Fe}(\text{CN})_6$ and a solution which has been boiled gives a precipitate of the composition $9\text{ZrO}(\text{OH})_2 \cdot 2(\text{ZrO})_2\text{Fe}(\text{CN})_6$. Potassium ferricyanide gives no precipitate with freshly prepared solutions of zirconyl chloride, but on boiling the mixture the very basic compound

$$21\text{ZrO}(\text{OH})_2 \cdot 2(\text{ZrO})_3\text{Fe}(\text{CN})_6$$

is precipitated.

J. F. S.

The Chemical Properties of Mesothorium. II. D. YOVANOVITCH (*Compt. rend.*, 1922, **175**, 307—309).—A concentrated solution of the chlorides of barium and radioactive elements was treated with hydrochloric acid in the cold. The precipitated barium chloride carried down with it mesothorium-*I*, thorium-*X*, and radium, leaving mesothorium-*II*, radiothorium, and the active residue in solution. By this process, repeated at intervals, mesothorium-*II* was obtained in the acid solution, nearly pure and practically free from barium. The final purification of mesothorium-*II* was carried out by repeated co-precipitation with salts of iron or aluminium, and further by reprecipitation as hydroxide. To eliminate radiothorium a trace of thorium was added and later removed by means of hydrogen peroxide. Thorium-*C* and thorium-*B* were removed by precipitation with lead and bismuth, which in turn were removed as sulphides. Mesothorium-*II* in solution with elements of the cerium group was fractionally precipitated as oxalate hydroxide, and as the double

sulphate. Mesothorium-*II* in the presence of lanthanum and praseodymium appeared in greater quantity in the early fractions, but when mixed with neodymium and samarium was more concentrated in the last fractions. In the fractionation of the double nitrates of the rare earths and ammonium, mesothorium-*II* tends to accumulate with lanthanum rather than with samarium.

A. G. P.

Crystal Structure of Germanium. N. H. KOLKMEIJER (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 125—126).—In continuation of previous work (A., 1921, ii, 200), the author has investigated the crystal structure of germanium, by the powder method. The structure, deduced from the observations, resembles that of the diamond, the lattice parameter a being equal to 5.61 \AA ., compared with the value 5.594 \AA . deduced from the value of the density and atomic weight, taking Avogadro's number equal to 6.062×10^{22} . As modifications of carbon, silicon, germanium, and tin resembling the diamond in structure are known, whilst the same is not true of titanium, zirconium, and thorium, it is concluded that carbon and silicon are more closely associated with the elements of group IVb than with those of group IVa.

J. S. G. T.

The Anode Oxidation of Gold. I. Anode Oxidation of Gold in Sulphuric Acid. FR. JIRSA and OT. BURYÁNEK (*Chem. Listy*, 1922, **16**, 189—194).—A detailed examination is made of the oxidation of a gold anode in dilute sulphuric acid. The product obtained is shown to be auric hydroxide, which loses a molecule of water on keeping over phosphoric oxide, giving the compound AuO(OH) , and this, on further dehydration, yields the oxide Au_2O_3 . It was observed that ozone is evolved during the passage of the current, and the amount produced per ampere-hour for various concentrations of acid is determined. The yields of hydroxide obtained with different currents and acid concentrations are also measured.

The solubilities of auric hydroxide, both freshly prepared and stale, and prepared both electrolytically and by hydrolysis, are determined for different concentrations of sulphuric acid, and from these results it is concluded that the product of solution is auric sulphate, and not the compound Au(OH)SO_4 .

R. T.

Mineralogical Chemistry.

The Composition and Calorific Power of Coal from the Deeper Strata of the Kenadza (Algerian) Mine. A. FOIX (*Bull. Soc. chim.*, 1922, [iv], **31**, 813—816).—Coal from the deeper workings differs from that obtained nearer the surface by reason of its greater proportion of ash, nitrogen, and sulphur. The heat of combustion is about 8·255 calories per gram, H. J. E.

Colloidal Phosphates. CARL ELSCHNER (*Kolloid Z.*, 1922, **31**, 94—96).—The author describes the colloidal formation of a clay found in the Fanning Islands which contains no silicates but is chiefly made up of calcium phosphates and organic materials. The mineral *naurite* is stated to be formed from a jelly-like mass containing tricalcium phosphate with uric acid and purine derivatives, which through the action of nitrifying bacteria has lost its organic matter and formed a substance of the composition $3(\text{Ca}_3\text{P}_2\text{O}_8), \text{Ca}(\text{OH})_2, x\text{H}_2\text{O}$. Another mineral, *meyersite*, found in the Hawaii Islands, is described. This is an aged gel of the composition AlPO_4 , 66·33%; FePO_4 , 2·52%; H_2O , 26·10%; and is to be distinguished from variszite, $\text{AlPO}_4, 2\text{H}_2\text{O}$. It is lighter in colour and is particularly characterised by its banded structure. The mineral is formed by the decomposition of lava by the constituents of guano.

J. F. S.

Olivine from Lithosiderites. P. CHIRVINSKII (*Bull. Soc. franç. Min.*, 1921, **44**, 170).—Olivine isolated from the pallasites of: I, Ahumada; II, Finmarken (*d* 3366); III, Mt. Dyrning; and IV, Molong, gave:

	SiO_2	FeO	MnO	MgO	CaO	Total
I.	38·43	14·93	trace	46·27	0·40	100·03
II.	39·32	16·61	—	44·07	—	100·00
III.	40·52	13·13	—	47·30	trace	100·95
IV.	39·32	13·13	trace	47·70	trace	100·15

L. J. S.

Cyprine and Associated Minerals from Franklin, New Jersey. J. VOLNEY LEWIS and LAWSON H. BAUER (*Amer. J. Sci.*, 1922, [v], **4**, 249—251).—Sky-blue, granular to fibrous cyprine (a variety of idocrase), which was apparently homogeneous, was found on microscopical examination of thin sections to enclose about 33% of rounded grains of willemite. Analysis I gives, after deducting willemite, the figures under II agreeing approximately with the composition of idocrase. Associated with this mineral is pale pink, cleavable to coarsely fibrous rhodonite (var. bustamite), which gave analysis III; brown, granular garnet—the polyadelphite variety of andradite (analysis IV); also phlogopite, felspar, etc.

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	ZnO
I.	32·42	14·07	—	0·77	1·50	21·71
II.	35·14	20·86	—	—	—	—
III.	46·72	1·34	—	0·46	26·51	1·34
IV.	34·28	3·12	25·53	—	7·41	—

	CuO	CaO	MgO	H_2O	Total
I.	0·99	25·22	1·08	2·38	100·14
II.	1·47	37·40	1·60	3·53	100·00
III.	—	22·24	1·27	—	99·88
IV.	—	29·20	0·39	—	99·93

L. J. S.

Analytical Chemistry.

Refractometric and Interferometric Quantitative Analysis.

J. BEČKA (*Z. physiol. Chem.*, 1922, **121**, 288—299).—The author has extended the observations of de Crinis (A., 1920, ii, 700) on the use of the refractometer for the analysis of solutions so as to make it more generally applicable. He has also described the use of the interferometer for more dilute solutions. The experiments have special reference to urine analysis. H. K.

Recovery of Solvents from Extracted Substances. A. B.

PICHLER (*Chem. Ztg.*, 1922, **46**, 698).—In the ordinary method of extracting substances in a Soxhlet apparatus a considerable quantity of the solvent is retained by the extraction thimble and its contents, particularly if the latter are of a bulky nature; this solvent may be recovered by transferring the thimble, at the end of the extraction, to a large flask and, when a suitable number of thimbles have thus been collected, submitting them to distillation. To recover solvent from a single thimble, the latter may be transferred to a tube which fits on to the lower end of the Soxhlet apparatus and the solvent then distilled into and collected in the Soxhlet apparatus. W. P. S.

Apparatus for Measuring the Hydrogen-ion Concentration of a Solution. ANDRÉ KLING and A. LASSIEUR (*Ann. Chim. Analyt.*, 1922, [ii], **4**, 232—238).—A further description of the electrometric method previously reported (this vol., ii, 234). G. F. M.

Colorimetric Estimation of Hydrogen Peroxide. M. L.

ISAACS (*J. Amer. Chem. Soc.*, 1922, **44**, 1662—1663).—A rapid method of estimating the concentration of hydrogen peroxide colorimetrically based on the method described by Denigès (A., 1890, 1185) and Crismer (A., 1892, 381) is worked out and fully described. About 30 c.c. of water, 10 c.c. of a 5% solution of citric acid, and 1 c.c. of the unknown hydrogen peroxide are placed in a 50 c.c. graduated flask and, after mixing, 1 c.c. of a 10% solution of ammonium molybdate is slowly added. Water is then added to make the volume 50 c.c. and the whole well shaken. The yellow colour develops at once and the solution is then compared with a standard potassium chromate solution (0.4 gram/litre) in a Dubosq colorimeter. When the standard is set at 20 the quantity of hydrogen peroxide is given by $x=0.05467/y$, where y is the colorimeter reading and x the number of grams of peroxide in the 50 c.c. of solution. The results obtained by this method compare extremely favourably with those obtained by direct titration with potassium permanganate. J. F. S.

The Error in Estimating Chloride by Bang's Micro-Method. RICHARD PRIGGE (*Biochem. Z.*, 1922, **130**, 442—447).—The sources of error in this method have been examined

and full details of the technique required for the greatest exactitude are given. H. K.

Micro-analyses by Bang's Methods. I. LUDWIG PETSCHACHER (*Biochem. Z.*, 1922, **131**, 116—123).—The estimation of chlorides by microanalysis in drops of blood gives sufficiently accurate results, but the estimation of dextrose and residual nitrogen is not sufficiently accurate. H. K.

Colorimetric Estimation of Blood Chlorides. M. L. ISAACS (*J. Biol. Chem.*, 1922, **53**, 17—19).—The method is applicable to the tungstic acid blood filtrates and depends on the conversion of silver chromate into sodium chromate by the action of the blood chlorides. Excess of silver chromate (about 0.05 gram) is stirred into 10 c.c. of the blood filtrate previously neutralised by addition of a small quantity of magnesium carbonate. After centrifuging, the supernatant liquid (plus washings) is clarified by the addition of 1 c.c. of a 2% ammonium hydroxide solution, and diluted to 25 c.c. The colour is then compared with a potassium chromate solution which has been standardised by means of a solution of sodium chloride in the above manner. E. S.

Estimation of Chlorine in Tissues. O. M. PRICO and J. MURTAGH (*Compt. rend. Soc. Biol.*, 1922, **86**, 405—406; from *Chem. Zentr.*, 1922, ii, 922).—The tissue is dissolved in concentrated sodium hydroxide solution and the proteins are precipitated by phosphotungstic acid. The chlorine is estimated in the filtrate by the method of Austin and Van Slyke. G. W. R.

Detection of Iodates in Potassium Iodide according to the French Codex, 1908. LACHARTRE (*J. Pharm. Chim.*, 1922, [vii], **26**, 134—138).—The test for iodates in potassium iodide described in the Codex lacks precision, and takes no account of the influence of such factors as the strength of the iodide solution, the amount of acid added, the duration of the reaction, etc. The following method is suggested. A 10% solution of the iodide in distilled water is prepared, and to 10 c.c., 3 c.c. of chloroform and 5 drops of glacial acetic acid are added. After shaking for thirty seconds, the chloroform, examined immediately after separation, should not be coloured. Performed in this manner, the limit of sensitiveness of the test is 0.08 part of iodate per 1000, which is considered to be all that is required for a reasonably pure product. The presence of copper in small quantities, for example, 0.0015 part per 1000, has no effect on the reaction with a perfectly pure iodide, but it appreciably accelerates the development of the iodine coloration when traces of iodate are present. The amount of copper in ordinary distilled water is, however, too small to have any effect on the reaction in either case. G. F. M.

Detection and Estimation of Fluorides. N. K. SMITT (*Bull. Bureau Biotech.*, 1922, 176—178).—Greeff's volumetric method for the estimation of fluorides (A., 1913, ii, 975) may be simplified somewhat by the use of an alcoholic solution of ferric chloride. The presence of fluoride in neutral solution may be detected by

adding a little ammonium thiocyanate solution and then ferric chloride solution drop by drop; in the absence of interfering substances, rapid disappearance of the colour of the ferric thiocyanate indicates the presence of fluoride. Even insoluble fluorides, such as that of calcium, may be similarly detected if the substance is vigorously ground in a mortar with thiocyanate and ferric chloride solutions. A colorimetric method for estimating traces of fluorides, based on the above reaction, is also described. [Cf. *J. Soc. Chem. Ind.*, 1922, Oct.] T. H. P.

The Estimation of Oxygen in Organic Compounds. H. TER MEULEN (*Rec. trav. chim.*, 1922, **41**, 509—514; cf. Boswell, A., 1913, ii, 334).—The substance to be analysed is heated in a current of pure hydrogen and the resulting gases are passed first over metallic nickel in the form of thin wire and secondly over nickelised asbestos. The function of the former is that of transforming the decomposition products of the substance into compounds which are suitable for hydrogenation, which reaction occurs in the presence of the latter. With proper precautions, all the oxygen is transformed into water and weighed as such; but as a portion may remain as carbon dioxide, a second absorbent is required to obviate error due to incomplete transformation. Analyses carried out by this method have yielded satisfactory results, details of which are given. Halogens and sulphur act as poisons to the catalyst; the method is therefore not applicable to substances containing these elements. As calcium chloride is used to absorb the water formed in the reaction, nitrogenous substances may not be dealt with by this method on account of the ammonia which they yield on hydrogenation. H. J. E.

Estimation of Sulphides by Oxidation by means of Ferric Sulphate. P. P. BUDNIKOV and K. E. KRAUZE (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1921, **4**, 157—159).—The method described is based on the reactions $3\text{Na}_2\text{S} + \text{Fe}_2(\text{SO}_4)_3 = 3\text{Na}_2\text{SO}_4 + 2\text{FeS} + \text{S}$ and $2\text{FeS} + 2\text{Fe}_2(\text{SO}_4)_3 = 6\text{FeSO}_4 + 2\text{S}$, the ferrous sulphate thus formed being estimated by titration with permanganate solution. If the ferric sulphate is used in aqueous solution, it undergoes hydrolysis, whereas in presence of acid the sodium sulphide may be attacked with loss of hydrogen sulphide. These difficulties are avoided by adding sodium carbonate or hydroxide, and by acidifying, only after the oxidation, with phosphoric acid. Manganous sulphate is added prior to the titration. The method is applicable to calcium and zinc sulphides, but not to sulphides of copper, lead, silver, etc., which are insoluble. T. H. P.

Estimation of Non-protein Nitrogen by means of Ultra-filtration. M. RICHTER-QUITTNER and H. HOENLINGER (*Wiener Klin. Wochschr.*, 1921, **34**, 24).—Twenty c.c. of blood plasma or serum are diluted ten to twenty times with distilled water and filtered through a Buchner funnel and membrane (Zsigmondy and Jander, A., 1919, ii, 520), the non-protein nitrogen being estimated in the filtrate by Kjeldahl's or Pregl's micro-method.

CHEMICAL ABSTRACTS.

The Triketohydrindene (Ninhydrin) Reaction as a Quantitative Colorimetric Method for the Estimation of Amino-acid Nitrogen. H. RIFFART (*Biochem. Z.*, 1922, **131**, 78—96).—The ninhydrin reaction is suitable for the estimation of amino-acid nitrogen if certain precautions are taken. All the amino-acids with free amino-groups examined, except histidine, give at P_H 6.976 the same standard colour if the solutions be equal in amino-acid nitrogen content, say, 10 mg. or less per litre. This result is obtained by taking 2 c.c. of such a solution, neutralising with $N/400$ alkali to P_H 6.976 by comparison with phosphate standards and methyl-red, adding 2 c.c. of phosphate solution of the same P_H and 1 c.c. of 1% ninhydrin solution, and heating for thirty minutes in the boiling-water-bath. The solutions are then diluted to 100 c.c. and estimated colorimetrically. Histidine gives the standard colour at P_H 6.24, thus involving a small error where mixtures of amino-acids contain this acid. Some amines and ammonium salts also give the colour reaction, but only in concentrations higher than 15 mg. per litre. H. K.

Estimation of Phosphorus in Minerals and in Coke Ash by a Colorimetric Method. GEORGES MISSON (*Bull. Soc. Chim. Belg.*, 1922, **31**, 222—225).—The phosphorus to be estimated is obtained in solution as phosphate, and it is essential that the solution should be free from chlorine. Potassium permanganate is added, followed by a solution of sodium peroxide in dilute nitric acid. After addition of ammonium vanadate, the solution is boiled and treatment with ammonium molybdate produces the colour which is compared with the standard tint. Three modifications of the method are given, (a) for minerals of small phosphorus content, 0.01—0.20%; (b) for minerals of greater phosphorus content, 0.20—2.50%; (c) for coke ash, together with details of the procedure in each case. A comparison of the results with those obtained by gravimetric methods shows that they are substantially in agreement, but the colorimetric method gives somewhat lower results for a phosphorus content of 1.7% and upwards.

H. J. E.

Modification of the Bell-Doisy Phosphate Method. A. P. BRIGGS (*J. Biol. Chem.*, 1922, **53**, 13—16; cf. A., 1920, ii, 769).—In the modification described, the coloration produced in acid solution, which is more stable than that in alkaline solution, is used for the estimation. The blood or plasma is diluted with 3 volumes of water and 1 volume of 20% trichloroacetic acid, shaken vigorously for a few seconds, and filtered after ten minutes. To 5 c.c. of the filtrate (corresponding with 1 c.c. of plasma), 2 c.c. of the molybdate solution, 1 c.c. of a 20% sodium sulphite solution, 1 c.c. of the quinol solution, and water to bring the volume to 10 c.c. are added. After thirty minutes, the coloration produced is compared with a standard. In the presence of the sodium sulphite reagent a blue coloration is obtained which is more intense than the green coloration produced in its absence. The method is applicable to urine. E. S.

Estimation of Lipoid Phosphoric Acid ("Lecithin") in Blood by Application of Bell and Doisy's Method for Phosphorus. F. S. RANGLES and ARTHUR KNUDSON (*J. Biol. Chem.*, 1922, **53**, 53—59).—An alcohol-ether extract of blood or plasma is prepared according to Bloor's procedure (A., 1918, ii, 452). An aliquot part of this is evaporated, treated with sulphuric and nitric acids, and heated until the latter acid is completely driven off. Phosphoric acid is then estimated in the clear solution by Bell and Doisy's method (A., 1920, ii, 769). Disturbance of the final solutions produces bubbles which interfere with the reading. The solutions should therefore be left in the colorimeter cups for five minutes before making the comparison. E. S.

Conductometric Titration of Hydrofluosilicic Acid. NAOTSUNA KANÔ (*J. Chem. Soc. Japan*, 1922, **43**, 556—560).—Using two adjustable parallel platinum plates as electrodes, the author has carried out the conductometric titration of hydrofluosilicic acid. When a mixture of 100 c.c. of water and 170—200 c.c. of 95% alcohol was used as solvent for the 0.138*N*-acid, the titration was conducted with sodium hydroxide solution as well as with potassium hydroxide solution without causing hydrolysis of the acid. K. K.

Critical Examination of Methods commonly used in Determining the Durability of Glass. W. E. S. TURNER (*J. Soc. Glass Technology*, 1922, **6**, 30—45).—The methods investigated involved (1) the testing of the surface of glass vessels, (2) the use of plates, disks, or slabs of glass, (3) the treatment of the glass in the form of powder, and (4) the autoclave test. Whilst there are uncertainties in the results obtained by any of the methods, it is not difficult to distinguish qualitatively a good glass from a poor one. It is suggested that, in absence of a satisfactory general test, the tests should be made on plates of the glass or on the powder, preferably the latter. W. P. S.

New Apparatus for Estimation of Carbon Dioxide in Air. HENRIK LUNDEGÅRDH (*Biochem. Z.*, 1922, **131**, 109—115).—The author has modified the Pettenkoffer method by replacing the flask by a zinc vessel in the form of a beaker with detachable cover, and fitted with three tubes to facilitate withdrawal and entry of solutions. A larger apparatus is also described on similar lines, suitable for use in the open. H. K.

Estimation of Gases in Metals. HAROLD LESTER SIMONS (*Chem. and Met. Eng.*, 1922, **27**, 248—249).—A weighed quantity of the metal is introduced into a specially designed apparatus which is then exhausted by means of a Toeppler pump. Mercury is allowed to siphon over into the flask containing the metal and the whole is heated until the latter dissolves. The evolved gases are first examined spectroscopically in a Geissler tube, then transferred to the usual gas apparatus, and the quantity of each constituent estimated in the usual manner. [Cf. *J. Soc. Chem. Ind.*, 1922, 714A.] A. R. P.

Estimation of Small Quantities of Sodium in Aluminium and Alumina. R. GEITH (*Chem. Ztg.*, 1922, **46**, 745).—The precipitation of aluminium hydroxide by even a very slight excess of ammonia is invariably not quite complete and the traces in solution are weighed with the sodium chloride. By electrolysis of a nearly neutral solution of aluminium chloride or sulphate containing iron, magnesium, calcium, and sodium salts as impurities, all the sodium may be deposited in a mercury cathode as amalgam whilst the bulk of the other metals are precipitated as hydroxides in the solution and the chlorine escapes as gas from the carbon anode. In a suitably arranged divided cell the mercury is made the cathode in the inner compartment and the anode in the outer, which contains dilute neutral sodium chloride solution and a nickel rod dipping into the mercury and forming a voltaic couple. The sodium then redissolves as hydroxide in the salt solution and its amount may be estimated by titration. The current required for the method is 0.15 ampere at 3.5 volts for two to three hours. [Cf. *J. Soc. Chem. Ind.*, 1922, 714A.] A. R. P.

A New Method of Qualitative Separation of the Alkaline-earth Metals. MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 806—810).—The separation is based on the differences in solubility of the sulphites and thiosulphates of the three metals in ethyl alcohol–water mixtures. The carbonates as precipitated in the group are dissolved in acetic acid, and the solution is boiled and neutralised with ammonia. After addition of ethyl alcohol, the barium is precipitated by alcoholic sodium thiosulphate. A small proportion remains in solution; this is separated, after filtration, by addition of potassium sulphate, but not of sufficient concentration to precipitate any strontium. The strontium is then separated as sulphite by excess of alcoholic sodium sulphite or as sulphate by excess of potassium sulphate. The solution is then acidified with very dilute acetic acid and the calcium precipitated by ammonium oxalate. The concentrations of the reagents required to effect the separation are given, also the proportions in which they are to be used. H. J. E.

Approximate Volumetric Estimation of Barium. MICHEL POLONOVSKI (*Bull. Soc. chim.*, 1922, [iv], **31**, 810—813; cf. previous abstract).—The separation of barium from strontium and calcium as thiosulphate may be utilised as a means of volumetric estimation by using excess of a standard sodium thiosulphate solution which contains ethyl alcohol. After allowing the mixture to remain for twenty-four to thirty-six hours to obtain as complete a precipitation of barium thiosulphate as possible, the solution is filtered and the excess of the reagent estimated. The quantity of barium present is thus found by difference. A correction is necessary by reason of the slight solubility of barium thiosulphate; this is applied by a formula given by the author, as the temperature at which the precipitation takes place and the percentage of alcohol present are factors which influence the result. H. J. E.

Use of Amalgams in Volumetric Analysis. V. Estimation of Iron, Titanium, Uranium, and Methylene-blue. SUETARÔ KIKUCHI (*J. Chem. Soc. Japan*, 1922, **43**, 544—550; cf. A., 1921, ii, 596, 714; this vol., ii, 519, 529).—After the reduction of mixed solutions of two metals with liquid zinc- or cadmium-amalgam, their differential titration with two standard oxidising solutions was studied. A mixture of ferric oxide and titanium dioxide is titrated with potassium permanganate and iron alum, using ammonium thiocyanate as an indicator after reduction with zinc amalgam. They are quantitatively oxidised with iodine in the presence of sodium tartrate. Combining this reaction and that with iron alum, they can also be differentially titrated. A mixture of ferric oxide and uranium trioxide is titrated with potassium permanganate and iron alum, after reduction with cadmium amalgam in warm solution and in the presence of carbon dioxide. A mixture of titanium dioxide and uranium trioxide is titrated with potassium permanganate and iodine solutions, after reduction with cadmium amalgam in warm solution. Quadrivalent uranium is not oxidised by excess of iodine in the presence of sodium tartrate.

After a mixed solution has been oxidised with potassium permanganate, it is reduced with the amalgam and titrated differentially with iron alum or iodine. A definite quantity of titanous sulphate is reduced to tervalent titanium salt by the amalgam; methylene-blue is added at 60—70° until the solution is tinged with blue, and then it is titrated. The purity of Kahlbaum's methylene-blue B extra was 82.96%, and that of Merck's methylene-blue B.B., 85.07%.
K. K.

Use of Amalgams in Volumetric Analysis. VI. Electro-metric Titration of Iron, Molybdenum, Uranium, Vanadium, and Titanium. NAOTSUNA KANÔ (*J. Chem. Soc. Japan*, 1922, **43**, 550—556; cf. preceding abstract).—Solutions of iron alum, ammonium molybdate, uranyl sulphate, vanadic acid, and titanium sulphate are reduced with zinc amalgam, separated from the amalgam, connected to the platinum and calomel electrodes, and their *E.M.F.* estimated, the standard solution of potassium permanganate meanwhile being gradually added. In these estimations, the volumes of the solution should be maintained as small as possible. In the case of titanium, a slight deficiency of the permanganate solution is first added, then excess of iron alum solution to oxidise tervalent titanium, and the solution then titrated with the permanganate solution. A mixture of iron and titanium can be electrometrically titrated with the permanganate solution, two break-points in the *E.M.F.* curve showing the end points.

K. K.

Estimation of Tin in Bearing Metals. JOSEF NÁGEL (*Chem. Ztg.*, 1922, **46**, 698).—One gram of the metal turnings is dissolved by boiling in a flask with 100 c.c. of hydrochloric acid and 3 grams of potassium chlorate; after all free chlorine has been expelled, the solution is diluted with 30 c.c. of water, 7 grams of sodium chloride are added, and, after the addition of a strip of nickel having

an area of about 10 sq. cm., the solution is boiled for one hour. The stannic chloride is thus reduced to stannous chloride, whilst the antimony is deposited as flakes on the nickel plate. After the solution has been cooled in an atmosphere of carbon dioxide, the stannous chloride is titrated with standardised iodine solution.

W. P. S.

The Volumetric Estimation of Antimony and Tin in Red Brass. FRANZ JOHANN MÜCK (*Chem. Ztg.*, 1922, **46**, 790).—The alloy is dissolved in nitric acid and the precipitated stannic and antimonie acids are collected, washed, and dissolved in hot sulphuric acid and potassium sulphate. The cooled solution is treated with 0.5 gram of tartaric acid, 180 c.c. of water, and 7 c.c. of hydrochloric acid and the antimony estimated by titration with permanganate. The solution is then boiled with a further 30 c.c. of water, 60 c.c. of hydrochloric acid, and 2–3 grams of metallic antimony, and the tin is estimated by titration with iodine [cf. *J. Soc. Chem. Ind.*, 1922, Oct.].

A. R. P.

Decomposition and Analysis of Monazite. P. WENGER and P. CHRISTIN (*Ann. Chim. Analyt.*, 1922, [ii], **4**, 231–232).—The hitherto published methods for the attack of monazite are either long and delicate, or else leave large quantities of the rare earths undissolved. By the following method the whole of the mineral can readily be brought into solution. About 1 gram of the finely ground material is heated for five hours with 5 c.c. of sulphuric acid (*d* 1.84) at 230°. The resulting pasty mass is gradually poured into iced water, when all but a small residue passes into solution. This residue is collected on a filter and again heated with sulphuric acid, a little hydrofluoric acid being added to volatilise the silica. The residue in the crucible is then melted with six parts of sodium carbonate. On addition of water, the tantalum passes into solution, and any slight residue which still may remain will be zirconia, which is rendered soluble by fusion with potassium hydrogen sulphate. In the subsequent analysis the precipitation of the rare earths by oxalic acid should be conducted at 55° in a solution containing 0.15–0.75% of sulphuric acid and with an excess of 3% of oxalic acid. At this temperature the precipitation may be considered quantitative for yttrium, thorium, cerium, and didymium. Lanthanum oxalate, being the most soluble, is not completely precipitated, and 50 c.c. of the solution under the above conditions would retain 0.0011 gram of lanthanum in solution.

G. F. M.

The Use of Hanuš's Method for the Determination of the Iodine Figure of Mineral Oils. JAN HLADKÝ (*Chem. Listy*, 1922, **16**, 207–211).—The method of Hanuš, whereby the iodine figure of mineral oils and bitumens is determined by means of a solution of iodine bromide in carbon tetrachloride, is examined. It is found that the reagent does not depreciate as rapidly as those used in the methods of Hübl and of Wijs (*E. Graefe, Petroleum*, 1905, **12**, 631), and that the difference produced in the iodine

figure by increasing the time allowed for reaction is smaller than for the above methods. The concentration of the reagent, and the reaction temperature are not of great importance, whilst it is essential that the quantity of oil used is such as to leave a large excess of reagent after interaction. The presence of small quantities of water does not appear to affect the reaction. A further advantage of this method is that it permits the use of carbon tetrachloride, a universal solvent for the bitumens. The accuracy attainable is, for oils of a low iodine figure, from 1 to 2 units. R. T.

The Iodine Values of Aliphatic and Aromatic Unsaturated Compounds. D. HOLDE [with P. WERNER, IDA TACKE, and C. WILKE] (*Chem. Umschau*, 1922, **29**, 185—188).—In the case of oleic acid anhydride and erucic acid, the iodine values found by the Hanuš method or by the Hübl-Waller method agree with the calculated values. Cholesterol, however, yields an iodine value of 73 to 77 by the Hübl method and phytosterol a value of 50 to 68, according to the time of contact (five to forty-eight hours); when estimated by the Wijs method, the iodine value of these two substances is identical, namely, 135. A similar difference in values obtained by the two methods has also been noticed in the case of certain mineral oils. W. P. S.

A New Method for the Detection of Methyl Alcohol. REINO HÄMÄLÄINEN (*Acta Soc. Med. fennic. "Duodecim."*, 1921, **3**, 1—6; *Ber. Ges. Physiol.*, **11**, 262—263; from *Chem. Zentr.*, 1922, ii, 918).—Formaldehyde from the oxidation of methyl alcohol by potassium permanganate in ethyl alcohol-sulphuric acid solution is detected by addition of methyl violet-sulphurous acid decolorised by oxalic acid; a dark- to light-blue coloration is formed. G. W. R.

Estimation of the Alcohol Content of a Solution. A. LÉVÊQUE (*Bull. Sci. Pharmacol.*, 1921, **28**, 549—554; from *Chem. Zentr.*, 1922, ii, 819).—The method of Rosset (A., 1921, ii, 598) is applied, using for miscibility temperature determinations, menthol, aniline sulphate, and phenol. G. W. R.

Estimation of Glycerol by the Dichromate Method. J. KELLNER (*Z. deut. Oel-Fett Ind.*, 1922, **42**, 345; cf. this vol., ii, 399).—Complete oxidation of glycerol by dichromate is effected only when sulphuric acid, *d* 1.230, is employed. Sodium chloride, if present in the glycerol, should be removed by treatment with lead acetate and silver oxide, since chlorine is evolved even with sulphuric acid, *d* 1.1.

CHEMICAL ABSTRACTS.

Chemical Reaction of Phenol. ANGELO BELLUSSI (*Arch. Farm. speriment. Sci. aff.*, 1922, **33**, 190—191).—When 2 c.c. of 2% phenol solution is gently heated on a water-bath with a small crystal of ammonium phosphate or arsenate and a few drops of 3% hydrogen peroxide solution, a pink or cherry-red coloration appears after a few seconds, the phenol evidently undergoing oxidation. The same coloration is obtained, only far more tardily, when the phenol solution is heated with hydrogen peroxide or

even alone, so that the action of the ammonium phosphate or arsenate is catalytic in nature.

T. H. P.

Causse-Bonnan's Method for the Estimation of Dextrose. H. J. LEMKES and L. M. LANSBERG (*Pharm. Weekblad*, 1922, **59**, 936—939).—It is confirmed that the results obtained vary considerably with the time occupied in titration. Attempts to get uniform results by substituting sodium for potassium compounds were unsuccessful. The white precipitate obtained at the end of the titration was found to contain Cu 23.05, Fe 11.2, K 21.55, (CN) 32.0, and water of crystallisation about 12.5%, but no empirical formula could be deduced.

S. I. L.

Modification of Bang's Method for the Estimation of Sugar in the Blood. Z. ERNST and ST. WEISS (*Wiener klin. Wochschr.*, 1921, **34**, 174—175).—The blood sample of 0.115 c.c. is aspirated by means of a calibrated capillary pipette which is attached to a 15 c.c. flask, and the pipette is rinsed into the flask by aspirating through it Bang's diluting salt solution. The stopper and pipette are removed, the flask is filled with the salt solution to the mark, the contents are mixed, filtered and 13 c.c. of the filtrate, corresponding with 0.1 c.c. of blood, are analysed by Bang's method (A., 1918, ii, 278). Instead of the filtration, a centrifuge may be employed.

CHEMICAL ABSTRACTS.

The Estimation of the Total Oxygen-combining Power of the Blood in the Van Slyke Apparatus. CHRISTEN LUNDGAARD and EGGERT MÖLLER (*J. Biol. Chem.*, 1922, **52**, 377—378).—The blood is saturated with oxygen after, instead of before, introduction into the apparatus. The remainder of the estimation is then carried out by the modified method of Van Slyke and Stadie (this vol., ii, 78).

E. S.

Qualitative and Quantitative Demonstration of Blood in Urine. A. JOHANNESSEN (*Ugesk. Læger*, 1921, **83**, 1613; from *Physiol. Abstr.*, 1922, **7**, 280).—The reagent recommended is prepared by adding 1 gram of phenolphthalein and 25 grams of potassium hydroxide to 100 c.c. of distilled water and then boiling with 10 grams of zinc dust until decolorised. After filtration, an equal volume of 96% alcohol is added. This solution keeps for six months. Immediately before use 1 c.c. of hydrogen peroxide is added to each 9 c.c. Equal volumes of the reagent and the suspected urine are mixed; if blood is present up to 1 in 20,000 or 1 in 30,000 a pinkish-red colour is formed. With blood in water, a positive reaction is obtained with dilutions as high as 1 in 500,000. Copper, even in traces, interferes with the test.

E. S.

General and Physical Chemistry.

Influence of Pressure on the Refractive Index of some Organic Liquids. F. HIMSTEDT and IRMA WERTHEIMER (*Ann. Physik*, 1922, [iv], **67**, 395—406).—The experimental arrangement of Röntgen and Zehnder was used, together with the Loewe-Zeiss interferometer. The refractive index and dn/dp were found for the following liquids, bromobenzene, chlorobenzene, nitrobenzene, chloroform, dichloroethylene, pinene, and hexane, and from these the compressibilities were calculated from the Newton, Beer, and Lorentz formulæ. The discussion of these values is postponed until the compressibilities of these liquids have been determined experimentally. W. E. G.

The Establishment of the International System of Normal Wave-lengths. FRIEDRICH MÜLLER (*Z. wiss. Photochem.*, 1922, **22**, 1—20).—Wave-lengths of the carbon, iron, and nickel spectra were accurately measured and are tabulated. Methods of measurement and precautions taken are given. W. T.

Fine Structure of the Red Hydrogen Line. OTTO OLDENBURG (*Ann. Physik*, 1922, [iv], **67**, 253—277).—Previous measurements of the Zeeman effect for H_α disagree among themselves and with the Sommerfeld quantum theory of fine structure. The divergences are shown to be mainly caused by errors arising in the photography of the spectrum from an echelon grating, and in the measurement of narrow diffuse bands. The true separation of H_α in the absence of a magnetic field, and at the temperature of liquid air, was obtained by resolution of the intensity curve into two Gauss curves. The value obtained was $0.140 \text{ \AA.} \pm 0.008$, whereas the measured distance between the two maxima was about 5% smaller. In weak fields (3500 gauss) the anomalous partial fusion of the p -components observed by Erochin was confirmed, but was shown to be due to a widening of the lines, without any appreciable alteration in the distance between the two components. At 18000 gauss, the two lines run together to form a single line which is narrower than the original doublet.

For weak fields, the Zeeman effect for the s -component is normal, but the widening of the lines at higher fields leads to the disappearance of the fine structure. Since the lines of H, He^+ , and Zn, which are most sensitive to the Stark effect, also become diffuse in a magnetic field, it is possible that an unexpected Stark effect was present. However, this is unlikely, since no appreciable change in potential along the capillary tube was observed under the influence of the magnetic field. Also the widening of the lines caused by the Stark effect disappears on the application of a magnetic field. The Zeeman effect for small magnetic fields is normal,

but the fusion of the fine structure components observed in the higher fields is in opposition to the Sommerfeld theory.

W. E. G.

The Balmer Series of Hydrogen. E. GEHRCKE and E. LAU (*Ann. Physik*, 1922, [iv], **67**, 388—394).—Measurements of the fine structure of the Balmer series have been made at the temperature of liquid air, by means of a Lummer-Gehrcke interference spectroscope. The differences between the frequencies of the H_α , H_β , and H_γ doublets were, respectively, $\Delta\nu \cdot 10^{-9} = 8.69, 8.78, 8.74$. These values were independent of the time of exposure, so that no error due to the contraction of the gelatin of the photographic plate could have occurred. A considerable deviation occurs between these values and the theoretical fine structure constant, 10.95, of Sommerfeld. It is shown that this deviation from theory is not explained by the additional hypothesis of Sommerfeld, which states that each line of the doublet is composed of a number of sub-components. The experimental results are also in poor agreement with the theory of Silberstein. It is remarkable that the mean figure for $\Delta\nu$ is that derived by Lenz from the Abraham assumption of stationary electrons.

W. E. G.

Series and Other Regularities in the Spectrum of Manganese. MIGUEL A. CATALÁN (*Phil. Trans.*, 1922, 223A, 127—173).—The flame-arc, arc, and spark spectra of manganese have been photographed, using a Littrow spectrograph giving a linear dispersion of 16 Å. per mm. at λ 6300 and 5.5 Å. at λ 4700, a similar instrument with quartz prism giving a linear dispersion of 12 Å. per mm. at λ 4000, 4.5 Å. at λ 3000, and 2 Å. at λ 2300, and a concave grating ruled with 14438 lines per inch giving a normal dispersion of 5.5 Å. per mm. in the first order. It is shown that the flame, arc, and spark spectra of manganese, like those of other elements, are formed of two classes of lines, some belonging to the neutral atom and some to the ionised atom (Mn^+). In the spectrum of the neutral atom, triplet series and combination lines have been found. The series follows a Hicks formula with the Rydberg constant " N " and may be classified as follows: (a) A system of four triplets (sharp, diffuse, principal, and fundamental, the last two being rather doubtful), analogous to the ordinary triplet systems of series in the alkaline earths. (b) A system of three narrower triplet series (sharp, diffuse, and principal) which have strong analogies with the single line systems of series in the alkaline earths. (c) Another system of still narrower triplets (sharp, diffuse, and principal) which is parallel to the preceding system, the shift number being $C=10967.75$. The intercombination lines, $1S-1p_2$ and $1S-1p_3$ (λ 5394.677 and λ 5432.555), between the first two systems are found as two lines very prominent at low temperatures, and losing very much of their intensity at high temperatures. The ionisation and resonance potentials of manganese have been calculated from the term $1S$ and from the wave number of the line $1S+1p_3$. The values obtained are 7.4 volts and 2.3 volts, respectively. The lines of ionised manganese, enhanced lines, also

form triplets. The data do not permit of the series being traced, but there is evidence that they include a system of triplets (sharp, diffuse, and principal), and also another system of narrower triplets, corresponding with the single line systems in the alkaline earths, as in the case of the neutral atom. Each diffuse triplet, in neutral and ionised atom alike, is formed of nine lines, giving five d terms in contrast to the six lines giving three d terms which are found in the more familiar diffuse triplets of the alkaline earths. In the spectra of both the neutral and the ionised atom there are certain groups of prominent lines having the same character and showing similar variations with changes of temperature. The lines of each group are related by very exact numerical separations, and these lines are denoted by the term *multiplet*. It is pointed out that similar multiplets exist in the spectra of the neutral atoms of magnesium, calcium, barium, strontium, ionised aluminium, scandium, yttrium, and lanthanum, and neutral atoms of silicon and chromium, and that they may represent a form of regularity present in the spectra of many elements, and serve to indicate the most probable nature of the series in the spectra where the actual series have not been traced. The spectrum of manganese is discussed in connexion with the position of manganese in the periodic system. It seems most probable that the neutral atom of manganese has two electrons in the outermost ring, and that when this atom loses an electron, thus becoming ionised, another electron from the next ring comes out to take its place in the outermost ring, which again contains two electrons. This mechanism would account for the similarity of the neutral and ionised manganese atoms.

J. F. S.

Ultra-red Characteristic Frequencies of the Silicates.

CLEMENS SCHAEFER and MARTHA SCHUBERT (*Z. tech. Physik*, 1922, 3, 201—204; cf. this vol., ii, 179).—Since crystals containing CO_3 and similar groups show selective reflection which is characteristic of the group, and varies in a simple manner with the type of crystal, an analogous phenomenon was sought in the case of the silicates. The reflecting power of thirteen silicates was observed throughout the range 1 to 20μ , and twelve of these showed maxima near 10μ and 18μ . These maxima were complicated, varying greatly from one substance to another, and could not be correlated with the crystal structure in the simple manner noted in connexion with other groups such as CO_3 , ClO_3 , etc. One specimen, analcite, lacked the maximum of greater wave-length. Two specimens containing the group SiO_4 showed no particular similarity in their reflexion curves.

CHEMICAL ABSTRACTS.

The Regularities of Ultra-red Spectra and the Failure of the Classical Dispersion Theory. CLEMENS SCHAEFER (*Ann. Physik*, 1922, [iv], 67, 407—419).—A theoretical paper. In the absorption spectra of polyatomic gases, a simple relationship occurs between the various bands. In diatomic gases, the band with short wave-length is almost exactly the octave of the band with long wave-length. Similar octaves are present in the

absorption bands of solid substances. An explanation is put forward based on the assumption that the molecular vibrations are asymmetrical, which supports the quantum theory and is opposed to the classical theory of dispersion and absorption. W. E. G.

Absorption of Light by Sulphur at Various Temperatures.

MITSU HARU FUKUDA (*Mem. Coll. Sci. Kyōtō*, 1921, **4**, 351—354).—The absorption spectrum of a layer of sulphur 0.3 mm. thick, prepared by heating the element slowly until melted, extends from the ultra-violet up to $\lambda 0.408\mu$ at 0° , and extends a further 2μ towards the red end for every 10° rise of temperature up to 300° . No discontinuity, such as might be anticipated from the view of Kellas as to the constitution of the sulphur molecule (T., 1915, **113**, 903), was observed in the absorption spectrum at about 160° . The absorption spectrum of plastic sulphur depends on the initial temperature to which the sulphur is heated during its preparation. The higher this temperature, the further does the absorption extend from the ultra-violet towards the red end. J. S. G. T.

Absorption of $\lambda 5460.97 \text{ \AA}$. by Luminous Mercury Vapour.

J. C. McLENNAN, D. S. AINSLIE, and (Miss) F. M. CALE (*Proc. Roy. Soc.*, 1922, [A], **102**, 33—45).—It has been shown that when the radiation constituting the green line of mercury is passed through moderately luminous mercury vapour the main component and the components No. +1, $\Delta\lambda = 0.0086 \text{ \AA}$. and No. -1, $\Delta\lambda = -0.0087 \text{ \AA}$. can be strongly absorbed. No marked absorption by luminous mercury vapour was observed in the case of the other nine components of the green line. Of the nine members constituting the magnetically resolved green line, it was found that the central undisplaced member was the only one that could be markedly absorbed by luminous vapour. It is also shown that absorption by luminous mercury vapour of the light constituting the green line in the mercury spectrum affords a means of clearly and easily demonstrating the existence of the components of the line with separations $\Delta\lambda = +0.0182 \text{ \AA}$. and $\Delta\lambda = -0.021 \text{ \AA}$., that is satellites Nos. +2 and -2. Some considerations are presented in support of the view that the components of the green line of mercury, for which $\Delta\lambda = +0.0182 \text{ \AA}$., $+0.0086 \text{ \AA}$., -0.0087 \AA ., -0.021 \AA ., and zero, may originate in atoms of the element having, respectively, the atomic weights 197, 198, 202, 204, and 200. J. F. S.

The Absorption of Mercury Vapour. J. FRANK and W.

GROTRIAN (*Z. tech. Physik*, 1922, **3**, 194—197).—To test the theory that the absorption bands of mercury vapour are due to diatomic molecules, the absorption of the band at 2540 \AA . was observed in superheated vapour. A sample saturated at $200^\circ/20 \text{ mm}$. was observed at temperatures up to 1200° . The strength of the band was found to decrease with increasing temperature. A second sample, saturated at $240^\circ/35 \text{ mm}$., showed greater absorption at low temperatures, but became nearly transparent at 1200° . This behaviour confirms the belief that the band is due to the molecule which is dissociated at high temperatures. From the rate of

variation of absorption with temperature, it is concluded that the work required for dissociation is of the order of one Cal. The number of molecules involved in the absorption is remarkably small, even at the lowest temperatures, where the partial pressure of molecules is less than 10^{-5} mm. CHEMICAL ABSTRACTS.

A Simple Method for the Measurement of Ultra-violet Absorption. CHR. WINTHER, BAGGESGAARD-RASMUSSEN, and E. SCHREINER (*Z. wiss. Photochem.*, 1922, **22**, 33—46).—The photographic method of Merton (T., 1913, **103**, 124) for the quantitative measurement of absorption has been adopted for the ultra-violet. An improved fluorometer has been constructed for extinction measurements of certain wave-lengths and the accuracy of the instrument has been tested by thermo-electric controls. The quantitative photographic method was employed for the investigation of the nitrates of potassium and silver, the results differed from those obtained by qualitative methods. W. T.

The Emission of Light by Atoms. K. FÖRSTERLING (*Z. Physik*, 1922, **10**, 387—392).—Previous experimental observations require that the light emitted by excited atoms is coupled with the atom in a continuous manner. This is contrary to the views of Sommerfeld, and in agreement with those of Mie. An external magnetic or electrical field does not appear to exert any effect on light free in the ether. Thus, if the emitted light is discontinuous, such fields should exert no effect on the radiated energy once it has left the electron. Those atoms in which the electrons have returned to an inner quantum orbit, after emitting the energy of excitation, should not show the Stark effect. The emitted light should be unchanged by the action of an electrical field and Stark, in his experiments, should have observed the unchanged line. For the *p*-components of H_α , H_γ , and H_δ and for the *s*-component of H_δ this was shown not to be the case. On this account, the assumption is made that the electron in its passage from the initial to the final orbit should give up its light continuously to the ether. If the assumption of the spherical wave, and the correspondence principle of Bohr, are still maintained, it would appear necessary to postulate some new energy form in the atom. W. E. G.

The Luminescence of Gas in the Electrodeless Discharge : The Induction Spectra of Cæsium and Rubidium. M. L. DUNOYER (*J. Phys. Radium*, 1922, **8**, 261—292).—The vapours of cæsium and rubidium, when surrounded by a high frequency electromagnetic field, emit a brilliant luminescence at 100—300°. Rubidium vapour gives a feeble luminosity at the ordinary temperature, but no light can be detected from cæsium vapour below 90°. The colour of the luminescence of the saturated metallic vapour undergoes a sudden change at certain temperatures. It is uncertain to what extent this is due to an increase in density of the vapour. At the lowest temperatures, the induction spectra are very rich in lines, but the principal and secondary series are absent. At higher temperatures, all the cæsium and most of the

rubidium lines which occur in the spark spectra appear, and are present in great intensity. The secondary series are, however, completely absent, and only a few lines from the flame and arc spectra are to be found in the induction spectra of these metals. The ionised atoms are believed to be the source of the induction spectra, and not the emission of an electron by the Bohr mechanism. Such ions should resemble the atoms of the rare gases, and points of resemblance should occur between the induction spectra of the two groups of elements.

W. E. G.

The Luminescence of Decomposing Ozone. MAX TRAUTZ and WALTER SEIDEL (*Ann. Physik*, 1922, [iv], **67**, 527—572).—No chemiluminescence is observed when a carefully purified mixture of ozone and oxygen is heated to 400°. On the admission of coal gas to this mixture, light is emitted at the ordinary temperature, frequently with the formation of a mist. Purified air, carbon dioxide, and hydrogen do not give rise to this effect. Carbon monoxide when mixed with ozone produces chemiluminescence at temperatures above 150°, and a band of light is emitted between the wave-lengths 400 and 560 μ . This spectrum is independent of the thickness of the radiating gas.

The light emitted by mixtures of carbon monoxide and ozone is measured by means of an argon-filled rubidium cell. By a streaming method, it was shown that the amount of light is proportional to the product of the concentrations of the two gases; thus $\Delta a = K_1[\text{CO}][\text{O}_3]/1 + K_2[\text{O}_3]/t$, where Δa is the electrometer deflexion, K_1 and K_2 are constants depending on the velocities of two simultaneous reactions, and t is the time of streaming for 50 c.c. of gas. These conclusions were confirmed by a study of the reaction in a stationary gas mixture. The velocity of emission of light obeys the second order law, and the deviations which were observed are probably due to irregularities in the temperature of the gas mixture. The velocity of emission increases with increase in temperature, but the total quantity of light emitted increases to a limiting value. The law of constant light summation propounded by Lenard for phosphorescent substances (*Heidelb. Akad.*, 1912, A, 5 Abh.) applies equally well to the chemiluminescence from the mixture of carbon monoxide and ozone, the quantity of light being independent of both the velocity and the temperature. The presence of indifferent gases such as nitrogen or carbon dioxide is without effect on the emission of light. The conclusion that the reaction is of the second order is supported by the observations of Angerer (*A.*, 1921, ii, 257) on the decomposition of N_3 .

W. E. G.

Catalysis. XVI. Radiation as a Factor in Thermal and Photochemical Reactions. N. R. DHAR (*Z. anorg. Chem.*, 1922, **122**, 151—158).—The author has studied the velocity of certain chemical reactions in tropical sunshine and found that the light rays accelerated the reaction in all cases, more particularly so in the case of those reactions with a high temperature coefficient. The paper concludes with a brief review of the radiation hypothesis.

W. T.

The Effect of Colloids on Silver Bromide Emulsions.

ROBERT SCHWARZ and HEINRICH STOCK (*Z. wiss. Photochem.*, 1922, **22**, 26—32).—The influence of catalysts on the photochemical decomposition of pure silver bromide has been investigated, the amount of decomposition being determined by the method previously described (A., 1921, ii, 614). Platinum sol delays the inversion point and solarisation. Silver and silicic acid sols act as positive catalysts, whilst aluminium hydroxide has a negative effect. Ferric hydroxide and stannic acid coagulated the emulsion. W. T.

The Photochemical Reduction of Titanium Salts. A.

BENRATH and A. OBLADEN (*Z. wiss. Photochem.*, 1922, **22**, 65—71).—The sulphate and oxalate of titanium were not reduced by ethyl alcohol on long exposure to light, whereas the chloride reacted violently. For quantitative work, ethyl alcohol was an unsatisfactory reducing agent owing to the formation of hydrogen peroxide. Mandelic and lactic acids were found to be suitable, and measurements were carried out with the former, which was the more powerful reducing agent. The temperature coefficient of the reaction for 10° was found to be 2.21. The reaction obeyed the law of mass action, and was found to be bimolecular. Chlorides decreased the velocity, probably owing to the decrease of ionisation of the tetrachloride. W. T.

Elimination of Carbon Dioxide from Organic Compounds.**VI. The Action of the Light of the Electric Arc on Aqueous Oxalic Acid Solutions in Presence of Ferric, Chromic, and Mercuric Chloride, of Uranyl Acetate, and of Iodic Acid.**

HERMANN KUNZ-KRAUSE and PAUL MANICKE (*Ber. Deut. pharm. Ges.*, 1922, **32**, 209—216; cf. this vol., i, 6).—Many observations are recorded on the action of sunlight in decomposing aqueous solutions of oxalic acid, but none on the effect of artificial light. Experiments have been made on the decomposing effect of the light from an electric arc on oxalic acid in presence of a number of "catalysts." In presence of ferric chloride, 61.7% of the oxalic acid was decomposed into carbon dioxide in sixteen hours, the reaction being represented by the equation $\text{H}_2\text{C}_2\text{O}_4 + \text{Fe}_2\text{Cl}_6 = 2\text{FeCl}_2 + 2\text{HCl} + 2\text{CO}_2$. When chromic chloride was used, no decomposition occurred, but ammonium oxalate was oxidised in presence of mercuric chloride, the latter being reduced to mercurous chloride. The decomposition of oxalic acid was also promoted by uranyl acetate and by iodic acid, in the latter case with formation of free iodine. So far as qualitative experiments show, sunlight and the arc light are equivalent for the decomposition of oxalic acid in presence of the above substances. E. H. R.

Chemistry of Actinometers. A. BENRATH, E. HESS, and

A. OBLADEN (*Z. wiss. Photochem.*, 1922, **22**, 47—64).—The mercuric chloride-ammonium oxalate actinometer was found to be trustworthy within narrow limits only. The ferric chloride and the oxalic acid-uranyl acetate actinometers were found to be in good agreement. Electrolytes retard the reduction of ferric chloride

and the decomposition of oxalic acid. The authors argue that the added electrolytes have no influence on the photochemical reaction, but decrease the dissociation of the iron salt and the oxalic acid, and they draw the conclusion that the ferric ion and the oxalate ion are photochemically active, whilst the undissociated molecules are inactive. W. T.

The Photoelectric Effect of the Alkaline-earth Phosphors.

KARL GÖGGL (*Ann. Physik*, 1922, **67**, 301—319).—The relation between the photoelectric effect and the wave-length of the exciting light have been studied for $\text{CaBi}\alpha$ and $\text{SrBi}\alpha$ phosphors (cf. Lenard and Saeland, A., 1909, ii, 283). In order to maintain the phosphor in a condition of least excitation, it was illuminated simultaneously by the exciting radiation, and by either green or red light. On account of the low conductivity of the phosphor as compared with the metals, the photoelectric effect of these substances increases more slowly than the intensity of the exciting light. The normal photoelectric effect becomes appreciable at the violet end of the visible spectrum, and increases rapidly with decrease in wave-length. In addition, in the region of the wave-length of the phosphorescent light, selective effects are observed, which are especially large in the presence of green light. In the case of the $\text{CaBi}\alpha$ phosphor, the maxima for the photoelectric effect correspond exactly with the maxima of phosphorescence, but a shift of the photoelectric effect towards the red occurs with the $\text{SrBi}\alpha$ phosphor. The normal phosphors show a much greater photoelectric effect and phosphorescence than the decinormal phosphors. This is associated with the larger number of small phosphorescence centres in the normal phosphor. Phosphors when destroyed by pressure in the presence of light, become coloured, show practically no phosphorescence, and give the normal photoelectric effect. When destroyed in the dark, however, a much larger effect is obtained which decreases with time. It is suggested that this is caused by the destruction of the closed chain compounds forming the phosphorescence centres, into molecules containing free valency electrons. The magnitude of the photoelectric effect is proportional to the amount of the colouring of the phosphor.

The *d*- and *u*-emission of phosphorescent light is accompanied by the separation of electrons, whereas the *m*-emission, the fluorescence, is not accompanied by a photoelectric effect, and hence is not a consequence of electron emission. The electrons emitted from a phosphorescence centre do not necessarily return to the same centre or by the same path. W. E. G.

β -Ray Spectra and their Connexion with γ -Radiation.

LISE MEITNER (*Z. Physik*, 1922, **11**, 35—54).—By means of a more precise investigation, it is shown that the thorium-*B* line, which was previously and erroneously classified as a line belonging to the L_2 ring (this vol., ii, 416), in reality belongs to a second γ -radiation group, as was indicated by Ellis (A., 1921, ii, 422). Measurements of thorium-*C* and thorium-*C'* confirm those of von Baeyer, Hahn, and Meitner (A., 1911, ii, 567) as to the existence of a group of

β -rays of velocity about 95% that of light, which Ellis (*loc. cit.*) was unable to find, and, further, these measurements show that on using the exact energy of the K -disintegration of thallium some of these lines must be interpreted otherwise than was done by Ellis. Very exact experiments with radium- D which have been controlled by photometric registration show that the three L levels found by Ellis are not present in radium- D ; one only could be found and that is the L_2 level. It is concluded from the above-mentioned results and those of Ellis for radium- B that in the excitation of the characteristic radiation by γ -radiation proceeding from the nucleus of the atom itself practically only the L_2 level is affected, in contrast to the relationships in the excitation by Röntgen rays from outside the atom. An attempt is made to explain this result on the basis of the unsymmetrical atomic configuration postulated in Bohr's hypothesis. The criticism of the author's interpretation of the β -change put forward by Ellis is discussed, and it is shown that this interpretation is in keeping with the experimental facts.

J. F. S.

Wave-lengths of γ -Rays. LISE MEITNER (*Naturwiss.*, 1922, 10, 884; from *Chem. Zentr.*, 1922, i, 1352—1354; cf. this vol., ii, 416).—The lattice of crystals is too coarse for the determination of the wave-length of hard γ -rays. Primary β -rays from the disintegration of an atomic nucleus have in the simplest case uniform velocity, and energy corresponding with this velocity. The β -radiation may either pass out of the atom with unchanged velocity or else γ -rays may originate in the nucleus from the β -rays, having the same energy and the relation $E_\beta = h\nu_\gamma = hc/\lambda_\gamma$ (1) holds. The resultant γ -radiation detaches K -, L -, and M -electrons from the atom in which it originates and the energy of this secondary radiation is equal to the energy of the γ -radiation, less the energy used for disintegration or $h\nu_\gamma = E_\beta - E_k$ (2), where E_k is the energy used in detaching K electrons. E_β and E_k may be determined from the deviation of the β -rays in a magnetic field, and E_k from the K , L , and M absorption wave-lengths obtained by the lattice method. Applying equations (1) and (2), the author found the wave-length of the γ -rays from thorium- B to be 5.2×10^{-10} cm., those from radium 6.6×10^{-10} cm., and those from radium- D 2.9×10^{-9} cm. The shortest wave-length obtained by this method was that of the γ -rays from thorium- C'' , namely, 2.45×10^{-10} cm., approximately one-fifth of the wave-length of the shortest characteristic Röntgen rays. γ -Rays of even shorter wave-length may be expected to occur. The γ -rays originating from the nucleus may in some circumstances have a greater wave-length than the corresponding K -series. In the case of radium- D where the wave-length of the K series is 1.385×10^{-9} , the γ -rays cannot set free any K electrons.

G. W. R.

Excitation and Ionisation Potentials of Neon and Argon. G. HERTZ (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, 25, 179—187).—The excitation potentials of argon and neon have been

determined by plotting the number of electrons which have a velocity below a definite small value (in the present experiments that below the velocity corresponding with 0.2 volt) against the applied tension. In this way, the excitation potentials are shown as sharp maxima in the curves. This method is unsuitable for measuring the ionisation potential, and a new method for measuring this quantity has been employed. The results show that, starting from the value 20.45 volts as the lowest excitation potential of helium, two pronounced excitation potentials are found at 17.35 and 19.15 volts for neon. The ionisation potential of neon is found to lie at 22.2 volts. In the case of argon, excitation potentials are found at 12.25 and 13.7 volts and the ionisation potential at 16.0 volts. It is shown in the case of neon that the values found are in harmony with the optical measurement of the spectrum, and, further, there is no room in the series spectrum for a resonance potential of 11.8 volts and ionisation potentials at 16.7 and 20 volts, as found by Horton and Davies (A., 1919, ii, 210), neither did the author find any indication of a resonance potential or ionisation potentials at the values stated. In the case of argon, a comparison with the series spectrum is not possible, but assuming that the argon spectrum is constituted similarly to the neon spectrum, then calculating from the observed excitation and ionisation potentials, the following mean values for the first groups of the terms are to be expected : $0.5s=130000\pm1000$, $1.5s\sim30400$; $2p\sim18600$, and higher terms <10500 . J. F. S.

Chemical Reactions induced by the Corona Effect in Circuits traversed by Continuous Currents. C. MONTE-MARTINI (*Gazzetta*, 1922, 52, ii, 96—97).—The corona discharge is capable of effecting the following reactions: Formation of ozone from air; decomposition of carbon dioxide into carbon monoxide and oxygen; synthesis of ammonia from its elements; formation of carbon dioxide and hydrogen from carbon monoxide and water vapour; formation of hydrogen cyanide from acetylene and nitrogen; formation of formaldehyde from carbon dioxide and hydrogen; formation of benzoic acid from carbon dioxide and benzene vapour; decomposition of hydrogen sulphide into its elements and the inverse reaction; decomposition of hydrogen antimonide and its synthesis from its elements. T. H. P.

Resistance Temperature Coefficient of Concentrated Solutions of Sodium in Liquid Ammonia. CHARLES A. KRAUS and WALTER W. LUCASSE (*J. Amer. Chem. Soc.*, 1922, 44, 1941—1949).—The resistance temperature coefficients of concentrated solutions of sodium in liquid ammonia have been measured from the saturation point up to $V=5.02$ and at temperatures from the boiling point of liquid ammonia down to -60° . Near the saturation point, the temperature coefficient of sodium in liquid ammonia has a value approximately 0.066%. With decreasing concentration, the temperature coefficient increases markedly, passing through a maximum value of approximately 3.6% at $V=1.1$ and then decreasing to a value of approximately 1.55 at dilutions above 4.0 litres

per atom. Taking into account the earlier work on the temperature coefficient of more dilute solutions, it is evident that the temperature coefficient passes through a minimum value. From the form of the curve at high concentrations, the temperature coefficient is seen to be approaching a negative value at high concentrations, although this value is not actually realisable, since the saturation point of the solution is reached. At the highest concentrations the solutions of the metals in liquid ammonia closely resemble metallic alloys. At lower temperatures, the temperature coefficient increases markedly at higher concentrations. As the concentration decreases, the influence of temperature on the coefficient decreases, and at a dilution $V=5.3$ the coefficient is relatively independent of temperature. From previous work on the influence of temperature on the temperature coefficient of more dilute solutions, it is clear that the influence changes sign, since at low concentrations the coefficient increases markedly with increasing temperature.

J. F. S.

Effect of Substitution on the Free Energy of Oxidation-reduction Reactions. I. Benzoquinone Derivatives. VICTOR K. LAMER and LILLIAN E. BAKER (*J. Amer. Chem. Soc.*, 1922, **44**, 1954—1964).—The oxidation reduction potentials of the substituted derivatives of quinone—quinol mixtures have been determined at 25°. The method consisted in adding the quinone to a measured volume of buffer solution, removing the oxygen by nitrogen, and then reducing a portion of the quinone to quinol with titanium chloride solution and measuring the potential of the mixture against a calomel electrode, using gold or platinum electrodes. Other measurements were made starting with the quinol and oxidising it with potassium dichromate. The concentration of hydrogen ions was also measured in each solution. The cells measured were therefore of the types: $\text{Hg} | \text{Hg}_2\text{Cl}_2, \text{KCl}(\text{sat}) || Q + Q\text{H}_2(yM) + \text{H}^+(xM) / \text{Pt}$; and $\text{Hg} | \text{Hg}_2\text{Cl}_2, \text{KCl}(\text{sat}) || \text{H}^+(xM) | \text{H}_2(1 \text{ atm.}) / \text{Pt}$. The following values of the normal potentials and the reduction of free energy in the various cases are recorded: bromo-*p*-benzoquinone, 0.7151 volts, 138.0 kilojoules; chloro-*p*-benzoquinone, 0.7125, 137.5; *p*-benzoquinone, 0.6990, 134.9; toluquinone, 0.6454, 124.6; *p*-xyloquinone, 0.5900, 113.9; *p*-thymoquinone, 0.5875, 113.4; dimethoxy-*p*-benzoquinone, 0.5139, 99.2; naphthaquinone, 0.4698, 90.7. The effect produced by the substitution of the various groups is discussed in the light of the positive-negative rule of Michael. The validity of the method of work adopted has been established by (1) the constancy and reproducibility of the potentials under widely varying concentrations and following anodic or cathodic polarisation, (2) the use of different electrodes, (3) the agreement of the *E.M.F.* with those obtained by the method of pure mixtures, and (4) the approach of the equilibrium from both sides. The *E.M.F.* values are reproducible to 0.2 milli-volt.

J. F. S.

Stability of Phthalate Solutions as Standards in Hydrogen-ion Work. C. J. WOOD and P. P. MURDICK (*J. Amer. Chem. Soc.*, 1922, **44**, 2008—2009).—An answer to the criticisms of Oakes

and Salisbury (this vol., ii, 468), who have shown that phthalate solutions when measured against a hydrogen electrode a drift of the *E.M.F.* is observed (cf. also Merrill, this vol., i, 326). The authors have repeated their measurements with a 0.2*M.*-solution of potassium hydrogen phthalate, which are shown to agree with those of Clark ("Determination of Hydrogen Ions," Baltimore, 1920). It is therefore contended that potassium hydrogen phthalate may be obtained in a sufficiently pure state to give constant potentials with the hydrogen electrode.

J. F. S.

An Electrolytic Current Intensification Effect, A New Electrolytic Displacement Effect, and the Connexion between Electrolysis and the Emission of Electrons in a Vacuum.

III. D. REICHINSTEIN and M. ROTHSCILD (*Z. physikal. Chem.*, 1922, 102, 209—234; cf. A., 1921, ii, 729, this vol., ii, 112).—A continuation of previous work. It is shown that the new displacement effect makes clear the mechanism of electrolytic detectors with a subsidiary source of current. It is shown experimentally that in such detectors the mechanism does not depend on a conversion into direct current, but that these detectors act as current intensifiers; the ratio of the direct current energy brought into existence by an alternating current to that of the alternating current itself may be greater than eighty-eight. An account is given of a new condenser commutator effect. A new electrolytic detector is described which does not make use of an external subsidiary current; this is characterised by the fact that in the absence of an alternating current it has an *E.M.F.*=0. An electrical current is capable of bringing about a reaction in an electrolyte without making any use of the migrations of the ions. When the new intensifier is connected with a source of alternating current, it intensifies the entering current one thousand times, consequently the intensifier and detector can be directly connected with the antennæ which collect high frequency undamped oscillations.

J. F. S.

The More Recent Conception of Electrolytes. IV. The Dissociation State of Acids of Medium Strength, especially Dichloroacetic Acid in Water and in Salt Solutions. ERLING SCHREINER (*Z. anorg. Chem.*, 1922, 122, 201—235).—Pure dichloroacetic acid was prepared and was found to be dimorphous with m. p. 12.15° and 13.25°, $d_{15}^{25}=1.5727$. The *E.M.F.* of this acid was measured in aqueous solutions as well as in 0.2 molar solutions of potassium chloride, sodium acetate, and magnesium sulphate. The quinhydrone electrode was used (Büllmann, A., 1921, ii, 372). The conductivities of the acid and its sodium salts were also measured. Assuming the activity constant of the hydrogen ion to be 0.2, that of the dichloroacetate ion was found to be 0.37. Calculations based on the *E.M.F.* measurements and on the conductivity measurements were in complete agreement with the general law of mass action.

W. T.

Chromate Electrolysis with Diaphragms. A. LOTTERMOSER and KURT FALK (*Z. Elektrochem.*, 1922, 28, 366—376).—When

sodium chromate is electrolysed in a two or three compartment cell, the current yields of sodium dichromate and sodium hydroxide theoretically possible depend on the composition of the solutions originally present in the anode and cathode compartments. It was shown by Müller and Sauer (A., 1912, ii, 1037) that if the anolyte is a solution of sodium chromate and the catholyte one of sodium hydroxide, the yields are lower than they are when sodium chromate is used in both compartments. Their conclusions are now confirmed by extended observations on two compartment cells of the above types and on three compartment cells (*a*) with sodium hydroxide as the catholyte and sodium chromate in the other two compartments, and (*b*) with chromate in all three. The best yields of dichromate are obtained under the last conditions, as circumstances are then the least favourable for the migration of hydroxyl-ions into the anode compartment. The paper concludes with a mathematical discussion of the possible yield obtainable with these types of cell both with and without taking account of the influence of diffusion. [See *J. Soc. Chem. Ind.*, 1922, 857A.]

E. H. R.

Thermal Expansion of Concentrated Salt Solutions.

ROBERT MEYER (*Physikal. Ber.*, 3, 149; from *Chem. Zentr.*, 1922, i, 1214—1215).—The thermal expansions of aqueous solutions of sodium nitrate, potassium nitrate, zinc sulphate, and potassium carbonate, saturated at 20—70°, were measured at temperatures up to 90°. The coefficient of expansion of concentrated solutions increases with rise of temperature, but whilst in the case of water the rate of increase of the coefficient of expansion decreases smoothly with rise of temperature, the curves obtained for concentrated salt solutions are irregular and show points of inflexion the positions of which depend on the concentration of the solution. G. W. R.

Approximate Rule for the Specific Heats of Gases and Vapours.

RUDOLF MEWES (*Z. Sauerstoff Stickstoff Ind.*, 1922, 14, 26; from *Chem. Zentr.*, 1922, i, 1129—1133).—From the formulæ $cp_t = cp_0(1+\gamma)^t$ and $cp_t/cp_0 = (c'p_t/c'p_0)^n$ the specific heat of a substance can be calculated for all temperatures. Values are given of $\log(1+\gamma)$ and n , respectively, for a number of gases and vapours. The values of $\log(1+\gamma)$ are simple multiples of each other, whilst the values of n are simple integers. G. W. R.

The Specific Heats of Gases with Special Reference to Hydrogen. CHRISTOPHER KELK INGOLD and EDITH HILDA USHERWOOD (T., 1922, 121, 2286—2291).

The Isotherms of Nitrogen, Oxygen, and Helium. L. HOLBORN and J. OTTO (*Z. Physik*, 1922, 10, 367—376).—The isothermals of oxygen and nitrogen at temperatures of 0°, 50°, and 100°, and at pressures up to 100 atm., and of helium from 50 to 100 atm. have been determined (cf. A., 1915, ii, 743; 1921, ii, 15). The coefficients are given for the equations $pv = A + Bp +$

Cp^2 , and $pv=(pv)_0(1+B'/v+C'v^2)$; the pv values for helium may be expressed by a linear relationship.

	A.	B 10 ² .	C 10 ⁶ .	B' 10 ² .	C' 10 ⁶ .
Nitrogen...	0° : 1.00057	-0.58100	4.76327	-0.57070	4.58106
	50° : 1.18368	-0.02500	3.80816	-0.03281	4.79200
	100° : 1.36682	+0.36057	3.15102	+0.35016	4.98088
Oxygen ...	0° : 1.00130	-1.30143	0.46452	-1.27335	4.07229
	50° : 1.18456	-0.63543	0.27755	-0.62750	3.26394
	100° : 1.36782	-0.20357	0.22571	-0.20149	3.02964
Helium ...	0° : 0.99930	+0.69543	—	+0.69565	0.50594
	50° : 1.18223	+0.68887	—	0.68797	0.51689
	100° : 1.36518	+0.66804	—	0.67453	0.53306

Amagat's pv -values for 100 atm. are greater by 0.7% for nitrogen and 0.3% for oxygen, and the results of Kamerlingh Onnes and Hyndman for oxygen are, at the lower pressures, about 0.4% greater and, at the higher pressures, about the same amount smaller. The pv -values for air have been calculated for air from those for oxygen and nitrogen: the differences between these and the experimental values for air are within the error of the observations, except at 0° and 50° for the higher pressures. W. E. G.

Thermodynamic Treatment of the Possible Formation of Helium from Hydrogen. RICHARD C. TOLMAN (*J. Amer. Chem. Soc.*, 1922, **44**, 1902—1908).—A theoretical paper in which it is shown that by combining the older ideas as to the possible formation of helium from hydrogen with the newer ideas as to the entropy of monatomic gases, it becomes possible to subject the reaction $4H=He$ to complete thermodynamical treatment. The equilibrium constant calculated from this treatment shows that hydrogen should combine practically completely to form helium at all temperatures below a million degrees and pressures above 10^{100} atmospheres. The conflict between this conclusion and the mutual presence of hydrogen and helium under solar, stellar, and terrestrial conditions has been discussed. Of the various possibilities presented for reconciling the thermodynamic conclusion as to equilibrium constant and the facts, the author regards the following as most hopeful; (1) the reaction to form helium from hydrogen is an extremely slow one even at 20000°, (2) hydrogen consists of a mixture of isotopes one of which has an atomic weight nearly unity, and (3) helium is decomposed in the sun and stars by the action of an extremely short wave-length radiation which is so penetrating as not to be in temperature equilibrium with the helium affected. J. F. S.

Correlation of Entropy and Probability. GEORGE A. LINHART (*J. Amer. Chem. Soc.*, 1922, **44**, 1881—1886).—In a recent paper (this vol., ii, 257), the author has put forward two equations, the one $S=C\infty/K.\log C\infty/(C\infty-C)$, connecting entropy and probability, and the other, $C=C\infty kT^K/(kT^K+1)$, connecting specific heats and temperature. The validity of the former equation was substantiated for eighteen substances and the latter equation by a single example. In the present paper the second equation has been shown to hold for the specific heat of all substances which

have been measured by the thermo-electric methods. The results calculated for thirty-one substances agree with the experimental values in many cases better than the individual experiments agree with one another. Only in the case of ice and silver iodide is the agreement poor, and here it is shown that the specific heat data are quite erroneous. J. F. S.

The Relation of Melting Point to Boiling Point. R. LORENZ and W. HERZ (*Z. anorg. Chem.*, 1922, **122**, 51—60).—The ratio of the absolute melting point to the normal boiling point has been calculated for 412 elements and compounds (inorganic and organic).

No. of cases.	Ratio.	No. of cases.	Ratio.	No. of cases.	Ratio.
1	0.198	118 between	0.5—0.599	25 between	0.8—0.899
14 between	0.3—0.399	99 „	0.6—0.699	26 „	0.9—0.999
66 „	0.4—0.499	61 „	0.7—0.799	2 above	1.0

The mean of all the ratios (A) was found to be 0.62, or taking only those shown to occur more frequently (4, 5, 6, 7) the mean (B) was 0.5946. The following are the quotients for the different categories examined. Elements (A) 0.5583, (B) 0.4542. Inorganic compounds (A) 0.7183, (B) 0.6857. Organic compounds (A) 0.5839, (B) 0.5745. W. T.

Fused Salts. W. HERZ (*Z. Elektrochem.*, 1922, **28**, 390—391).—It has been shown that at the critical temperature the refractive index of non-associated liquids is a constant, 1.126 (A., 1921, ii, 529; this vol., ii, 97). From the measurements of Meyer and Heck of the molecular refractions of fused potassium and sodium nitrates (this vol., ii, 241), the critical refractive indices have been calculated and are, respectively, 1.136 and 1.138. It appears probable, therefore, that the requirements of the theory are fulfilled by fused salts. The critical densities, calculated from the law of corresponding states, are, respectively, 0.599 and 0.612. The boiling points of the alkali fluorides calculated by Lorenz and Herz from the surface tensions (this vol., ii, 261) are compared with the values found by von Wartenberg (this vol., ii, 146). The agreement is good except in the case of caesium fluoride. The critical pressures of the alkali fluorides, chlorides, bromides, and iodides are now calculated from the known relation between surface tension at the boiling point and critical pressure, $\gamma_s = 0.427p_k$. The values obtained are probably minimum values. They are used to calculate the constant of Cederberg's vapour pressure formula. When the differences between melting and boiling points of the alkali haloids are compared, regular variations are found as the atomic weight of the metal or halogen increases. E. H. R.

The Vapour Pressure of some Salts. III. H. VON WARTENBERG and O. BOSSE (*Z. Elektrochem.*, 1922, **28**, 384—386).—Continuing the work previously described on the vapour pressures of salts (this vol., ii, 156), the following new data have been obtained. Silver chloride, m. p. 449° , b. p. 1554° , $\log p = -44257/4.571T +$

5.298. Cuprous chloride, m. p. 430° , b. p. 1367° , $\log p = -19258/4.571T + 2.573$. Cuprous bromide, m. p. 483° , b. p. 1345° , $\log p = -19075/4.571T + 2.5794$. Cuprous iodide, m. p. 588° , b. p. 1293° , $\log p = -19257/4.571T + 2.690$. Lead chloride, m. p. 498° , b. p. 954° , $\log p = -28518/4.571T + 5.085$. Lead bromide, b. p. 916° , $\log p = -28180/4.571T + 5.183$. Lead fluoride, m. p. 818° , b. p. 1292° , $\log p = -39425/4.571T + 5.510$. Thallous chloride, m. p. 430° , b. p. 806° , $\log p = -25108/4.571T + 5.093$. Thallous bromide, m. p. 456° , b. p. 815° , $\log p = -25164/4.571T + 5.059$. Thallous iodide, m. p. 440° , b. p. 824° , $\log p = -25168/4.571T + 5.021$. Thallous fluoride, b. p. 298° , $\log p = -25152/4.571T + 9.639$. The thallous salts are abnormal in that the iodide has the highest boiling point and the fluoride the lowest. No vapour pressures of barium chloride, calcium chloride, calcium bromide, and boric anhydride could be measured at the highest attainable temperature, 1536 — 1546° . The opinion previously expressed that the fluorides form double vapour molecules is now withdrawn, an experimental error having been detected. The dissociation temperatures of the following acid fluorides were determined: lithium hydrogen fluoride, below 200° ; sodium hydrogen fluoride, about 270° ; potassium hydrogen fluoride, 310 — 440° ; caesium hydrogen fluoride, 500 — 600° ; rubidium hydrogen fluoride, 550 — 670° . E. H. R.

Calorimetric Determinations. P. E. VERKADE (*Chem. Weekblad*, 1922, **19**, 389—393; cf. this vol., ii, 474).—The Third Conference of the International Union of Pure and Applied Chemistry, held at Lyon, June—July, 1922, recommended for the standardisation of calorimetric bombs the use of pure benzoic acid, prepared by the Bureau of Standards at Washington, and tested calorimetrically before issue; this special material is obtainable from the Bureau of the Institut International d'Etalons physico-chimiques at Brussels (The University, Rue des Sols). The other materials generally employed are reviewed, and the values given for the heats of combustion criticised. Pending exact determination of the mechanical equivalent of heat, which will permit of electrical measurements for standardisation, the Brussels benzoic acid should be used for all thermo-chemical determinations. The heat of combustion accepted by the Conference is 6324 cal. per gram weighed in air at 15° (6319 , weighed in a vacuum). S. I. L.

Apparatus for the Rapid Determination of the Specific Gravity of Small Amounts of Liquid. ERICH WIEDBRAUK (*Z. anorg. Chem.*, 1922, **122**, 167—170).—Water and the liquid in question are contained in two communicating U-tubes which also communicate with a manometer, the heights of the liquids which balance various pressures are measured, and hence the specific gravity is calculated. W. T.

Kinetic Theory of Adsorption. D. C. HENRY (*Phil. Mag.*, 1922, [vi], **44**, 689—705).—A theoretical paper in which a kinetic theory of adsorption of gases has been developed by means of assumptions derived from Langmuir's conception of a unimole-

cular layer. Equations for the adsorption isotherm and isostere are deduced which are in keeping with experimental results. A method is suggested for applying these equations to adsorption from solution, and the results are compared with experimental data. A theoretical derivation of the well-known exponential formula is given which attributes a theoretical significance to the index $1/n$, which is in qualitative agreement with experimental data.

J. F. S.

Adsorption of Activated Sugar Charcoal. I. F. E. BARTELL and E. J. MILLER (*J. Amer. Chem. Soc.*, 1922, **44**, 1866—1880).—The adsorption of methylene-blue, a basic dye of the electrolyte type, by activated ash-free sugar charcoal has been investigated. The results show that this adsorption is partly, if not entirely, hydrolytic in character. Ash-free sugar charcoal will completely adsorb a certain maximum amount of methylene-blue from solution and still leave the solution neutral. During this process of adsorption a considerable quantity of hydrochloric acid is set free which is readily and completely adsorbed. Adsorption of quantities of methylene-blue greater than the above-mentioned maximum results in the liberation of hydrochloric acid which is not subsequently removed from solution by adsorption. The contradictory results obtained by previous investigators who have used blood charcoal as adsorbent have been reproduced with pure sugar charcoal and an explanation of these results is put forward.

J. F. S.

Adsorption and Catalysis in Fuller's Earth. ERIC KEIGHTLEY RIDEAL and WILLIAM THOMAS (T., 1922, **121**, 2119—2123).

Adsorption and Orientation of the Molecules of Dibasic Acids and their Ethereal Salts in Liquid-Vapour Interfaces. H. H. KING and R. W. WAMPLER (*J. Amer. Chem. Soc.*, 1922, **44**, 1894—1902).—Surface tension measurements have been made at 20° by the drop-weight method of aqueous solutions of a series of concentrations of tartaric, malonic, succinic, fumaric, oxalic, malic, and maleic acids and the diethyl esters of the four first-named acids. The adsorption has been found for each solution by means of the Gibbs equation $u = -1/iRT \cdot \delta\gamma/\delta \log C$. A general explanation of the chemical theory of capillarity is given and this is shown to serve as an explanation of catalysis. Tables are drawn up giving the adsorption, surface tension, drop weight, and density of all the above-named solutions. It is shown that the adsorption of the dibasic acids is less than that of the monobasic acids; the degree of adsorption of the dibasic acids increases with increasing carbon content, but the increase is not regular for each carbon atom added to the chain. The presence of a hydroxyl group in the molecule decreases the amount adsorbed, and raises the surface tension, as shown by malic and *d*-tartaric acids. The esters are adsorbed more than the acids, due to the replacement of the polar carboxyl group by the group $-\text{C}(=\text{O})-\text{O}-\text{C}_2\text{H}_5$. The molecules are oriented

in the surface with the polar groups in the liquid and the least active portions of the molecule forming the surface. J. F. S.

The Rate of Absorption of Carbon Dioxide by Ammoniacal Solutions. PAUL RIOU (*Compt. rend.*, 1922, 175, 472—474).—Investigation of the influence of temperature and of concentration on the rate of absorption of carbon dioxide by solutions of ammonium carbonate and hydrogen carbonate shows that at constant temperature it increases to a maximum with increase of concentration. In the presence of ammonium hydrogen carbonate, the absorption velocity is considerably less and a decrease takes place with higher concentration after the maximum has been reached. With increase of temperature, a maximum rate is also obtained; the presence of a larger proportion of hydrogen carbonate in the solution corresponds with a reduction in the temperature at which this maximum is reached. H. J. E.

Cataphoretic Charges of Collodion Particles and Anomalous Osmosis through Collodion Membranes Free from Protein. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 5, 89—107).—If a collodion membrane separate a solution of a salt at a definite P_H from pure water, it is found that at $P_H 3$ the rate of diffusion of the water into the salt solution is normal, and is determined almost entirely by osmotic forces. If, however, the P_H be increased, "anomalous osmosis" is obtained. Measurements have been made of the potential difference between the salt solutions and pure water, and also of that between collodion particles and such salt solutions. It is found that the anomalous diffusion rates can be largely explained as due to the potential difference between the solutions on the two sides of the membrane, and that between the membrane and the liquid in its pores. The former potential difference appears to be due to the diffusion potential. W. O. K.

Interpretation of the Influence of Acid on the Osmotic Pressure of Protein Solutions. JACQUES LOEB (*J. Amer. Chem. Soc.*, 1922, 44, 1930—1941).—The effect of adding acid to casein solutions has been investigated with regard to the changes brought about in the osmotic pressure. The results show that the addition of a little acid to isoelectric casein solutions increases the osmotic pressure until a maximum is reached, after which the addition of more acid depresses the osmotic pressure. This is explained on the basis of the dispersion hypothesis by the assumption that the addition of a little acid increases the degree of dispersion and consequently the osmotic pressure of the solution, whilst the addition of more acid diminishes the degree of dispersion and consequently the osmotic pressure. The present observations show that when osmotic equilibrium is established between a solution of casein chloride enclosed in a collodion bag and an outside aqueous solution free from protein, the hydrogen-ion concentration is always greater in the outer solution than in the casein solution. There exists a membrane potential between the casein chloride solution enclosed in a collodion bag and the surrounding

aqueous solution free from protein with which the casein solution is in osmotic equilibrium, and this membrane potential can be measured with indifferent calomel electrodes and a Compton electrometer. When this is done at 24° , it is found that the number of millivolts of the observed membrane potential is equal to 59 (P_{H} inside $-P_{\text{H}}$ outside), the latter values being measured with the hydrogen electrode. This is the result to be expected if the inequality of the hydrogen-ion concentrations inside and outside the casein chloride solution at equilibrium is determined by Donnan's equation for membrane equilibria (A., 1911, ii, 848). The fact that the hydrogen-ion concentration inside and outside the casein chloride solution is not the same as that of the outside free from casein chloride which is in osmotic equilibrium shows that the observed osmotic pressure of the protein chloride solution cannot be entirely due to the protein, but must be partly due to the difference in the concentration of the crystalloid ions, hydrogen and chloride, in the inside and outside solution. It is therefore necessary to correct the observed osmotic pressure of a protein chloride solution for this difference of concentration of the hydrogen and chloride ions on the opposite sides of the membrane on the basis of the Donnan equilibrium. The method of evaluating this correction is demonstrated. When this evaluation is made, it is found that within the limit of accuracy of the observations and calculations the entire effect of the hydrogen-ion concentration on the osmotic pressure of the casein chloride solution is covered by the correction required and that there is little if anything left for the dispersion hypothesis to explain. This is in keeping with the conclusion previously drawn by the author, that the influence of electrolytes on the osmotic pressure of protein solutions is entirely, or almost entirely, the consequence of the difference in the concentration of crystalloid ions inside the protein solutions and the outside aqueous solutions at equilibrium, this difference being caused by the establishment of a membrane equilibrium.

J. F. S.

Selective Solvent Action by the Constituents of Aqueous Alcohol. ROBERT WRIGHT (T., 1922, 121, 2251—2256).

Variations in the Solubility of a Compound in Presence of Other Compounds. I. Water-Phenol-Diphenols. P. LEONE and E. ANGELESCU (*Gazzetta*, 1922, 52, ii, 61—74).—The critical solubility temperature for the system water-phenol is raised by addition of naphthalene, benzophenone, calcium chloride, benzoic acid, tartaric acid, etc., lowered by addition of succinic acid, sodium oleate, or mercuric cyanide, and first raised and then lowered by increasing proportions of acetone. The addition to this system of resorcinol, quinol, or catechol produces marked increase in the reciprocal solubility and a considerable lowering of the critical temperature. Thus, the compositions of the two layers formed at any temperature in a water-phenol mixture gradually approach one another on addition of a dihydroxybenzene and, for a certain concentration of the latter, become equal. The critical temperature of the system is 66.6° ; Rothmund (A., 1898,

ii, 503) found a rather higher temperature. The results obtained are given both graphically and in tabular form. T. H. P.

Variations in the Solubility of a Compound in Presence of Other Compounds. II. Water-Epichlorohydrin-Acetic Acid. P. LEONE and M. BENELLI (*Gazzetta*, 1922, 52, ii, 75—86; cf. preceding abstract).—The reciprocal solubilities of water and epichlorohydrin increase as the temperature is raised, but the critical solution temperature cannot be ascertained since chemical reaction occurs at temperatures above 80°. The authors have measured the reciprocal solubilities at different temperatures and also the depressions of the temperature of saturation by addition of varying proportions of acetic acid, which is miscible in all proportions with both water and epichlorohydrin. T. H. P.

Electronic Structures of Crystals. I. MAURICE L. HUGGINS (*J. Amer. Chem. Soc.*, 1922, 44, 1841—1850).—A theoretical paper in which the author shows how the Lewis hypothesis of atomic and molecular structures (A., 1916, ii, 310) may be applied to ascertain the relative position of electrons and electronic groups in crystals for which the atomic arrangements are known from X-ray investigation. It is shown that the valency electrons, in the crystals discussed, tend to form complete shells round each atomic kernel, each shell consisting of four or six electron pairs. Except for the elements of the first series of the periodic table, these pairs tend to be opposite to the faces of the kernel polyhedra. The atoms are held together by single bonds, each of which is a valency pair in the shell of two atoms and on or near the centre line between them, or by double bonds in each of which there are two electron pairs common to two atoms; the latter case obtains between the carbon and oxygen, and the nitrogen and oxygen in carbonates and nitrates, respectively. There are isolated pairs, that is pairs not acting as bonds in arsenic, antimony, bismuth, and quartz. From the point of view of the foregoing statements, the following crystals have been discussed with regard to their electronic structure: diamond, silicon, germanium, grey tin, zinc sulphide (cubic and hexagonal), cuprous chloride, bromide and iodide, silver iodide (cubic and hexagonal), zinc oxide, cadmium sulphide, carborundum, chalcopyrite, marcasite, hauerite, iron-nickel sulphide, arsenoferrite, loellingite, smaltite, safflorite, cloanthite, rammelsbergite, cobaltite, willyamite, gersdorffite, wolfachite, ullmanite, kallilite, arsenopyrite, glaucodotite, arsenic, antimony, bismuth, quartz, calcite, aragonite, carbonates of calcium, magnesium, iron (ferrous), manganese, zinc, strontium, barium, and lead, and several mixed carbonates of the above-named metals, and sodium and potassium nitrate. J. F. S.

The Effect of Scratching the Wall of a Vessel with a Glass Rod. L. DEDE (*Z. Elektrochem.*, 1922, 28, 364—365). ROBERT FRICKE (*ibid.*, 365—366).—The first author criticises Fricke's explanation (*ibid.*, 244) of the manner in which crystallisation of a solution or liquid is started when the wall of the containing vessel

is rubbed with a glass rod, namely, that detached particles of glass act as nuclei. The view is put forward that the phenomenon is electrostatic in character, and experiments with ammonium magnesium phosphate are described supporting this view. Fricke replies, criticising Dede's experiments and maintaining his opinion.

E. H. R.

Crystallisation and Proteins. ÉMILE CAVAZZANI (*Arch. internat. physiol.*, 1921, **18**, 446—450; from *Chem. Zentr.*, 1922, i, 1214).—The crystallisation of ammonium chloride from saturated solutions is prevented by 0.05% of egg-albumin, or by 0.2—0.5% of gum arabic.

G. W. R.

An Electron Theory of Solids. (SIR) J. J. THOMSON (*J. Franklin Inst.*, 1922, **194**, 281—289).—A theoretical paper giving a summary of the author's theory of the solid state (cf. this vol., ii, 252, 355). The potential energy of atoms in the crystals of the elements and the bulk moduli have been calculated, on the assumption that the attractive force between the atoms and nuclei varies as the inverse cube of the distance. The values for the uni-, bi-, and ter-valent elements are in absolute agreement with the experimental values of Richards. The excess of energy in the surface, the surface tension, has been deduced, and it is shown that this is proportional to $K^{\frac{1}{3}}$, where K is the bulk modulus, a relation due to Richards. The calculation of the potential energy of the atoms in chemical compounds is complicated by the unequal distributions of the electrons about the atoms, but the numbers obtained for the bulk moduli are a useful guide to the distribution of the electrons in the crystal.

W. E. G.

Hardness of Solid Substances and its Relationship to Chemical Constitution. A. REIS and L. ZIMMERMANN (*Z. physikal. Chem.*, 1922, **102**, 298—358).—The method of determining hardness by Marten's sclerometric method has been investigated in connexion with a large number of substances of different types, including very soft substances which exhibit a scratch of 10μ in width when a load of only 1 gram is applied to the needle and shown to be trustworthy for this type of investigation. Experiments on the scratching of ninety crystals by one another yield results which on the whole are in agreement with those obtained by the foregoing method. The eroding action of a moving liquid on solid surfaces has been investigated and by using a stream of mercury from narrow nozzles it has been found possible to obtain trustworthy results on the resistance to erosion of solid substances. It is shown that the hardness and the resistance to erosion for the larger number of the substances examined (about one hundred and eighty) are parallel, but that the numerical value of the resistance to erosion, measured as time required for the removal of the same amount of material, increases much more than the hardness. The hardness depends on the particular crystal face employed, and on the direction of the scratch, whereas no such dependence could be observed in the erosion experiments. The relationship

between the hardness, crystal structure, and chemical constitution has been investigated for a large number of substances of all types. A general connexion is shown to exist on the basis of the classification of crystal lattices according to the strength and spacial partition of the forces of attraction between the atoms. In the case of those salts with lattices which are maintained by the electrostatic attractions of the ions, it is shown that generally the charges and distances between the ions are determinative of the hardness. In the case of compounds which have not the nature of salts, the hardness runs parallel with the strength of the residual affinities which the molecules exert outwardly. In keeping with the general chemical experience and with the tendency to association, it is shown from the hardness measurements that the residual affinity is smallest in the case of the hydrocarbons and increases most strongly under the influence of hydroxyl, carboxyl, and cyanogen groups. In the case of mixed crystals, it is shown that the mixture is harder than the mean of the components and in some cases harder than the harder component. The hardness of compressed pastilles has been compared with that of crystals of the same substances, and the two values are shown to be very nearly equal. A number of methods of producing large crystals have been investigated, and it is shown that the tendency of substances to form large crystals is to a certain extent a function of the chemical constitution and is often parallel with the hardness. J. F. S.

The Increase in the Size of Grain of Metallic Bodies (not previously Worked in the Cold) Formed from Powdered Material by Pressure or Sintering. F. SAUERWALD (*Z. anorg. Chem.*, 1922, 122, 277—294).—The application of pressure did not increase the size of the grain; nor does this occur at moderate temperatures, but at higher temperatures an increase in granular size was observed in the case of iron, nickel, cobalt, tungsten, and copper. This limiting temperature could be fixed within 100°, and an increase of temperature beyond this limit resulted in a rapid increase in the size of the grains. This limiting temperature is independent of the pressure applied in compressing the powder, and has a characteristic value for each metal. Increase in the size of grains was not observed in the cases of zinc and aluminium. These results are discussed in the light of Tammann's new theory of crystallisation (*A.*, 1921, ii, 172). W. T.

The Influence of Electrolytes on the Cataphoretic Charge of Colloidal Particles and the Stability of their Suspensions.
I. Experiments with Collodion Particles. JACQUES LOEB (*J. Gen. Physiol.*, 1922, 5, 109—126).—The potential difference between collodion particles and the aqueous solution in which they are suspended has been determined by measuring the mobility of the particles under a given potential gradient. It is found that the influence of acid and of alkali and of most salts is to cause the negative charge on the collodion particle to increase to a maximum and then to decrease with increasing concentration of the solution.

A tervalent kation, however (for example, in the case of lanthanum chloride), may cause a steady decrease in the charge and even reverse it. The effects of hydrochloric acid, sodium hydroxide, lithium chloride, sodium chloride, and potassium chloride are very similar. If the P_H of the solution be varied, the variation of the charge with changing concentration of salt in the solution remains similar.

When the potential difference between the particles and the solution is reduced below a certain critical value, about 16 millivolts, the suspension of colloidal particles becomes unstable, and precipitation occurs.

W. O. K.

Elasticity of Purified Gelatin Jellies as a Function of the Hydrogen-ion Concentration. S. E. SHEPPARD, S. S. SWEET, and ANBER J. BENEDICT (*J. Amer. Chem. Soc.*, 1922, **44**, 1857—1866).—The rigidity and hydrogen-ion concentration of demineralised gelatin jellies, which are free from products of hydrolysis, has been determined for 4, 5, 7, and 10% jellies. The effect on the rigidity of the addition of 0.001% to 0.10% of alum to the above-named jellies has also been investigated. It is shown that except at very high ($P_H > 2$) and very low ($P_H < 11$) hydrogen-ion concentrations, the rigidity does not vary rapidly with changes of the hydrogen-ion concentration, the maximum being at $P_H = 7-9$. The addition of quantities of aluminium equivalent to 0.01—0.1% of alumina based on the dry gelatin produced considerable changes in the rigidity- P_H curve, and markedly increased the rigidity. These results are discussed in connexion with the theory of the viscosity and elasticity of gelatin. A misleading statement on Poisson's ratio for gelatin jellies in a previous paper (A., 1921, ii, 311), and also in the literature, has been corrected.

J. F. S.

The Ultra-filtration of Soap Solutions: Sodium Oleate and Potassium Laurate. JAMES WILLIAM MCBAIN and WILLIAM JOB JENKINS (*T.*, 1922, **121**, 2325—2344).

The Reversibility of the Reaction between Nitrogen, Carbon, and Sodium Carbonate. CHRISTOPHER KELK INGOLD and DANIEL WILSON (*T.*, 1922, **121**, 2278—2286).

The Ammonium Carbonate-Carbamate Equilibrium. CARL FAURHOLT (*Z. anorg. Chem.*, 1922, **121**, 132—134).—A reply to Wegscheider's theoretical paper (this vol., ii, 376). The author shows that his results for the above equilibrium are in fair agreement with those obtained by Burrows and Lewis and by Fenton. The author also shows that the conclusions of Wegscheider (A., 1916, ii, 617) are incorrect, because the latter found that carbamic acid was very weak and the ammonium salt completely hydrolysed in aqueous solution. The present author carried out colorimetric hydrogen-ion estimations and found that the ammonium salt is not hydrolysed to any appreciable extent.

W. T.

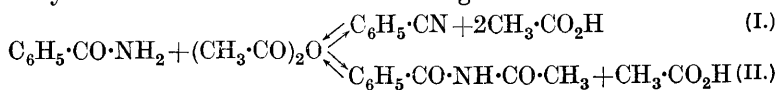
Equilibrium in the System Potassium Chlorate, Potassium Nitrate, and Water at 25°. SHIGERU TODA (*J. Chem. Soc. Japan*, 1922, **43**, 320—328; *Mem. Coll. Sci. Kyoto Imp. Univ.*, 1921, **4**, 377—382).—The equilibrium in the system potassium chlorate, potassium nitrate, and water at 25° has been studied. The solubility of potassium chlorate at 25° is 7.745 grams in 100 grams of solution or 8.395 grams in 100 grams of water, and that of potassium nitrate is 27.24 grams in 100 grams of solution or 37.44 grams in 100 grams of water. At 25°, potassium chlorate forms a solid solution with potassium nitrate taking up the latter to the extent of 14.37 molar %, whilst the nitrate takes up none of the chlorate. K. K.

Equilibrium in the System Copper Sulphate, Ammonium Sulphate, Potassium Sulphate, and Water at 25.0°. RYONOSUKE HAYAMI (*Mem. Coll. Sci. Kyoto*, 1921, **4**, 359—369; *J. Chem. Soc. Japan*, 1921, **42**, 421—441).—The equilibrium diagram for the system copper sulphate, potassium sulphate, ammonium sulphate, and water at 25° has been determined, and also the relation between the composition of the aqueous solutions and that of the solid solutions when the residue is either a mixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{CuSO}_4(\text{NH}_4\text{K})_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ or a mixture of $(\text{NH}_4\text{K})_2\text{SO}_4$ and $\text{CuSO}_4(\text{NH}_4\text{K})_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$. J. S. G. T.

Dynamics of the Formation of Nitriles from Acid-anhydrides and Amides. II. Kinetic Study of the Reaction between Acetamide and Acetic Anhydride, using Phase Rule Methods. ROBERT KREMANN, ALFRED ZOFF, and VICTOR OSWALD (*Monatsh.*, 1922, **43**, 139—144).—The reaction: acetamide + acetic anhydride \rightleftharpoons acetonitrile + 2 acetic acid, is followed kinetically, and shown to reach an equilibrium corresponding with 83% conversion (from left to right in the sense of the above scheme) at 98°, and with 87% conversion at 78°.

The method consisted in taking the freezing points of mixtures of the components which had been heated at the required temperature for different lengths of time. The percentage compositions were then read from an experimentally determined curve of the freezing points of mixtures of the two systems involved in the reversible reaction. C. K. I.

Dynamics of the Formation of Nitriles from Acid-anhydrides and Amides. III. Reaction between Benzamide and Acetic Anhydride. ROBERT KREMANN, WILHELM RÖSLER, and WILHELM PENKNER (*Monatsh.*, 1922, **43**, 145—159).—Two side reactions take place when equimolecular quantities of acetic anhydride and benzamide are heated together:



and in order to follow the process kinetically by the method previously employed (cf. preceding abstract) it was necessary

first to construct a ternary freezing-point diagram for the systems $[\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}_2 + (\text{CH}_3\cdot\text{CO})_2\text{O}]$, $[\text{C}_6\text{H}_5\cdot\text{CN} + 2\text{CH}_3\cdot\text{CO}_2\text{H}]$, and $[\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{NH}\cdot\text{CO}\cdot\text{CH}_3 + \text{CH}_3\cdot\text{CO}_2\text{H}]$. With the aid of this diagram the progress of the reactions is followed by a series of freezing-point determinations. The following values are deduced for the composition of the equilibrium mixture: benzamide 0.48, acetic anhydride 0.48, benzonitrile 0.14, acetylbenzoylimide 0.38, acetic acid 0.66 mol.

C. K. I.

Studies in Acidolysis. I. The Equilibrium between Acetic Acid, Trichloroacetic Acid, and their Ethyl Esters. II. The Equilibrium between Acetic Acid, Trichloroacetic Acid, and their Methyl Esters. J. J. SUDBOROUGH and D. D. KARVÉ (*J. Indian Inst. Sci.*, 1922, 5, 1—21).—As a preliminary to the study of the reaction between ethyl alcohol and a mixture of acetic and trichloroacetic acids, the equilibrium between the two acids and their ethyl esters was examined at 30°. The equilibrium constant of the reaction $\text{CH}_3\cdot\text{CO}_2\text{Et} + \text{CCl}_3\cdot\text{CO}_2\text{H} \rightleftharpoons \text{CH}_3\cdot\text{CO}_2\text{H} + \text{CCl}_3\cdot\text{CO}_2\text{Et}$ was found to be equal to unity, and the same result was obtained with the methyl esters. It follows that the relative affinities of the methoxy- and ethoxy-residues for acetyl and trichloroacetyl are practically identical, in spite of the difference between the dissociation constants of the two acids. In the absence of a catalyst the reaction $\text{CH}_3\cdot\text{CO}_2\text{Et} + \text{CCl}_3\cdot\text{CO}_2\text{H} \rightarrow \text{CH}_3\cdot\text{CO}_2\text{H} + \text{CCl}_3\cdot\text{CO}_2\text{Et}$ and the reverse reaction proceed very slowly at 30°, the time required for the attainment of equilibrium being 1200—1400 hours. The velocity constants in both directions are equal, the value of k/V being 0.00039, where $k/V = 1/2A_1 t \log A_1/A_1 - 2x$. In this expression, V_1 = volume of 1000 grams of the mixture, A_1 = the number of gram-mols. per 1000 grams, and x the number of molecules which have reacted after t hours. With the methyl esters, the reaction is still slower, and $k/V = 0.000097$.

E. H. R.

The Ignition of Gases. II. Ignition by a Heated Surface. Mixtures of Methane and Air. WALTER MASON and RICHARD VERNON WHEELER (*T.*, 1922, 121, 2079—2091).

The Explosions of Varieties of Organic Dust. Experimental Investigation of the Simple Case of Sugar Dust. P. BEYERSDORFER (*Ber.*, 1922, 55, [B], 2568—2596).—The experiments consist in a thermal and an electrical investigation of the causes leading to the exploding of mixtures of very finely divided sucrose and air.

The explosion chamber consists of a glass vessel of about 600 c.c. capacity which is suspended symmetrically in a copper pot surrounded by an asbestos mantle and heated from below by a Franke burner. The vessel is provided with inlet and outlet tubes for gases and at its centre a cage of thin aluminium foil is suspended against which the sugar dust is blown through a horizontal side tube. The temperature is measured by a silver-constantan thermo-element. The sugar dust is passed through a sieve having

ten thousand meshes to the square centimetre, dried at $105^{\circ}/100$ mm., and preserved over concentrated sulphuric acid. The apparatus is heated to slightly above the desired temperature, and then allowed to cool to the desired extent, when the dust is blown against the foil. In this manner, the latter is the hottest part of the apparatus at the moment of the experiment.

The author defines the following terms. Ignition is a process which leads to visible combustion. Its cause may be of a dynamic, thermal, or an electrical nature. The ignition may lead to inflammation or explosion. Inflammation is a visible process of combustion which takes place throughout the material with small velocity and little change of pressure and has the power of causing further thermal ignition. Explosion is a visible process of combustion which is propagated through the material with high velocity and great change of pressure, and has the ability to ignite other combustible material by thermal action or by shock.

The author draws the following conclusions. The explosion of dusts can be caused by thermal or electrical processes. The temperature of ignition of sugar dust in air is $410 \pm 1^{\circ}$, and in oxygen 371° . The presence of small quantities of ozone lowers the temperature of ignition by 3° in air and by 4° in oxygen. The temperature of ignition is dependent on the oxygen content of the gas and on the nature and thermal conductivity of the relatively inert gases which accompany the oxygen, carbon dioxide having a noticeably greater extinguishing action than nitrogen. The dependence of the temperature of ignition of sugar dust on the oxygen content of mixtures of the latter gas with nitrogen is represented graphically. The curve approaches asymptotically to the temperature axis. At a point corresponding with the presence of about 9% of oxygen, the region of ignition becomes divided into an inflammation and an explosion region. Ultimately, the thermal explosion of sugar dust is a gaseous explosion. The process occurs in two phases: (i) the gasification of sugar dust such as takes place in the case of coal, and (ii) the oxidation of the "sugar gas" until ignition sets in. [In experiments on the temperature of ignition of sugar dust in air in which such ignition just does not occur, a rapid initial drop of $10-15^{\circ}$ in temperature is invariably observed (due to gasification of the sugar) followed by a rise in temperature which generally exceeds the initial temperature ultimately (due to oxidation of the gas).] The upper limit of explosion is established at 13.5 kilos. of dust per cubic metre; the lower safety limit is calculated to be 17.5 grams per cubic metre.

Sugar dust becomes positively charged when projected through the air. If it is whirled through the air, tensions of multiples of ten thousand volts may be developed. Discharge of the loaded particles in a gas may occur silently, but they have no immediate connexion with the luminosity which accompanies the process and is readily visible in the dark. This luminosity is specific for each gas, and is identical with that observed for it in an alternating field.

Sugar dust may be caused to explode in an alternating field. The phases of the electrical explosion are: (1) the formation of

ozone and nitrogen pentoxide, (2) the reaction of these substances with the most minute sugar particles, and (3) explosion as a result of this reaction in the alternating field. Sugar dust forms an aerosol with air; if this suddenly approaches the isoelectric point, a flash occurs which ignites the dust cloud.

The conclusions elucidated for sugar dust are applicable to every explosive dust whether organic or inorganic.

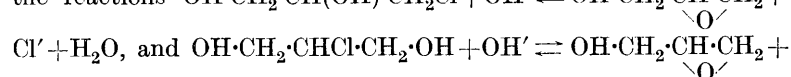
Magnetic phenomena have no influence on the occurrence of dust explosions.

The violence of a dust explosion is attributed to the adsorption of oxygen by the dust.

Triboluminescence cannot be regarded as a cause of sugar dust explosions.

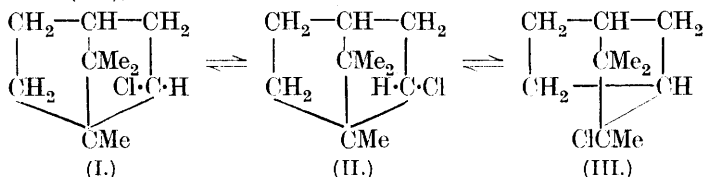
H. W.

Michael's Addition and Separation Rule. L. SMITH (*Z. physikal. Chem.*, 1922, **102**, 359—363).—A theoretical paper in which on the basis of the author's investigations on the velocity of the reactions



(A., 1920, i, 658), an attempt is made to explain Michael's addition and separation rule. This rule may be stated as follows: When two isomeric compounds may be formed from an unsaturated compound, a direct relationship exists between the relative quantities of the additive compounds produced and the velocities with which they may be reconverted into the original substance. J. F. S.

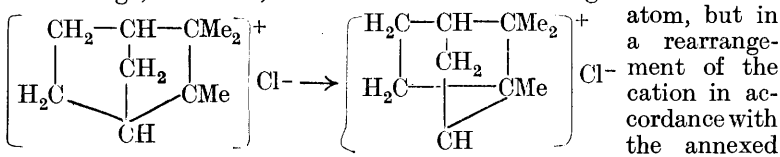
The Equilibrium Isomerism between Bornyl Chloride, isoBornyl Chloride, and Camphene Hydrochloride. HANS MEERWEIN and KONRAD VAN EMSTER [with JACOB JOUSSEN] (*Ber.*, 1922, **55**, [B], 2500—2528; cf. A., 1920, i, 855).—In the molten condition and in solution, an equilibrium is established between bornyl chloride (I), isobornyl chloride (II), and camphene hydrochloride (III), in accordance with the scheme:



The equilibrium is dependent on the temperature and to a slight extent on the solvent. At the atmospheric temperature, it is greatly displaced in the direction of bornyl chloride. The transformation from right to left occurs exothermally; bornyl chloride is therefore the most stable, camphene hydrochloride the most labile isomeride. With increasing temperature, the equilibrium becomes more and more displaced in favour of isobornyl chloride and camphene hydrochloride. The interconversion of isobornyl chloride and camphene hydrochloride takes place readily at the atmospheric temperature, whereas the transformation of bornyl

chloride into *isobornyl* chloride occurs with greater difficulty and only at a more elevated temperature.

The velocity of the conversion of camphene hydrochloride into *isobornyl* chloride at 20° or 40° has been examined in the following solvents: cresol, sulphur dioxide, nitromethane, acetonitrile, nitrobenzene, benzonitrile, anisole, bromobenzene, ethyl bromide, chlorobenzene, benzene, light petroleum, and ether. The rate of change is enormously influenced by the solvent. In cresol, it occurs so rapidly that it is complete almost as soon as the camphene hydrochloride has passed into solution; ether, at the other end of the scale, acts practically as a stabilising agent towards camphene hydrochloride. The transformation is a unimolecular change. In general, the values of *k* exhibit a decreasing tendency during the course of an experiment, which is due to the partial dissociation of camphene hydrochloride in solution into camphene and hydrogen chloride and the catalytic acceleration of the transformation by the latter; with decreasing content of camphene hydrochloride, the concentration of the hydrogen chloride also diminishes and the rate of change becomes smaller. The results indicate that the conversion of camphene hydrochloride into *isobornyl* chloride is due to an actual, intramolecular atomic displacement and cannot be explained by elimination and re-addition of hydrogen chloride. An intimate connexion is obvious between the dielectric constant of the solvent and its influence on the rate of conversion of camphene hydrochloride into *isobornyl* chloride, the latter being greatest in strongly ionising solvents (nitromethane and acetonitrile) and smallest in non-ionising solvents (benzene, ether, light petroleum). From this it appears that the velocity of the change depends on the degree of the electrolytic dissociation of camphene hydrochloride and that the conversion only occurs subsequently to ionisation. The change, therefore, consists not in a wandering of the chlorine



scheme, whereby the more strongly ionised camphene hydrochloride passes into the less strongly ionised *isobornyl* chloride. A perfect parallelism between rate of change and dielectric constant of the solvent is not observed, exceptions being encountered in the cases of cresol, sulphur dioxide, and anisole, on the one hand, and of ether on the other. Precisely these solvents have an anomalous action towards triphenylmethyl chloride, and it seems probable that their effect can be explained in a uniform manner, and that phenol, sulphur dioxide, and (to a less extent) anisole form complex compounds with camphene hydrochloride in which the mobility of the chlorine atom is increased or the ionisation of camphene hydrochloride occurs to a greater degree. The influence of complex formation on the ionisation and therefore on the rate of transformation of camphene hydrochloride is further

illustrated by the catalytic acceleration of the change by the halogen acids, antimony pentachloride, stannic chloride, ferric chloride, mercuric chloride, and antimony trichloride (all of which yield additive compounds with triphenylmethyl chloride), whereas phosphorus trichloride and silicon tetrachloride, which show no tendency to complex formation, are inactive. In the presence of catalysts, the change is unimolecular, and the constancy of k is more satisfactory than in their absence, since the effect of the hydrogen chloride (see above) is of relatively less importance.

The influence of the solvent on the degree of ionisation of camphene hydrochloride is also observed in the alcoholysis of this substance. The conversion of camphene hydrochloride into camphene hydrate methyl ether by methyl alcohol has been examined kinetically in the presence of nitromethane, acetonitrile, nitrobenzene, benzonitrile, anisole, bromobenzene, chlorobenzene, benzene, ethyl bromide, pyridine, and ether and it is found that the effect of the solvents is approximately the same as that observed in the conversion of camphene hydrochloride into *isobornyl* chloride. The analogy between triphenylmethyl chloride and camphene hydrochloride is illustrated further by a study of the alcoholysis of the former by amyl alcohol in the presence of nitrobenzene, benzonitrile, bromobenzene, chlorobenzene, anisole, ethyl bromide, benzene, pyridine, and ether, and the complete parallelism thus established justifies the assumption of the ionisation of camphene hydrochloride which cannot be measured directly on account of the ease with which it is converted into *isobornyl* chloride in all solvents which are suitable for measurements of conductivity.

Unfortunately, it is not possible to measure the rate of the reverse transformation of *isobornyl* chloride into camphene hydrochloride, but it is shown to be subject to the same catalytic influences by observation on the rate of decomposition of *isobornyl* chloride into camphene or camphene hydrate and hydrogen chloride under differing conditions, this decomposition being consequent on the transformation of *isobornyl* chloride into camphene hydrochloride.

The mutual transformation of *isobornyl* and *bornyl* chlorides takes place with much greater difficulty and in non-ionising solvents in the absence of catalysts is extremely slow at 130°. In cresol, sulphur dioxide, or chlorobenzene in the presence of stannic chloride, the change occurs with considerable rapidity at 70°, but the conditions are unsuitable for physico-chemical examination.

The authors have previously described (*loc. cit.*) the isolation of "true" pinene hydrochloride. The compound had been obtained previously in 1914 by Aschan (cf. A., 1921, i, 795), whose work, however, was not generally accessible until recently. It has now been obtained in the crystalline condition (although not quite free from *bornyl* chloride) by the action of hydrogen chloride on a dilute solution of pinene in light petroleum at -60°. It is instantly decomposed by water and alcohol, and can be titrated in alcoholic solution in the same manner as hydrochloric acid. It resembles camphene hydrochloride in that its solutions can be greatly stabilised by the addition of ether.

The estimation of camphene hydrochloride, *isobornyl* chloride, and free hydrogen chloride in their solutions is effected in the following manner. Camphene hydrochloride is determined by adding an excess of *N*/5-absolute alcoholic sodium ethoxide to the solution together with methyl alcohol, and titrating the excess of alkoxide after the mixture has been preserved for an hour at 20° with *N*/10-alcoholic hydrogen chloride in the presence of phenolphthalein as indicator. *isobornyl* chloride is estimated by boiling the mixture for an hour with *N*/5-alcoholic potassium hydroxide solution, with the addition of a little water. Free hydrogen chloride in the presence of camphene hydrochloride is estimated by taking advantage of the observation that the dissociation of the latter can be delayed to such an extent by the addition of ether that the free acid can be titrated with sodium ethoxide solution in the presence of iodoeosin as indicator.

Camphene hydrochloride is prepared by treating a solution of camphene in ether with hydrogen chloride and filtration of the product with exclusion of atmospheric moisture; the material, when most carefully prepared in this manner, contains about 9–10% of *isobornyl* chloride. A somewhat purer product (containing 93.3% of camphene hydrochloride) can be secured by using light petroleum as solvent, in which, however, the addition of the halogen acid occurs very slowly. *isobornyl* chloride is obtained by saturating a solution of camphene in ethyl bromide with hydrogen chloride at 10–20°, heating the mixture uninterruptedly under a reflux condenser during six days at 55°, removing the solvent, and crystallising the residue from amyl alcohol. It has m. p. 161.5°, and contains 99.6% of pure *isobornyl* chloride; the presence of camphene hydrochloride cannot be detected. H. W.

The Velocity of Reaction in Mixed Solvents. III. The Influence of Temperature on the Velocity of Saponification of Esters. HAMILTON MCCOMBIE, HAROLD ARCHIBALD SCARBOROUGH, and RICHARD HARDCASTLE SETTLE (T., 1922, **121**, 2308–2318).

Rate of Hydrolysis of Wheat Gliadin. HUBERT BRADFORD VICKERY (*J. Biol. Chem.*, 1922, **53**, 495–511).—Results are given of a large number of experiments in which measurements were made of the rate of hydrolysis of gliadin by acids of various concentrations and also by alkalis. Hydrolysis both of the amide nitrogen and of the peptide linkings proceeds more rapidly the greater the concentration of the acid. In the early stages, alkalis are more effective than acids. Owing to secondary decompositions, however, considerably larger quantities of ammonia are liberated by alkalis than by acids. Hydrolysis is more rapid with barium hydroxide than with sodium hydroxide of equivalent concentration. E. S.

Influence of the Catalyst on the Thermodynamic Quantities Regulating the Velocity of a Reaction. E. VAN THIEL (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, **25**, 199–209).—After a theo-

retical discussion of the velocity of chemical reactions in which the hypotheses of Trautz, Lewis, Scheffer, and Marcelin are considered, it is shown that the hypotheses of Trautz and Lewis demand that a reaction which is strongly catalysed shall have a smaller temperature coefficient than the same reaction uncatalysed or weakly catalysed, whilst Scheffer's hypothesis shows that a catalysed reaction can have a temperature coefficient and an energy increment which are greater than those of the uncatalysed reaction. An attempt has been made to decide between these two hypotheses by means of measurements of the rate of acetylation of diphenylamine at 0°, 20°, 30°, 40°, and 50° both without a catalyst and in the presence of *p*-bromobenzenesulphonic acid or *p*-toluenesulphonic acid as catalyst. The results of these experiments show that Scheffer's hypothesis is in keeping with the facts. J. F. S.

Dislocation Theory of Catalysis. J. BÖESEKEN (*Proc. K. Akad. Wetensch. Amsterdam*, 1922, 25, 210—215).—A theoretical paper in which the author discusses the mechanism of catalysis. He starts from the idea that ideal catalysts are those which are not temporarily fixed in intermediate compounds and so withdrawn from the reaction mass. Real catalysis is the interaction between the catalyst and the molecules which has nothing to do with the formation of a compound. This interaction is termed a *dislocation*, and may be regarded as consisting of a change in the paths of the electrons. The hypothesis is considered in the case of the photo-oxidation of alcohols in the presence of *p*-benzophenone and oxygen. In this case, the author has shown (A., 1921, ii, 500) that above a certain concentration of the ketone the velocity is independent of this concentration, and, further, it is proportional to the square of the intensity of the light and to the concentration of the alcohol, which is explained as follows: The ketone absorbs part of the light and is activated by it, the quantity of activated ketone is $I(1 - e^{-kcd})$, where k is the absorption coefficient, c the concentration of the ketone, and d the thickness of the layer. When k , c , and d are large, the quantity of activated ketone becomes proportional to I and independent of c . The whole process then is as follows: Under the influence of light a quantity of photo-ketone $kI(1 - e^{-kcd})$ is formed instantaneously, this amount approaches the value kI , so that the first stage of the process is represented by the equation (1) ketone + light = photo-ketone, and is followed by the reaction which regulates the process. (2) photo-ketone + alcohol = (photo-ketone), alcohol; the meeting of the two molecules activates two hydrogen atoms of the alcohol and is represented by (3) (photo-ketone), alcohol \rightarrow [(photo-ketone), active alcohol]. This process which probably takes place with the velocity of light, is the real catalysis, the dislocation. The alcohol molecules are thereby brought into the condition to react according to (4) $2[(\text{photo-ketone}) \text{ active alcohol}] + \text{O}_2 = 2 \text{ ketone} + 2 \text{ aldehyde} + 2 \text{H}_2\text{O}$, which also occurs with a great velocity. The photo-ketone may be replaced by palladium, and the same type of reaction will occur and is similarly explained. This explanation demands

intimate contact between the catalyst and the reacting molecules. It is shown that Scheffer's relation of the reaction constant, $\log_e k = (E_t - E)/RT + B$ represents the thermodynamic aspect of the above hypothesis (cf. Thiel, preceding abstract). J. F. S.

The Influencing of the Catalysis of Hydrogen Peroxide with Platinum by Röntgen Rays. ANTON KAILAN (*Ber.*, 1922, 55, [B], 2492—2494).—Recalculation of the experimental results of Schwarz and Friedrich (this vol., ii, 436) show that the catalytic decomposition of concentrated hydrogen peroxide is a bimolecular action and not unimolecular as stated by these authors.

In an addendum to the communication, the correctness of the criticism is recognised by Schwarz and Friedrich. H. W.

Catalysis. XIV. The Action of Nitric Acid on Metals and an Example of a Periodic Reaction. B. C. BANERJI and N. R. DHAR (*Z. anorg. Chem.*, 1922, 122, 73—80).—The rate of standard solution of copper, silver, lead, nickel, brass, mint silver, and of copper-nickel alloy, in nitric acid, was studied in the presence of different salts. Ferrous salts acted as catalysts; this catalytic effect is ascribed to the nitrous acid which is formed by the action of ferrous salts on nitric acid. Ferric salts were also found to act as positive catalysts; this is due to the formation of ferrous salts by the action of the metals copper, silver, etc., on the ferric salts. Oxidising agents, for example, potassium permanganate, potassium chlorate, are negative catalysts because they prevent the formation of nitrous acid. The dissolution of a 50% copper-nickel alloy in nitric acid takes place in well-defined periods of reaction, each period being followed by a period of no reaction. W. T.

Catalytic Action at Solid Surfaces. VIII. Action of Sodium Carbonate in Promoting the Hydrogenation of Phenol. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1922, [A], 102, 21—27; cf. this vol., ii, 41).—The results of a number of experiments on the hydrogenation of phenol in the presence of nickel powder and sodium carbonate at 180° and under a pressure of hydrogen of 80 lb. per sq. inch are described. The object of the experiments was to ascertain the part played by a promoter in a catalytic change. The products of the reaction are cyclohexanol 95%, some cyclohexanone, with practically no unchanged phenol. The presence of sodium carbonate has an accelerating action which is dependent on the amount of carbonate present; if an excess is present the hydrogenation is retarded. The optimum amount of sodium carbonate bears no relationship to the amount of phenol present, but is closely connected with the amount of nickel catalyst employed, and in the present experiments is found to be at the point where the amount of sodium carbonate is about 25% of the weight of the nickel. The exact mechanism by which the sodium carbonate assists the hydrogenation has not been discovered, but it appears that the stimulation is not a true acceleration but the restoration of the nickel to its normal function by the suppression of a retardation, which is probably of the nature of a

poisoning of the catalyst by the phenol. It is found that the curvilinear nature of the time-absorption relationship in the absence of sodium carbonate becomes linear in the presence of this substance. This fact furnishes further evidence that the rôle of the promoter in this case is a protective one with respect to the catalyst, rendering the latter free to exert its normal functions.

J. F. S.

Catalytic Action at Solid Surfaces. IX. Action of Copper in Promoting the Activity of Nickel Catalyst. E. F. ARMSTRONG and T. P. HILDITCH (*Proc. Roy. Soc.*, 1922, [A], 102, 27—32; cf. preceding abstract).—It is shown that a copper-nickel catalyst may be produced in hydrogen when suitably supported compounds are heated at 180°, whereas supported nickel compounds alone are not reduced by hydrogen below 300° and not rapidly below 350—400°. It is shown that for the reduction of the nickel at this low temperature an intimate mixture of the two compounds must be used, which must be more intimate than can be obtained by mechanical mixture. Co-precipitation is not always sufficient to obtain the desired degree of intimacy, for a comparison of the activity of the catalysts with the nature of the nickel cupricarbonates from which they are produced shows that both the nickel and copper must be in the same complex molecule to obtain any degree of catalytic activity. On the basis of the foregoing, the relatively low temperature of the reduction of the nickel is explained as follows: the reduction of copper carbonate or cupric oxide is strongly exothermic, and even although the exterior temperature is only 180°, it is evident that the temperature inside the molecule must momentarily, at least, be far above the outside temperature.

J. F. S.

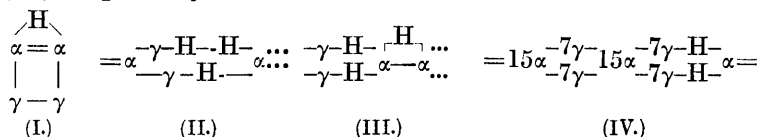
Influence of *s*-Trinitrobenzene on Reactions in which Arylamines are involved. J. J. SUDBOROUGH and R. C. SHAH (*J. Indian Inst. Sci.*, 1922, 5, 29—35).—To determine whether, on account of the readiness with which polynitro-aromatic compounds form additive compounds with most of the simple arylamines, such nitro-compounds would have a catalytic influence on reactions involving aromatic amines, a number of such reactions which are readily catalysed by iodine were carried out in presence of *s*-trinitrobenzene. The reactions studied were the methylation of aniline, formation of phenyl- α -naphthylamine from aniline and α -naphthylamine, condensation of aniline with benzophenone, the formation of thiodiphenylamine from diphenylamine and sulphur, and the acetylation of aniline. In no case had the *s*-trinitrobenzene any catalytic influence, whilst iodine was a powerful catalyst for all except the last of these reactions.

E. H. R.

Atoms and Electrons. ROBERT N. PEASE (*Nature*, 1922, 110, 379—380).—In view of the facts (1) that the distances between the atomic centres in crystals of cerium and thorium are practically the same, the number of electrons being 58 and 90,

respectively, and (2) that in the atom of uranium (atomic volume 12.8) there are concentrated 32 more electrons than in the atom of neodymium (atomic volume 20.7), it is significant that elements of higher atomic number than uranium are not known to exist, and that most of those of immediately lower atomic number are unstable. In the case of elements of high atomic number, the electron-density must therefore be greater than in other cases, and be accompanied by a greater attractive force on the nucleus. It is suggested that periodical exertion by numbers of electrons of attractive forces on the positive nucleus in the same direction may result in the extraction of a positively charged constituent of the latter and its expulsion as an α -particle. The rate of decay would depend primarily on the stability of the nucleus, and the suggested mechanism would constitute the trigger action. A. A. E.

Periodic Structure of Atoms and Elements. H. NEWMAN ALLEN (*Nature*, 1922, **110**, 415).—In one of the models postulated by Crehore (A., 1921, ii, 632; this vol., ii, 438, 494), one of the particles marked 4 is also marked with a dot, evidently indicating that it has a charge $+e$ only. By calling these particles γ , it has been found possible to construct hypothetical models for a considerable number of atoms of the form indicated by the following examples representing nitrogen (I), fluorine (II or III), and uranium (IV), respectively:



The strokes represent electrons; in II, the α 's join to form a ring, in III, two γ 's join to the α to form a ring, and in IV, a ring structure is also obtained. A. A. E.

The Rare Earths in the Periodic System. CARL RENZ (*Z. anorg. Chem.*, 1922, **122**, 135—145).—The author reviews the literature on the subject and discusses the difficulties. He suggests as a solution a modification of Soddy's helical representation of the periodic law. W. T.

Determination of the Molecular Weight of Substances in Alcoholic Solution from the Elevation of the Flash Point. ROBERT WRIGHT (T., 1922, **121**, 2247—2250).

Polar and Non-polar Valency in Organic Compounds. W. E. GARNER (*Nature*, 1922, **110**, 543—544).—Two explanations may be given of the positive and negative relationships of groups in organic compounds: (a) there may be a partial transference of an electron between the group and the residue of the molecule, or (b) there may be a varying concentration of polar molecules in the typically non-polar substance. In the consideration of the second possibility, an equilibrium may be imagined to exist between the polar and non-polar substances which will be affected by the

temperature, nature of the solvent, etc. Thus, in those substances where the stability of the non-polar arrangement is very great, the occurrence of both forms, $\bar{A}\bar{X}^+$ and $\bar{A}^+\bar{X}$, will be possible, and in the presence of a suitable solvent these may give rise to the respective ions. A. A. E.

Melting Point Tubes as Reaction Vessels. AUGUST FUCHS (*Monatsh.*, 1922, **43**, 129—137).—Details are given for carrying out the commoner manipulations, using very small quantities of material (2—5 mg.). That satisfactory preparations and purifications can be effected by the methods indicated is proved by a record of examples actually worked out. C. K. I.

Perforation Apparatus for the Extraction of Liquids by Liquids. Non-miscible Liquids. FAYOLLE and CH. LORMAND (*Chim. et Ind.*, 1922, **8**, 273—274).—Two types of apparatus are described for the extraction of a liquid by another liquid with which it does not mix. One type is for use where the solvent is heavier than the liquid to be extracted, and the other where the solvent is the lighter of the two liquids. In either case the extraction is continuous. W. G.

A Shaking Machine for Large Quantities of Fluid. HARTWIG FRANZEN (*Z. physiol. Chem.*, 1922, **122**, 86—87).—An apparatus is described suitable for stirring large amounts of lead precipitates in aqueous suspension, while treating them with carbon dioxide or hydrogen sulphide. W. O. K.

Inorganic Chemistry.

Vapour Pressure of Hydrogen. Determinations in the Region of Liquid Hydrogen. H. KAMERLINGH ONNES and J. PALACIOS MARTINEZ (*Anal. Fis. Quím.*, 1922, **20**, 233—242).—The vapour pressures of liquid hydrogen at temperatures near its normal boiling point were measured using a helium thermometer. By interpolation, the boiling point of hydrogen at a pressure of 759·549 mm. of mercury is given as $20\cdot35^{\circ} K$ (Kelvin international scale).
G. W. R.

Spontaneous Incandescence of Substances in Atomic Hydrogen Gas. R. W. WOOD (*Proc. Roy. Soc.*, 1922, [A], **102**, 1—9).—A number of experiments with very long hydrogen discharge tubes are described from which it is shown that some metals, oxides, and other substances are raised to incandescence when introduced into a stream of atomic hydrogen, the surface of the substance acting as a catalyst in bringing about the recombination of the atoms. Atomic hydrogen, practically free from molecular hydrogen, may be drawn by a pump from the central portion of a long discharge tube excited by a current of high potential. Fire
28—2

polished glass surfaces, such as the walls of a glass tube, have a comparatively feeble catalysing power whilst fractured surfaces cause the recombination of the atoms, and are strongly heated. The action of water vapour or oxygen in enhancing the Balmer spectrum, and suppressing the secondary spectrum of hydrogen, is probably due to its action on the walls of the tube, which, when dry, catalyse the atomic hydrogen as fast as it is formed by the current. The peculiar spectroscopic phenomena observed with long hydrogen tubes, described in an earlier paper (A., 1920, ii, 569) are explained. Methods are suggested for determining the physical and optical properties of atomic hydrogen gas. J. F. S.

Evidence of the Existence of Isotopes of Chlorine. MATAKICHI ISHINO (*Mem. Coll. Sci. Kyōtō*, 1921, 4, 311—315).—Employing the method of positive-ray analysis, using the crossed-deflexion method devised by Thomson, the author has obtained evidence of the existence of chlorine isotopes of respective atomic weights 34 and 36, and of positively charged chlorine atoms.

J. S. G. T.

The Decomposition of Chlorine into Atoms. MAX TRAUTZ and WALTER STÄCKEL (*Z. anorg. Chem.*, 1922, 122, 81—131).—The apparatus employed and methods of working are described in detail. The amount of chlorine decomposed was 1.50% at 1200°, 2.10% at 1240°, and 3.05% at 1280°. The limit of the absorption band for chlorine was found to be 390—420 $\mu\mu$. This corresponds with 67,500—73,000 cal. as the heat of decomposition according to Trautz's "approximate" equation $q_0 = Ah\nu$ (A., 1918, ii, 151). The heat of decomposition of chlorine calculated from the temperature coefficient was found to be $71,000 \pm 3,000$ cal. The same result was obtained by the use of the quantum theoretical constants and also by the use of Victor Meyer's vapour density measurements. With the exception of hydrogen, the heat of decomposition of the diatomic elements found experimentally agrees with the value obtained from the equation $d_0 = (5.78 \times 10^5 / \sqrt{M})$ cal., where M is the molecular weight. W. T.

Vapour Pressure of Solid Chlorine and Bromine. F. A. HENGLEIN, G. VON ROSENBERG, and A. MUCHLINSKI (*Z. Physik*, 1922, 11, 1—11).—The vapour pressure of solid and liquid chlorine and solid bromine has been determined over a wide range of temperature. The following values are recorded for chlorine, 119.2° 0.0013; 126.0°, 0.0063; 133.0°, 0.028; 146.6°, 0.30; 161.1°, 2.75; 177.6°, 17.40; 194.5°, 64.40, and for bromine 177.6°, 0.0020; 210.0°, 0.26; 228.8°, 1.12; 227.0°, 1.71; and 241.1°, 6.44; the temperatures are expressed in absolute degrees and the pressures in millimetres of mercury. Vapour pressure formulæ have been deduced for both cases and have the form: $\log p = -1160/T + 7773$ for liquid chlorine; $\log p = -1530/T + 9950$ for solid chlorine; these formula are representative over the temperature ranges -95° to -78° and -154° to -112° , respectively, $\log p = -12150/T^{1.368} + 75030$ for solid bromine over the range -32° to

—96°. From the above data a number of constants have been calculated which include the following: Chlorine, m. p. 170·0° Abs.: vapour pressure at the melting point 8·9 mm., molecular heat of vaporisation at the melting point 5300 cal., heat of sublimation of solid chlorine at the melting point 6960 cal., molecular heat of fusion 1660 cal.; bromine: vapour pressure at the melting point 44·12 mm., molecular heat of sublimation at the melting point 9740 cal., specific heat of sublimation 60·91 cal., specific heat of vaporisation at the melting point 48·4 cal., molecular heat of fusion 12·5 cal. From the dissociation equilibrium of the chlorine molecule and the chemical constant as determined by Stern and Tetrode the vapour pressure of diatomic chlorine has been calculated and the chemical constant for diatomic chlorine in its normal condition has also been obtained.

J. F. S.

Physical Constants of Ozone. E. H. RIESENFELD and G. M. SCHWAB (*Z. Physik*, 1922, **11**, 12—21; cf. this vol., ii, 637).—An account of the determination of a number of physical constants of pure ozone which was prepared as previously described by the authors (*loc. cit.*). The following values are put on record: m. p. —249·7°, b. p. —112·4°; critical temperature, —5°; specific gravity at —183°, $1·71 \pm 0·1$; change of density with temperature, $1/d = a + bT + cT^2$, where $a = 0·51193$, $b = 0·0004559$, $c = 0·000003929$; density at the boiling point, 1·46; coefficient of expansion, 0·0025; critical density, 0·537; critical pressure, 64·8 atmospheres. The authors show that neither in the gaseous nor in the liquid state is there any other molecular species present than that represented by the formula O_3 .

J. F. S.

Solubility of Sulphur Dioxide in Suspensions of Calcium and Magnesium Hydroxides. WM. THOMPSON SMITH and REGINALD B. PARKHURST (*J. Amer. Chem. Soc.*, 1922, **44**, 1918—1927).—The solubility of sulphur dioxide has been determined in water, milk of lime, and milk of magnesia, at partial pressures of sulphur dioxide up to 760 mm., and temperatures from 5° to 60°. All proportions of calcium and magnesium hydroxides were used in suspensions of a total alkalinity of one equivalent per litre. It is shown that the concentration of sulphur dioxide as sulphurous acid is proportional to its partial pressure. With solutions of the same alkali concentration, the percentage salting-out effect increases with, but more than in proportion to, the temperature. With solutions of constant temperature, the percentage salting-out effect increases with the alkali concentration, but is less than proportional to it. Varying proportions of calcium and magnesium hydroxide have no effect on the equilibrium concentration of sulphur dioxide as sulphurous acid.

J. F. S.

The Physico-chemical Study of the Lead Chamber Process. MAX FORRER (*Bull. Soc. chim. Belg.*, 1922, **31**, 254—293).—A detailed description of a form of apparatus in which sulphur dioxide, nitrogen peroxide, water, oxygen, and nitrogen may be brought into contact with each other under definite conditions

of pressure, temperature, and, in the case of liquids, surface of reaction. The proportions of these substances could be varied at will. It is shown that, in such a system, the formation of sulphuric acid only occurs in presence of a liquid phase, so that the system must be heterogeneous; the formation of the acid takes place in a shorter time and the yield is increased if a liquid, either sulphuric acid or water, is present at the outset. Further, the rate at which water vapour is supplied during the course of the reaction exerts a considerable effect both on the velocity of reaction and on the concentration of the product. Under certain conditions, the acid formed may disappear, which appears to indicate that the reactions assumed to take place in the chambers are at least partly reversible. For low concentrations of the gases, there is an optimum rate of intake for water vapour: this gives the best yield and, at the same time, the most concentrated acid. As the gas concentration increases, the optimum point shifts in the direction of diminution of water supply; a curve is given showing the speed of reaction plotted against concentration of gas. The relation between these two factors is much less complex when the composition of the liquid phase is constant. The author infers from his experimental results the existence of an intermediate substance of which water is a constituent; it is, however, decomposed in presence of an excess of water. He points out that, of the series of reactions which occur, the slowest is the "limiting reaction" in that it conditions the rate of formation of the product and shows that, in practice, the reaction velocity is strongly influenced by the rate of supply of nitrogen peroxide and water, but is practically unaffected by the supply of sulphur dioxide.

An attempt is made to calculate the order of the reaction, and, for this purpose, the heterogeneity of the system and the non-equivalence of the reactants are neglected. The values obtained vary from 1.26 to 3.67. However, when the concentration of the liquid phase does not vary, the values are in the neighbourhood of 2. In the case of temperature variations which have a similar effect to that of variations in water supply, it was not found possible to obtain a coefficient in agreement with the experimental data.

H. J. E.

Density of Atmospheric Nitrogen. A Small Anomaly in the Air of Madrid. M. PAYÁ and E. MOLES (*Anal. Fis. Quím.*, 1922, 20, 247—254).—The normal density of nitrogen obtained from the air of Madrid is given as 1.25681. The density of air in Madrid corresponds with a slightly higher proportion of oxygen than the normal for other places. The anomaly is attributed to the presence of higher proportion than normal of ozone and gases of the argon group.

G. W. R.

The Reactions between Gaseous Oxides of Nitrogen and Alkaline Solutions. A. SANFOURCHE (*Compt. rend.*, 1922, 175, 469—472).—The action of oxides of nitrogen on solutions of alkali hydroxide in which the calculated proportions of nitrate and nitrite are formed only occurs if the alkali is in excess at all points

in the solution. Otherwise, reaction with the water takes place with formation of nitric acid and nitric oxide, the latter being further oxidised if oxygen is present. Moreover, if all the oxides of nitrogen are not absorbed in their first passage through the solution, this reaction with water continues in the gaseous phase with water vapour. This is shown by the formation of a nitric acid mist and by its subsequent deposition as acid dew on the upper portion of the walls of the vessel in spite of the presence of excess of alkaline solution. It is pointed out that estimation of nitrous vapours by the method of absorption in alkali hydroxide is liable to lead to considerable error and for this reason it is preferable to use sulphuric acid as the absorbent. H. J. E.

The Solubility of Arsenic Trichloride in Concentrated Hydrochloric Acid at 100°. W. D. TREADWELL [with CH. MUSSLER] (*Helv. Chim. Acta*, 1922, 5, 818—821).—The solubility of arsenic trichloride in concentrated hydrochloric acid at 100° was determined by an indirect method which consisted in measuring the rate of volatilisation of the trichloride from the solution in a current of hydrogen chloride at 100°. From Henry's law, it follows that $\log (x_0 - x)/x_0 = -kV/V_0$, where x is the quantity of trichloride volatilised by the volume V of gas in a given time, x_0 is the quantity of trichloride originally present, V_0 the volume of the solution, and k the solubility coefficient. Experiments showed that the value of k remained constant for a considerable period of time, its mean value being 0.0233. From this it can be calculated that to volatilise 99% of the arsenic trichloride present in 100 c.c. of solution at 100° requires 19.8 litres of hydrogen chloride. From the known vapour pressure of arsenic trichloride, a litre of the vapour contains 2.34 grams. Hence the solubility in concentrated hydrochloric acid at 100° is $2.34/k = 100.3$ grams per litre. E. H. R.

Boric Acid Phosphors. RUDOLF TOMASCHEK (*Ann. Physik*, 1922, [iv], 67, 612—648; cf. Tiede and Wulff, this vol., ii, 245).—A number of boric acid phosphors have been prepared by the addition of phthalic anhydride, terephthalic acid, the sodium salt of fluorescein (uranin), naphthalic anhydride, and phenanthrene. The phosphorescence of these organic phosphors is in many ways simpler than that of the metal phosphors. In general, the bands of the former are all excited by the same wave-lengths of light, and owe their origin to the same phosphorescence centre. Thus the three mercury lines, 365.4, 313, and 253.6 $\mu\mu$, all appear to excite the four components of the band of the phenanthrene-phosphor. On the other hand, the different bands of the metal phosphors are excited independently. The relative intensities of the components of the bands of the boric acid substances may change with temperature; the uranin-phosphor emits a yellow light at -70° , but, when heated on metal foil, this radiation rapidly changes into a bluish-green phosphorescence. In opposition to the heavy metal phosphors, the duration and intensity of the emitted light are influenced only slightly by changes in temperature, being, in many

cases, the same at the temperature of liquid air as at the ordinary temperature. Neither can the phosphorescence be extinguished by exposure to red light. Phenanthrene-phosphor is especially sensitive to light, and it is shown that the decolorisation which occurs is not in any way the cause of the phosphorescence, as suggested by Perrin. The wave-lengths of the absorption bands of the transparent phosphor frequently coincide with those of the exciting radiation, and in the case of phenanthrene, correspondence is found to occur between the fluorescence bands and the absorption bands in the ultra-violet. The duration of the phosphorescence for organic boric acid phosphors is about one minute, and this comparatively short period points to the presence of very small centres; this is supported by the difficulty of fully exciting these centres. When the terephthalic acid phosphor is fully excited by an intense beam of light, the larger portion of the total phosphorescence takes place within the first second, so that the centres are mainly of very short duration. The centres do not all possess the same duration. The I/L curves indicate that a bimolecular chemical reaction is not the cause of the phosphorescence, which can be explained satisfactorily on the assumption of a photo-electric process. Three kinds of emission take place, phosphorescence, fluorescence, and an emission in the ultra-violet. The conclusion is drawn that the fields of force are almost exclusively in the interior of the organic molecules.

W. E. G.

Borates. The System $(\text{NH}_4)_2\text{O}-\text{B}_2\text{O}_3-\text{H}_2\text{O}$. Temperature-Concentration Diagram. U. SBORGI and L. FERRI (*Mem. Accad. Lincei*, 1922, [v], **13**, 570—591).—The results previously obtained (A., 1913, ii, 213, 318; 1915, ii, 686; this vol., ii, 568) are collected.

T. H. P.

The Modifications of Silicon. II. Silicon from Copper Silicide. WILHELM MANCHOT and HERBERT FUNK (*Z. anorg. Chem.*, 1922, **122**, 22—26).—Specimens of silicon obtained from a copper silicide regulus have been studied; the results were similar to those obtained by the authors when employing aluminium and silver reguli (this vol., ii, 286). Conditions which favour the formation of crystals produce silicon which reacted but slowly with hydrofluoric acid. Crystalline silicon very soluble in this acid could not be obtained.

W. T.

Alkali Iodides. L. W. WINKLER (*Pharm. Zentr.-h.*, 1922, **63**, 386—387).—Analyses of samples of commercial potassium iodide and sodium iodide showed that these substances have a high degree of purity. The respective quantities of iodide found corresponded with 98.6 to 99.6% of potassium iodide and with 97.0 to 99.9% of sodium iodide.

W. P. S.

Composition of the Liquid Phases in a Univariant System, Liquid-Liquid-Vapour, for Mixtures of Sodium and Ammonia. CHARLES A. KRAUS and WALTER W. LUCASSE (*J. Amer. Chem. Soc.*, 1922, **44**, 1949—1953).—In an earlier paper (A., 1907, ii, 935), it has been shown that at low temperatures concentrated

solutions of sodium in liquid ammonia separate into two liquid phases which have an upper critical end-point at about -45° . The concentrations of these liquid phases have now been determined by electrical conductivity measurements and it has been found that the upper critical end-point lies at -41.6° and at a composition of 4.15 atom % of sodium. The phase relations in the system sodium-ammonia are briefly discussed. J. F. S.

Nature of the Complexes formed between Sodium and Tellurium in Liquid Ammonia. CHARLES A. KRAUS and C. Y. CHIU (*J. Amer. Chem. Soc.*, 1922, **44**, 1999—2008).—The reaction between sodium and tellurium in liquid ammonia has been investigated and the composition of the resulting solutions has been determined under various conditions. The initial compound formed is normal sodium telluride of the formula Na_2Te . In equilibrium with the normal telluride, the complex in solution has a composition corresponding with the formula Na_2Te_2 . In equilibrium with free tellurium the solution has a composition which varies as a function of the concentration. The maximum amount of tellurium present corresponds approximately with the formula Na_2Te_4 . J. F. S.

Crystal Structure of Silver Molybdate. RALPH W. G. WYCKOFF (*J. Amer. Chem. Soc.*, 1922, **44**, 1994—1998).—Making use of the data obtained from the reflection spectra and Laue photographs of silver molybdate, the crystal structure of this substance has been shown to be the same as that of the spinels and magnetite. The length of the side of the unit cube, which contains eight molecules, is 9.26 \AA.U. , and the parameter defining the position of the oxygen atoms is very close to $3/8$. The distance between molybdenum and adjacent oxygen atoms is 2.00 \AA. , between silver and the nearest oxygen atom 2.31 \AA. , and between the nearest molybdenum atom and silver 4.02 \AA. J. F. S.

The Dissociation of the Chlorides of Bivalent Metals in Aqueous Solution. A. GÜNTHER-SCHULZE (*Z. Elektrochem.*, 1922, **28**, 387—389).—In a previous paper it was shown from a study of the basic exchange between copper salts in solution and permutite that the copper salt solution, even at high dilutions, contains complex kations (this vol., ii, 504). The investigation has now been extended to salts of barium, strontium, calcium, cadmium, manganese, cobalt, and nickel, using the chlorides of the metals and ammonium permutite. If a represents the number of equivalents of metal passing into the permutite in exchange for ammonia, and c the number of equivalents of chlorine likewise disappearing from the solution, then if the metallic chloride is present in solution only in the form of M^{++} and Cl^- ions, $c=0$ and $a/c=\infty$. If, however, the ions are MCl^+ and Cl^- , the MCl^+ ion passing into the permutite, $a/c=2$. If still more complex ions are formed, such as M_2Cl_3^+ , $a/c < 2$. Applying this reasoning to the experimental results, it is found that at the highest concentrations of all the above salts, some MCl^+ ions are present and,

in the cases of magnesium, nickel, and copper, still more complex ions. The first stage of dissociation into MeCl' and Cl' preponderates in the case of those metals having the smallest ionic radius. At a dilution of $1.0N$, a considerable proportion of MeCl' ions is found only in the case of those metals having the smallest ionic radius, namely, nickel and copper. E. H. R.

Transference of the Acid Radicle in the Solid Phase. I. Carbonates of the Alkaline Earths and Magnesium. J. ARVID HEDVALL and J. HEUBERGER (*Z. anorg. Chem.*, 1922, **122**, 181—187).—It was found that if the oxides of the elements considered are arranged in order of increasing basicity MgO , CaO , SrO , BaO , then the oxide of the more basic will on heating with the carbonate of the less basic element be changed into the carbonate without the evolution of gas and at a temperature well below the temperature of dissociation of the carbonate taken. The temperature of the reaction decreases and the heat effect increases with increasing difference of basicity, for example, $\text{MgCO}_3 + \text{BaO} = \text{BaCO}_3 + \text{MgO} + 19 \text{ cal. } (t=230^\circ)$; $\text{SrCO}_3 + \text{BaO} = \text{BaCO}_3 + \text{SrO} + 6.14 \text{ cal. } (t=280^\circ)$. W. T.

The Crystal Structure of Glucinum and Glucinum Oxide. L. W. MCKEEHAN (*Proc. Nat. Acad. Sci.*, 1922, **8**, 270—274).—The glucinum was obtained by electrolysis of sodium glucinum fluoride, $2\text{GlF}_2, \text{NaF}$, and contained a few per cent. of glucinum oxide. The diffracting centres in the metal and its oxide lie at the points of two symmetrically interpenetrating hexagonal space lattices. For glucinum oxide, the axial ratio, $c/a=1.63$, and $a=2.696 \times 10^{-8} \text{ cm.}$; for glucinum, $c/a=1.58$ and $a=2.283 \times 10^{-8} \text{ cm.}$ These values give computed densities within 1% of the best previous values. Glucinum more closely resembles magnesium, zinc, and cadmium, rather than calcium, strontium, and barium; the oxide is an analogue of zinc oxide, and the structure suggested by W. L. Bragg (*A.*, 1920, ii, 433) for the latter substance is also possible for glucinum oxide. W. E. G.

Physical Chemistry of the Oxides of Lead. VI. The Anodic Behaviour of Lead and Lead Dioxide. SAMUEL GLASTONE (*T.*, 1922, **121**, 2091—2098).

The Isomerism of Metallic Oxides. I. Lead Monoxide. MALCOLM PERCIVAL APPLEBEY and ROBERT DOUGLAS REID (*T.*, 1922, **121**, 2129—2136).

The Hindrance of Precipitations with Hydrogen Sulphide by Neutral Chlorides. L. DEDE and P. BONIN (*Ber.*, 1922, **55**, [B], 2327—2331).—The action of hydrogen sulphide on a $1/1000$ -molar solution of lead chloride in water at 20° in the presence of hydrochloric acid and of neutral chlorides has been investigated. Precipitation of lead sulphide is completely inhibited by hydrochloric acid alone if present in a concentration of $1.4N$. In the presence of increasing quantities of calcium, ammonium, or potass-

ium chlorides, decreasing concentrations of hydrochloric acid are sufficient to prevent precipitation entirely. In the presence of considerably smaller concentrations of hydrochloric acid, the precipitation of lead sulphide is incomplete. At higher temperatures, the effect of hydrochloric acid in the presence of neutral chlorides is still more marked. Similar results are obtained with cadmium salts, and apparently also with tin salts. The precipitation of lead sulphide is also hampered, although to a less degree, by the presence of perchloric acid. In this case, however, the addition of sodium perchlorate favours precipitation presumably by depressing the dissociation of the acid.

The precipitation of lead chromate in acetic acid solution is not quantitative in the presence of much chloride; in ammoniacal solution this is not the case.

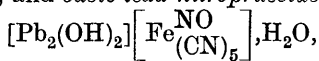
H. W.

The Constitution of Basic Lead Salts. R. WEINLAND and RUDOLF STROH (*Ber.*, 1922, **55**, [B], 2706—2718).—It has been assumed by Werner (A., 1908, ii, 42) that certain basic salts are to be regarded as aquo-salts in which the water molecules are replaced by metallic hydroxide, that is, as compounds containing a polynuclear kation; thus, atacamite, $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$, has been formulated $\left[\text{Cu} \left(\begin{smallmatrix} \text{OH} \\ \diagup \quad \diagdown \\ \text{OH} \end{smallmatrix} \right) \text{Cu} \right]_3 \text{Cl}_2$. The presence of such ions in several forms has been established by preparative substitution in the case of lead salts. Thus, in the basic perchlorates, $[\text{Pb}_2(\text{OH})_2](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ (I) and $[\text{Pb}_3(\text{OH})_4](\text{ClO}_4)_2$ (II), the perchlorate residues could be replaced by other acid radicles. The stability of the metal-ol kations is not to be compared with that of the typical metal amines in aqueous solution, since the above basic perchlorates are to some extent decomposed into new basic salts when their solutions are diluted, so that, at any rate, a partial change has occurred in the complex. This instability is also shown by the fact that potassium ferricyanide and potassium cobalticyanide give salts with differently constituted lead kations from those obtained with alkali chlorides. The presence of such lead-ol complexes in basic lead acetates has also been established by the substitution method in the case of the basic lead acetate; one such ion is identical with that contained in the perchlorate (I).

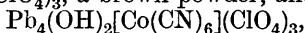
Polynuclear lead kations are also present in the neutral lead acetate-perchlorates and lead acetate-nitrates (Weinland and Stroh, this vol., i, 981). They are distinguished from those contained in the basic salts only by containing acetato- instead of ol-bridges, thus: $[\text{Pb}_2(\text{OH})_2](\text{ClO}_4)_2 \cdot 1.5\text{H}_2\text{O}$ and $[\text{Pb}_2(\text{CH}_3\text{CO}_2)_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$. Application of these considerations to lead acetate itself causes the authors to regard it as the acetate of a polynuclear lead acetato-kation. In aqueous solution, undoubtedly more than one such kation is present, since the action of perchloric acid on lead acetate in neutral and acetic acid solution yields the perchlorates of four different lead acetato-kations. It has not yet been found possible to decide which kation is present in solid lead acetate, $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$.

Basic lead perchlorate (I) is readily prepared from a solution of

lead monoxide in the calculated quantity of perchloric acid; its electrical conductivity indicates that three ions are present in its solutions. It is converted by double decomposition into basic lead chloride, $[\text{Pb}_2(\text{OH})_2]\text{Cl}_2$, a colourless powder which does not appear under the microscope to be crystalline; basic lead nitrate, $[\text{Pb}_2(\text{OH})_2](\text{NO}_3)_2$, *basic lead dithionate*, $[\text{Pb}_2(\text{OH})_2]\text{S}_2\text{O}_6$, lustrous leaflets and needles, and *basic lead nitroprusside*,

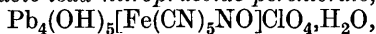


pale brownish-red cubes. With potassium ferricyanide and potassium cobalticyanide, it gives the analogously constituted *compounds*, $\text{Pb}_4(\text{OH})_2[\text{Fe}(\text{CN})_6](\text{ClO}_4)_3$, a brown powder, and



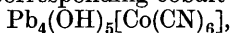
a colourless, heavy powder.

Basic lead perchlorate (II), tetrahedra and octahedra, is prepared by cooling a hot solution of perchloric acid which has been saturated with lead monoxide. It is converted by double decomposition into basic lead chloride, $[\text{Pb}_3(\text{OH})_4]\text{Cl}_2$, a yellowish-white powder; basic lead iodide, a yellow powder; basic lead nitrate, $[\text{Pb}_3(\text{OH})_4](\text{NO}_3)_2$, a heavy, white powder, and *basic lead dithionate*, $[\text{Pb}_3(\text{OH})_4]\text{S}_2\text{O}_6$, a colourless, crystalline precipitate. The following salts, also prepared by double decomposition, do not contain the original kation: *basic lead chromate*, $[\text{Pb}_2(\text{OH})_2]\text{CrO}_4$, a fine, red powder; *basic lead ferricyanide-perchlorate*, $\text{Pb}_3(\text{OH})_5[\text{Fe}(\text{CN})_6](\text{ClO}_4)_2$, a pale brown powder which explodes violently when heated; *basic lead ferri-cyanide*, $\text{Pb}_5(\text{OH})_7[\text{Fe}(\text{CN})_6] \cdot 3 \cdot 5\text{H}_2\text{O}$, a yellow powder; *basic lead cobalticyanide-perchlorate*, $\text{Pb}_5(\text{OH})_5[\text{Co}(\text{CN})_6](\text{ClO}_4)_2 \cdot 1 \cdot 5\text{H}_2\text{O}$, a heavy, white powder; *basic lead nitroprusside-perchlorate*,



pale, brownish-red, crystalline aggregates.

Basic lead acetate is shown to contain the same kation as the perchlorate (I) by the fact that it gives by double decomposition the same basic chloride and dithionate. Concentrated solutions of the salt and potassium ferricyanide give the *salt*, $\text{Pb}_6(\text{OH})_7[\text{Fe}(\text{CN})_6](\text{CH}_3\text{CO}_2)_2 \cdot \text{H}_2\text{O}$, brownish-red crystals, whereas dilute solutions yield a dark yellow, amorphous precipitate which fairly rapidly passes into the *compound*, $\text{Pb}_4(\text{OH})_5[\text{Fe}(\text{CN})_6]$, garnet-red prisms (the corresponding cobalt *compound*,



is prepared similarly). Treatment of the ferricyanide last mentioned with dilute acetic acid leads to the formation of the salt $\text{Pb}_3(\text{OAc})_5[\text{Fe}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$, brownish-red needles. Solutions of lead acetate and sodium perchlorate give, under different conditions, the *salts*, $\text{Pb}(\text{OAc})_2 \cdot \text{NaClO}_4$, rectangular prisms capped by pyramids at either end; $\text{Pb}_2(\text{OAc})_4 \cdot \text{NaClO}_4 \cdot 3\text{H}_2\text{O}$, colourless needles, and $\text{Pb}_4(\text{OH})_4(\text{ClO}_4)_4 \cdot \text{NaClO}_4 \cdot 3\text{H}_2\text{O}$, large, many-sided plates. H. W.

The Complex Cuprammoniates $\text{Cu}(\text{CN})_2, \text{CuCN}, 2\text{NH}_3$; $\text{Cu}(\text{CN})_2, 4\text{CuCN}, 4\text{NH}_3$; $\text{Cu}(\text{CNS})_2, \text{Cu}(\text{CN})_2, 5\text{CuCN}, 6\text{NH}_3$, and the **Analytical Methods for their Identification**. F. HALLE and K. HIRSCHKO (*Z. anorg. Chem.*, 1922, 122, 188—194).—The

above three new complex cuprammoniates have been prepared, and details are given of their analysis. W. T.

Critical Constants of Mercury. SOPHUS WEBER (*K. Danske Vid. Medd.*, 1920, **3**, No. 4, 1—12; from *Chem. Zentr.*, 1922, iii, 27).—From theoretical considerations, the author derives the following critical constants for mercury: t_c 1450°; d_c 5.0; p_c 1042 atmospheres. The same value for p_c is given by extrapolation at 1450° with Knudsen's vapour pressure formula. The correlation of the Trouton constants with the critical data established by Cederberg is valid for the above values. The reduced vapour pressure curve for mercury approximately coincides with the curve for hydrogen. G. W. R.

Oxychlorides of Mercury. Equilibrium in the System Mercuric Chloride, Yellow Mercuric Oxide, and Water at 35°. SHIGERU TODA (*J. Chem. Soc. Japan*, 1922, **43**, 312—320; *Mem. Coll. Sci. Kyōto Imp. Univ.*, 1921, **4**, 305—310).—The equilibrium in the system mercuric chloride, yellow mercuric oxide, and water at 35° has been studied. The solubility of mercuric chloride, 9.39 grams in 100 grams of water, and that of yellow mercuric oxide is 0.0014 gram in 100 grams of water. In the system investigated, two oxychlorides of mercury were found to exist: $\text{HgCl}_2 \cdot 2\text{HgO}$, purplish-scarlet needles, and $\text{HgCl}_2 \cdot 4\text{HgO}$, a brownish-yellow, amorphous substance. It is probable that the latter forms a solid solution with mercuric oxide. K. K.

The Rare-earth Magnesium Sulphide Phosphors. ERICH TIEDE and ARTHUR SCHLEEDE (*Ann. Physik*, 1922, [iv], **67**, 573—580).—Phosphors containing cerium, lanthanum, didymium, praseodymium, neodymium, samarium, yttrium, gadolinium, erbium, ytterbium, scandium, thorium, and zirconium were prepared by the methods previously described (Tiede and Richter, this vol., ii, 215). They were all yellow in colour and, like the phosphors of the heavy metals, this colour was destroyed by pressure. The temperature relationships, and the spectrum of the phosphorescent light of the magnesium samarium phosphor were very similar to those of the calcium samarium phosphor of Hauer and Kowalski (*A.*, 1914, ii, 320). Cerium, didymium, praseodymium, samarium, gadolinium, and scandium gave the best phosphors in the ordinary sense of the word, although the other metals gave strong phosphorescence in the cathode ray tube. The colour of the phosphorescence ranged from orange-yellow to pale green, and the duration of the emitted light was approximately twenty minutes. The spectra differed considerably from those of the phosphors of the heavy metals, being composed of intense sharp lines and bands. The exciting light, in all cases, lay in the ultra-violet. W. E. G.

The Separation of the Rare Earths by Basic Precipitation. IV. WILHELM PRANDTL and JOHANNA RAUCHENBERGER (*Z. anorg. Chem.*, 1922, **122**, 311—314).—The influence of cadmium nitrate on the equilibrium between the nitrates of the rare earths and ammonia in ammonium nitrate solutions of various concen-

trations has been investigated. The conditions were the same as in previous experiments (cf. this vol., ii, 298). The presence of cadmium nitrate increased considerably the amount of rare earth kept in solution, especially lanthanum, this increase being much more marked than in the case of zinc nitrate. W. T.

Rare Earths. III. Atomic Weight of Lanthanum. B. S. HOPKINS and F. H. DRIGGS (*J. Amer. Chem. Soc.*, 1922, **44**, 1927—1929).—The atomic weight of lanthanum has been determined by a comparison of lanthanum chloride with silver. The material used was the less soluble portion of the magnesium rare-earth nitrates from which the whole of the cerium had been removed by James and Pratt's method (A., 1911, ii, 935). The sparingly soluble fractions containing lanthanum and praseodymium were fractionated further as double ammonium nitrates until the first twenty fractions failed to show the faintest trace of the praseodymium absorption spectrum. Fractions 7 and 8 of this series were precipitated with hot dilute oxalic acid solution, the precipitate filtered, washed, and ignited to oxide which was dissolved in nitric acid, and the solution treated with ammonia gas to precipitate the hydroxide. The alternate precipitation as oxalate and hydroxide was repeated four times, the last two taking place in conductivity water. The final oxide was suspended in conductivity water and treated with hydrogen chloride in a quartz flask. This material showed no spectroscopic lines of any of the related elements. The solution of lanthanum chloride was dried in a quartz flask in a current of air and hydrogen chloride until crystallisation commenced, the air current was shut off, and hydrogen chloride alone passed in until, at 85°, the first five molecules of water of crystallisation had come off, then the temperature was raised to 125°, when the final molecule of water commences to come off. As soon as this evolution was complete, the temperature was raised to 325°, and kept there for an hour, after which the salt was rapidly melted over a bunsen flame and then allowed to cool. The hydrogen chloride was displaced by dry air and the material weighed. The chloride was treated with silver solution and exact equivalence between the two substances determined nephelometrically. Using the data: density, $\text{LaCl}_3=3.947$, $\text{Ag}=10.5$; atomic weights, $\text{Ag}=107.88$, $\text{Cl}=35.457$, it was found that 1.02450 grams LaCl_3 is equivalent to 1.35189 grams of silver, whence the mean atomic weight of lanthanum (10 expts.)= 138.89 ; the extreme values being 138.84 and 138.97 . This value is very close to 138.91 , the value found by Baxter, Tani, and Chapin (A., 1921, ii, 454), and seems to indicate that the value 139.0 adopted by the International Atomic Weight committee is slightly too high. J. F. S.

The Separation of the Rare Earths by Basic Precipitation. III. The Quantitative Separation of Cerium from the Other Earths. WILHELM PRANDTL and JOSEPH LÖSCH (*Z. anorg. Chem.*, 1922, **122**, 159—166).—The separation is based on the fact that ceric hydroxide is a weak base and its salts are highly hydrolysed. Cerous nitrate mixed with the nitrates of the other rare

earths was oxidised by trinitratocobalttriammine in acid solution with quantitative precipitation of the ceric hydroxide, $\text{Ce}(\text{NO}_3)_3 + [\text{Co}(\text{NH}_3)_3(\text{NO}_3)_3] + 4\text{H}_2\text{O} = \text{Ce}(\text{OH})_4 + \text{Co}(\text{NO}_3)_2 + 3\text{NH}_4\text{NO}_3 + \text{HNO}_3$. The formation of free acid prevents the precipitation of the other rare earths.

W. T.

Intermetallic Actions. The System Aluminium-Arsenic. QASIM ALI MANSURI (T., 1922, 121, 2272—2277).

The Constitution of Aluminates. JAROSLAV HEYROVSKY (*Chem. News*, 1922, 125, 198—199).—In order to investigate further the monobasicity of "aluminic acid" (cf. T., 1920, 117, 1013), cryoscopic and conductivity determinations were made on solutions of the alkaline-earth hydroxides when gradually saturated with aluminium hydroxide in the nascent condition, generated by the action of the solution on amalgamated aluminium. The regular fall in conductivity observed and the slight changes in the lowering of the freezing point show that only univalent aluminate ions exist. In contact with crystalline aluminium hydroxide, all the solutions are about 50% hydrolysed; with nascent aluminium hydroxide, the hydrolysis is only 1—1.5%. The process by which aluminium hydroxide dissolves in alkali is undoubtedly by complex-ion formation, $\text{Al}(\text{OH})_3 + \text{OH}' \rightarrow \text{Al}(\text{OH})_4'$, and not, as is often stated, by sending into solution one, two, or three of its hydrogen atoms as hydrions. The hydrolysis of aluminates is therefore, on this view, not due to scarcity of hydrions, but to the incompleteness of the complex formation.

G. F. M.

The Properties of Potassium Permanganate. G. FESTER and G. BRUDE (*Z. angew. Chem.*, 1922, 35, 527).—Crystals of pure potassium permanganate prepared in the dark and in air free from carbon dioxide and organic matter, are brown and have a bronze, metallic lustre. The finely powdered crystals, however, show a dark violet colour. When exposed to subdued daylight and ordinary air, the surfaces of the crystals develop a violet colour in a few hours and a steel blue lustre after two days. This change is confined to the surface layer, which acts as a protective layer to the remainder of the crystal. The change is particularly rapid in an atmosphere containing mineral acid. The crystals of potassium permanganate should be described as bipyramidal rhombs rather than as prisms. Potassium permanganate oxidises paper and most other organic substances, so that the statement that it is without action on litmus paper is untrue.

H. C. R.

Mechanism of the Reduction of Permanganate and its Physico-chemical Basis. IV. Reduction of Permanganate by Formate in Alkaline Solutions. JOSEF HOLLUTA (*Z. physikal. Chem.*, 1922, 102, 276—297; cf. this vol., ii, 448, 628, 700).—A continuation of previous work. It is shown that the reduction of permanganate by formates in alkaline solution takes place in two stages which are sharply separated from one another. In the first stage, the reduction of permanganate to manganate takes place, and this is reduced to an alkali manganite in the second

stage. The first stage takes place according to the equation $2\text{MnO}_4' + \text{HCO}_2' + 3\text{OH}' = 2\text{MnO}_4'' + \text{CO}_3'' + 2\text{H}_2\text{O}$, and it is shown that a disturbance occurs in the reaction at a point immediately before the completion of the reduction to manganate due to the commencement of the reduction of the manganate. The first stage is shown to be a second order reaction, inasmuch as one molecule of permanganate apparently oxidises one molecule of formate. To explain the behaviour of the manganate and the low order of the reaction it is assumed that it is not the permanganate itself which oxidises the formate, but atomic oxygen which is split off from the permanganate under the influence of the hydroxyl ions. It is further assumed that the hydroxyl ions, through the formation of an additive compound with the permanganate, act as oxygen carriers. It is shown that the above assumptions can be justified on the basis of the experiments and calculations of Sackur and Taegener (A., 1912, ii, 916). The temperature coefficient of this reaction is found to be 2.06. From the potential measurements of Sackur and Taegener (*loc. cit.*), the equilibrium constant of the reaction $2\text{MnO}_4'' + 2\text{H}_2\text{O} \rightleftharpoons 2\text{MnO}_2 + 4\text{OH}' + \text{O}_2$ is calculated to be 53.1 for 18–20°. It is shown that the presence of hydroxyl ions accelerates the reaction, the cause of which being in all probability that the hydroxyl ions affect the equilibrium pressure at which oxygen is separated from the permanganate hydroxyl ion complex.

J. F. S.

The Diffusion of Carbon in Metals and in Mixed Crystals of Iron. G. TAMMANN and K. SCHÖNERT (*Z. anorg. Chem.*, 1922, 122, 27–43).—Carbon was found to diffuse into iron at 750°, whereas no diffusion into the other metals took place at 980°. In mixed crystals of iron with tungsten, molybdenum, nickel, cobalt, and manganese containing a large amount of iron, the diffusion was found to increase with the addition of the second element until a maximum was reached; the diffusion then diminished. In the cases of tungsten and molybdenum, the maxima corresponded with 0.0306 molar concentration, and the diffusion increased by 0.166; with nickel, cobalt, and manganese as added metals, the maxima required a molar concentration of 0.114, and the increase in diffusion was 0.057. The diffusion coefficients found for different pieces of iron were found to vary; this was due to the foreign matter between the crystallites.

W. T.

Photochemical Examination of the Reaction between Ferric Salts and Iodides. NOBUJI SASAKI (*Mem. Coll. Sci. Kyōtō Imp. Univ.*, 1922, 5, 315–327).—The reaction between ferric salts and iodides is retarded by exposure to sunlight or bright artificial light, whilst that between ferrous salts and free iodine is accelerated. These photochemical reactions are discussed, and are shown to follow a simple law.

W. P. S.

System $\text{Fe}_2\text{O}_3\text{--SO}_3\text{--H}_2\text{O}$. E. POSNJAK and H. E. MERWIN (*J. Amer. Chem. Soc.*, 1922, 44, 1965–1994).—The system ferric oxide-sulphur trioxide-water has been investigated over the

temperature range 50—200°, by heating various mixtures of the components at various temperatures and analysing the phases produced. The following crystalline phases have been obtained: Fe_2O_3 ; $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$; $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot \text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3 \cdot 5\text{H}_2\text{O}$; $2\text{Fe}_2\text{O}_3 \cdot 5\text{SO}_3 \cdot 17\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ (2 forms); $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 6\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 \cdot 3\text{SO}_3 \cdot 7\text{H}_2\text{O}$; $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 3\text{H}_2\text{O}$; and $\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$. The conditions under which these substances are formed, the ranges of their stability, and some of their crystallographic and optical properties have been determined. J. F. S.

Some Poly-acids of the Elements of the Sulphur Group.

JULIUS MEYER and VALENTIN STATECZNY (*Z. anorg. Chem.*, 1922, **122**, 1—21).—The poly-acids formed by elements of the sulphur group are formulated according to the co-ordination system with a co-ordination number equal to four. The authors have succeeded in preparing the following heteropoly-acids and some of their salts: chromosulphuric acid, $\text{H}_2[\text{CrO}_3(\text{SO}_4)]$, and its potassium, sodium, ammonium, barium, strontium, and calcium salts; chromoselenic acid, $\text{H}_2[\text{CrO}_3(\text{SeO}_4)]$, together with its potassium and barium salts. Methods of preparation are given in detail. The solubilities of chromic anhydride in sulphuric and selenic acids of various concentrations were determined and a method was given for the preparation of the pure anhydride. The existence of the sulphoselenic acids, $\text{H}_2[\text{SeO}_3(\text{SO}_4)]$ and $\text{H}_2[\text{SeO}_2(\text{SO}_4)_2]$, was indicated by thermal analysis. Sulphomolybdic acid, $\text{H}_2[\text{MoO}(\text{SO}_4)_2(\text{MoO}_4)]$, was also prepared, but the corresponding selenic acid could not be isolated. Indications were obtained of the existence of chromyl-sulphuryl chloride, CuSO_3Cl_2 . W. T.

Experimental Attempts to Decompose Tungsten at High Temperatures. GERALD L. WENDT and CLARENCE E. IRION (*J. Amer. Chem. Soc.*, 1922, **44**, 1887—1894).—Attempts have been made to decompose tungsten by rapidly discharging a condenser holding 30,000—45,000 volts through a tungsten wire 4 cm. long and 0.035 mm. diam., either in a vacuum or in carbon dioxide at 1 atm. pressure. In this way, momentary temperatures above 20,000° were produced in the wires which were entirely dissipated, no smoke, dust or solid residue being found after the explosion. Abundant quantities of gas were present after the explosions in a vacuum, and a spectroscopic examination of this showed the strong yellow helium line, and two red, one bright blue, and one pale violet line were also observed but have not been identified. The gas from the explosions in carbon dioxide was collected and measured, and it was found that about the same weight (mean 0.713 mg.) of tungsten yields in different experiments from 3.62 to 0.30 c.c. of gas unabsorbable by potassium hydroxide. It is pointed out that if the whole of the tungsten had been decomposed into helium the volume of gas would have been 4.0 c.c. J. F. S.

The Hydrates of Tungsten Trioxide. GUSTAV F. HÜTTIG and BRUNO KURRE (*Z. anorg. Chem.*, 1922, **122**, 44—50).—The

existence of hydrates of tungsten trioxide was investigated by the Hüttig tensi-eudiometer (A., 1921, ii, 195). Solutions of the pure white and yellow acids were employed, and the process of dehydration was followed. No compound was indicated in the case of the white acid, the temperature-composition curve indicating adsorption as the water content changes gradually. The dehydration of the yellow acid showed the existence of a monohydrate $\text{WO}_3 \cdot \text{H}_2\text{O}$. The authors found that at temperatures above 188° and below 76° the white acid is the more stable, whereas between 76° and 188° the yellow variety is the stable form. W. T.

Sodium Tungstates. I. EDGAR F. SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 2027—2036).—Tungstates in which the basic and acidic oxides are present in the ratio 4 : 10 constitute a very definite series of salts. The sodium compound, $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$, can be prepared by the method of Forcher and Gibbs, by passing carbon dioxide during several days through an aqueous solution of normal sodium tungstate or by the gradual addition of formic acid, until the action is distinctly acid, to a solution of normal sodium tungstate (100 grams) in water (100 c.c.). A mixture of the salts $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$ and $5\text{Na}_2\text{O} \cdot 12\text{WO}_3 \cdot 28\text{H}_2\text{O}$ is produced by the action of glacial acetic acid on a solution of sodium tungstate; the product, $9\text{Na}_2\text{O} \cdot 22\text{WO}_3 \cdot 51\text{H}_2\text{O}$, appears to be a mixture of the two salts described above. The salt $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$ forms monoclinic crystals which effloresce rapidly in dry air. It is soluble in water to the extent of 19 parts in 100 parts at atmospheric temperature; and has d 4.3. The following melting points are recorded for the various sodium tungstates: $\text{Na}_2\text{O} \cdot \text{WO}_3$, 665° ; $5\text{Na}_2\text{O} \cdot 12\text{WO}_3$, 705.8° ; $4\text{Na}_2\text{O} \cdot 10\text{WO}_3$, 680.8° ; $9\text{Na}_2\text{O} \cdot 22\text{WO}_3$, 683.3° ; $\text{Na}_2\text{O} \cdot 4\text{WO}_3$, 706° . Addition of an excess of the respective metallic chlorides to a boiling aqueous solution of the salt $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$ leads to the formation of the following compounds: *calcium* salt, $4\text{CaO} \cdot 10\text{WO}_3 \cdot 25\text{H}_2\text{O}$, a white, granular powder which does not melt when heated to intense redness; the *barium* salt, $4\text{BaO} \cdot 10\text{WO}_3 \cdot 22\text{H}_2\text{O}$, and the *strontium* salt, $4\text{SrO} \cdot 10\text{WO}_3 \cdot 26\text{H}_2\text{O}$, white, insoluble, granular powders; the *nickel* salt, $4\text{NiO} \cdot 10\text{WO}_3 \cdot 34\text{H}_2\text{O}$, a greenish-white powder; the *cobalt* salt, $4\text{CoO} \cdot 10\text{WO}_3 \cdot 35\text{H}_2\text{O}$, pink granules; the *manganese* salt, $4\text{MnO} \cdot 10\text{WO}_3 \cdot 30\text{H}_2\text{O}$, a colourless, granular powder. The action of a solution of the sodium salt, $4\text{Na}_2\text{O} \cdot 10\text{WO}_3 \cdot 23\text{H}_2\text{O}$, towards solutions of salts of many inorganic and organic bases has been examined qualitatively. The sodium salt loses the whole of its water of crystallisation when it is strongly ignited, but when dried at 100° until constant in weight it retains six molecular proportions. It therefore appears that it may be formulated definitely as an acid salt, $4(\text{Na}_2\text{O} \cdot \text{WO}_3) \cdot 6(\text{H}_2\text{O} \cdot \text{WO}_3) \cdot 17\text{H}_2\text{O}$, and similar considerations are extended to the tungstates of other series. Confirmation of its acidic character is found in the ready neutralisation of its solutions with *N*-sodium carbonate solution and also in conductivity experiments during its neutralisation with barium hydroxide solution. H. W.

The Binary Systems Na_2SiO_3 – Na_2WO_4 , K_2SiO_3 – K_2WO_4 , and Na_2WO_4 – K_2WO_4 . J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1922, **122**, 175–180).—Klooster (A., 1911, ii, 111) examined the system Na_2WO_4 – Na_2SiO_3 and found no indications of a compound; the liquid salts were found to be immiscible. The present author has examined the viscosity and conductivity of aqueous solutions of the mixture. Curves representing the results showed no maxima or minima. The system K_2WO_4 – K_2SiO_3 gave similar results. The equilibrium curve for the system K_2WO_4 – Na_2WO_4 was obtained by the cooling method; a minimum freezing point was found for a mixture containing 80% of the sodium and 20% of the potassium salt. W. T.

Preparation and Reactions of Stannous Oxide and Stannous Hydroxides. FRANK WARD BURY and JAMES RIDDICK PARTINGTON (T., 1922, **121**, 1998–2004).

Reduction of Thorium Oxide by Metallic Tungsten. THE RESEARCH STAFF OF THE GENERAL ELECTRIC CO., LTD., LONDON (work conducted by COLIN JAMES SMITHELLS) (T., 1922, **121**, 2236–2238).

Germanium Hydride. JOHN H. MÜLLER and NICOL H. SMITH (*J. Amer. Chem. Soc.*, 1922, **44**, 1909–1918).—Germanium may be detected by a modification of Marsh's test in quantities as small as 0.00006 gram of the metal. The delicacy of the hydride relation is greatly increased by use of an alkaline generator as source of nascent hydrogen. Aluminium and dilute potassium hydroxide solution serve best for the formation of large quantities of germanium hydride, whilst sodium amalgam is best for small quantities. A modification of the usual form of Marsh apparatus is described which permits of the formation of a richer mixture of the hydride than has hitherto been prepared and still further increases the delicacy of the test. The apparatus is arranged as follows:—an electrolytic hydrogen generator, using 15% sodium hydroxide as electrolyte and having nickel electrodes, a washing tower containing a solution of a silver salt, a sulphuric acid drying tower, and a trap for exit of excess of hydrogen from the generator. The gas prepared and purified in the above train passes into the germanium hydride generator, which consists of a small wash-bottle the inner tube of which is cut off at a height 5 cm. above the bottom of the bottle; the generator is fitted with a funnel and stopcock through which the sodium amalgam and germanium solution may be added after the whole system has been filled with electrolytic hydrogen. To the generator is attached a small drying tube and to the end of this a constricted tube in which the germanium mirror may be formed. A rich mixture of germanium hydride and hydrogen is obtained by placing dry sodium amalgam in the generator and expelling the air by means of electrolytic hydrogen. The hydrogen stream is then interrupted and an aqueous solution of the germanium salt added and washed in with water. The germanium hydride is then allowed to form in the

closed apparatus, and when the action is over swept through the heated constricted tube by means of electrolytic hydrogen, when a mirror of germanium is immediately formed. The decomposition temperature of germanium hydride lies between 340° and 360° , and the deposition of the mirror is best obtained below a red heat. The reverse action, involving the loss of germanium in hydrogen, has been quantitatively investigated and shows that at $750\text{--}800^{\circ}$ 1.41855 grams of germanium loses 0.00647 gram when in a stream of hydrogen for thirty-eight hours. The dissimilarity of films of arsenic and germanium as obtained by the Marsh test is shown by a spectroscopic examination of the light transmitted by the films, and the thickness of the films has been determined. A study of the composition of the substance described by Voegelen (A., 1902, ii, 401) shows this substance to be a mixture which may contain little or much silver germanide Ag_4Ge along with metallic silver, depending on the method used in the preparation of the hydride. The precipitate contains much more germanide if the hydride is generated by the action of potassium hydroxide on aluminium and passed slowly through a solution of a silver salt, whilst if the formation of the hydride is brought about by means of sodium amalgam or the gas passed rapidly through the silver salt, the precipitate contains little germanide and the solution contains germanic acid. Evidence is put forward which indicates the presence of at least one hydride other than the tetrahydride, but the presence of this hydride has not been finally established. The richest mixture of hydrogen and germanium hydride examined contained 0.176% of the hydride. J. F. S.

Germanium Hydride. FRITZ PANETH and EDGAR SCHMIDT-HEBBEL (*Ber.*, 1922, 55, [B], 2615—2622).—Germanium hydride has been described previously by Voegelen, but its composition has not been settled definitely. The substance has now been re-examined, and since the authors had only a very limited amount of material at their disposal they have found it most convenient to prepare the gas by the action of zinc or, preferably, magnesium on a solution of germanium in the presence of 3—4*N*-sulphuric acid; the yield varies between 0.2 and 1.5%. The gas evolved from the solution is dried by passage over granulated calcium chloride and phosphoric oxide and subsequently led through a Landsiedl apparatus filled with potassium hydroxide solution (50%), a U-tube immersed in pentane cooled to -110° and finally through three U-tubes cooled in liquid air. The almost invisible white condensate in the last three tubes is analysed by the method used previously for antimony and tin hydrides (this vol., ii, 383). It is thus shown that the atomic ratio of hydrogen to germanium is exactly 4:1. The accuracy of the analyses excludes the possibility of the presence of more than the merest traces of possible hydrides, such as Ge_2H_6 , and the existence of these is the more improbable, since, under the conditions of the condensation, they must have become concentrated in the condensate; the pentane tube does not retain any germanium compounds, and about 15%

of germanium hydride passes uncondensed through the apparatus. It is shown that the molecular formula of germanium hydride is GeH_4 .

Germanium hydride is unusually stable, being unaffected by potassium hydroxide solution (50%) or phosphoric oxide, and requiring a relatively very high temperature to cause its certain decomposition. The colours of the germanium mirrors are extraordinarily varied and in this respect the metal is differentiated from all others which yield hydrides decomposable by heat. In doubtful cases, confirmation may be obtained by oxidising the mirror to colourless germanium dioxide by heating it in a current of oxygen and subsequently reducing it in hydrogen to copper-coloured germanium, which can then be dissolved in sodium hypochlorite. Arsenic exhibits greater solubility in the reagent, but its oxide would be volatilised completely under the experimental conditions.

H. W.

The System $\text{Bi}_2\text{O}_3\text{-PbO}$. L. BELLADEN (*Gazzetta*, 1922, 52, ii, 160—164).—The occurrence in nature of a series of minerals constituted of double sulphides of bismuth and lead which may mostly be regarded as derivatives of hypothetical ortho-, meta-, and pyro-sulphobismuthous acids renders possible the existence of similar compounds containing oxygen in place of the sulphur atoms. The author has investigated the fusion diagram of the system $\text{Bi}_2\text{O}_3\text{:PbO}$, the results obtained indicating the formation of the compounds: (1) $4\text{Bi}_2\text{O}_3\text{,PbO}$, m. p. 695° (decomp.); (2) $3\text{Bi}_2\text{O}_3\text{,2PbO}$, m. p. 686° , stable when fused; (3) $\text{Bi}_2\text{O}_3\text{,2PbO}$, m. p. 625° , stable on fusion. These indications are fully confirmed by micrographic examination.

Litharge has m. p. 870° and bismuth trioxide, m. p. 817° .

T. H. P.

Polonium Hydride. II. FRITZ PANETH and ADOLF JOHANNSEN (*Ber.*, 1922, 55, [B], 2622—2637).—Polonium hydride closely resembles bismuth hydride in the order of magnitude of its yields by all methods of preparation, its great instability during the condensation of minimal amounts, and its ready decomposability by chemical reagents.

The preparation of polonium hydride has been affected previously by the action of dilute acids on an electrolytic deposit of polonium on magnesium (A., 1919, ii, 76). Since it is difficult by this method to secure highly activated magnesium foil in uniformly good yield, a process has been evolved which depends on the deposition of polonium on magnesium powder by distillation. For this purpose, the polonium is first deposited electrolytically from a lead nitrate solution containing radium-*D* on the central portion of a thin piece of platinum foil. The latter is now suspended in a glass dish, the bottom and sides of which are covered with magnesium powder; the apparatus is brought into an evacuated desiccator and the foil is raised electrically to a bright yellow heat. The volatilised polonium is deposited mainly on the powder, which, after being carefully mixed, gives a preparation of uniform activity.

(A method for the recovery of polonium from its residual solutions and again precipitating it on magnesium is described in detail.) The yield of polonium hydride obtained by the solution of the activated powder in dilute acid is practically the same as from the activated foil, and lies intermediate between those of lead and bismuth hydrides. The formation of the hydride cannot be ascribed to the decomposition of a compound of magnesium and polonium, since the gas is also obtained by adding magnesium powder to a solution containing polonium. The method of "spark electrolysis" is also applicable to the production of polonium hydride, but the evolution of the gas by this method is too irregular for use for the present purposes.

Polonium hydride which has been condensed at the temperature of liquid air is very extensively decomposed during re-evaporation. The action appears to depend to some extent on the accompanying gases; thus, for example, it has not been found possible to re-volatilise polonium hydride which has been prepared by "spark electrolysis." The condensation and partial re-volatilisation of polonium hydride affords the most conclusive evidence of the gaseous nature of the compound.

Phosphoric oxide causes very extensive decomposition of the hydrides of polonium and thorium-C, whereas calcium chloride has a less strongly marked action; the latter, however, can only be used for the desiccation of polonium hydride when a very high initial activity can be used. Under the experimental conditions adopted, unboiled distilled water only allows 3% of polonium hydride to pass unchanged, whereas 50% of the gas passes through air-free, distilled water. *N*/10-Sodium hydroxide and *N*/10-silver nitrate solution cause very extensive decomposition of polonium hydride.

The rates of spontaneous decomposition of polonium and bismuth hydrides have been examined; the former is decomposed to the extent of 50% after four minutes, the latter after about twenty-five minutes. A more exact calculation is not warranted by the accuracy of the experiments, which suffer under the disadvantages that the gases cannot be dried. It is, however, established that moist polonium hydride is considerably more easily decomposed than bismuth hydride.

H. W.

The Recrystallisation of Pure Mechanically Unworked Gold, obtained by Solidification from the Fused Mass. W. FRAENKEL (*Z. anorg. Chem.*, 1922, **122**, 295—298).—Pure mechanically unworked gold showed no change in size or form of crystals on heating at 1000—1040°. The purity could not be guaranteed to be such that the crystallites might not be surrounded by films of impurity (cf. Tammann, A., 1921, ii, 172).

W. T.

Mineralogical Chemistry.

Colour of Fluorites. TOKUTARO SAKAO and MITSUIE HIROSE (*Mem. Coll. Sci. Kyōtō*, 1921, 4, 349—350).—The colour of fluorite crystals has been attributed by Blount and Sequeira (T., 1919, 15, 705) to the presence of a small amount of organic matter. Employing the ultra-microscope, the authors were unable to detect the presence of such matter in a state of colloidal suspension in five varieties of coloured fluorite crystals. J. S. G. T.

Analytical Chemistry.

Qualitative Chemical Analysis. V. MACRI (*Boll. Chim. Farm.*, 1922, **61**, 417—418).—By means of the following scheme, the use of sulphur compounds is avoided. The hydrochloric acid solution is placed, together with a rod of zinc, in a flask fitted with a gas delivery tube, the latter being heated so as to make a Marsh apparatus; the flask is eventually heated. The liquid is filtered, the precipitate containing silver, mercury, lead, bismuth, copper, cadmium, platinum, gold, tin, antimony, and arsenic. The filtrate is heated to boiling with zinc acetate, aluminium, iron, and chromium being precipitated. The filtrate from this is heated with hydrogen peroxide, which precipitates manganese. The filtrate from the latter is heated and treated with zinc oxide in presence of chlorine, nickel and cobalt being thus precipitated. Reference is made to various circumstances which prevent the subdivision into groups from being rigorously exact. [Cf. *J. Soc. Chem. Ind.*, 1922, 839A.] T. H. P.

Quantitative Microanalysis. MAURICE NICLOUX and GEORGES WELTER (*Chim. et Ind.*, 1922, **8**, 269—272).—A summary of Pregl's methods of microanalysis for use with which a Longue's aperiodic microbalance is recommended. A micro-method for the estimation of urea in blood is outlined (cf. this vol., ii, 170). W. G.

Use of Resorcinol in Qualitative Inorganic Analysis. LAVOYE (*J. Pharm. Belg.*, 1921, **3**, 889—890; from *Chem. Zentr.*, 1922, ii, 1154).—One c.c. of a 10% solution of resorcinol mixed with 2 c.c. of 10% ammonia solution gives characteristic colorations when added to 2 c.c. of different metallic salt solutions. The following colorations are obtained. Zinc salts, a yellowish-green colour, changing to deep blue; cadmium salts, a less intense blue colour; manganese salts, in the presence of ammonium salts, a bluish-green colour; nickel salts, bluish-green; copper salts, reddish-violet, changing to bluish-violet. With salts of the latter two metals the solutions should be so dilute that ammonia alone

gives no coloration. Platinum salts give a garnet-red colour; mercury salts give no colour, but the solution on evaporation gives crystalline needles. All the colorations mentioned change to red on the addition of acid. The reactions are sensitive with very small amounts of the metals in question.

G. W. R.

Analysis of Minerals by the Röntgen Spectrograph.

ASSAR HADDING (*Z. anorg. Chem.*, 1922, **122**, 195—200).—The suitability of this method is shown by the fact that monazite, which contains twelve oxides, only gives twelve lines. Quantities of substances are indicated roughly by the strength of the lines. Very small amounts of substances are shown by weak lines and the author suspects the presence of the unknown element of atomic number 61 in "fluocerite."

W. T.

Use of Mixed Indicators.

A. COHEN (*J. Amer. Chem. Soc.*, 1922, **44**, 1851—1857).—It is shown that differences of subjective colour are enhanced when two indicators are partially transformed at the same hydrogen-ion concentration. The colorimetric determination of hydrogen-ion concentration can, therefore, be rendered more precise by the use of suitable mixed indicators and in certain titrations sharper end-points can be obtained, particularly in coloured liquids. Thus with the indicator bromothymol-blue the value P_H 6.8 is indicated by a pure green colour, but in a yellow medium the colour is yellowish-green and difficult to observe; if, however, an indicator is added which is violet at this concentration, then the total effect of the mixed indicators will be a green end-point. This may be achieved by adding equal quantities of bromothymol-blue and bromocresol-purple. Several cases of the use of mixed indicators are described.

J. F. S.

Modification of the Chlorometric Method of Hayem and Winter. J. MALGOYRE (*Bull. Soc. pharm. Bordeaux*, 1922, **60**, 59—64).—Gastric juice is treated with a reagent prepared by dissolving 2 grams of chromic acid in 100 c.c. of 95% ethyl alcohol to remove proteins, and then titrated directly. The free and total hydrochloric acid are estimated by the Topfer-Linossier method, and the combined acid found by difference. The total chlorine is estimated by neutralising 10 c.c. of gastric juice with a saturated solution of sodium carbonate, adding 10 c.c. of the chromic acid reagent, filtering, and titrating with 0.1*N*-silver nitrate. The fixed chlorine is equal to the difference between the total chlorine and total acidity.

CHEMICAL ABSTRACTS.

Reductions with Cadmium and Lead in Volumetric Analysis. III. W. D. TREADWELL (*Helv. Chim. Acta*, 1922, **5**, 806—818).—[With P. HRISTIE, L. EGGER, and P. STURZENEGGER.] A warm solution of a chlorate in presence of sulphuric acid can be reduced quantitatively to chloride by passing it through a cadmium reduction tube (A., 1921, ii, 523), and the chloride can then be titrated by the Volhard process. Since perchlorates are not reduced under these conditions, chlorate can be determined in presence of perchlorate by this method. Perchlorate can be reduced to chloride

by boiling in sulphuric acid solution (about 10 c.c. of concentrated acid to 50 c.c. of 0.1*N*-chlorate solution) in presence of titanium sulphate for one-half to one hour with finely divided cadmium. The cadmium is only attacked to a slight extent by the acid, and a small amount of cadmium sulphide is formed which, however, does not interfere with the estimation of perchlorate. After cooling, the solution is diluted, the titanous sulphate present is carefully oxidised with permanganate and the chloride is titrated either by the Volhard process or electrometrically.

[With A. FREULER and A. WEBER.]—A reduction method for the estimation of columbium was described by Metzger and Taylor (A., 1909, ii, 702), depending on the stabilising effect of succinic acid on a solution of columbic acid in sulphuric acid. The solution was reduced with amalgamated zinc to the constant stage $\text{Cb}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$. It has now been found that the succinic acid solution of columbic acid prepared in this manner is far from stable. In course of a few days it becomes opalescent and its reducibility gradually becomes less. The reducibility also becomes less when a solution of columbic acid in sulphuric acid is diluted, confirming the view that the reducibility depends on the dispersity of the colloidal acid. Consistent results were obtained when the reduction was carried out in a cadmium reduction tube in presence of ammonium molybdate or vanadate or of titanium sulphate, the subsequent titration being carried out with permanganate. The most stable solutions of columbic acid were obtained by dissolving the fluoride in concentrated hydrochloric acid, and consistent results were obtained when such solutions were reduced in a cadmium tube and titrated electrometrically with ferric chloride.

[With R. F. EDELMANN.]—A concentrated hydrochloric acid solution of a molybdate can be reduced quantitatively to the Mo^{III} stage by finely divided lead. Lead in a suitable form for a reduction tube was obtained by immersing a zinc rod in an acidified solution of lead acetate. The crystals of lead must be carefully washed with alcohol and ether, not pressed together. Stannic chloride was also reduced quantitatively to stannous chloride by means of lead. The oxidation titrations were carried out with permanganate.

E. H. R.

Chlorination of Mixed Silver Haloids in Gooch Crucibles.

M. G. MELLON and J. C. SIEGESMUND (*Proc. Indiana Acad. Sci.*, 1921, 197—199).—The crucible containing the silver haloids is placed inside a larger crucible which is covered with a watch glass with a hole in the centre. Chlorine is passed into the crucible through a tube extending to within 1 cm. of the bottom, the outer crucible being gently heated meanwhile.

CHEMICAL ABSTRACTS.

Electrometric Titrations with Lead Nitrate. I. M. KOLTHOFF (*Z. anal. Chem.*, 1922, **61**, 369—377).—Electrometric titration of iodide solutions, of not too low concentration, with lead nitrate solution yields trustworthy results, even in the presence of chlorides and bromides; the method is applicable to the estim-

ation of ferrocyanides and also of sulphates provided that mineral acids, ferric salts, and aluminium salts are not present. The titration of pyrophosphates with lead nitrate solution gives unsatisfactory results, but the method may be used in the case of a few organic salts such as oxalates, tartrates, and succinates.

W. P. S.

A New Iodometric Method Based on the Formation and the Estimation of Cyanogen Iodide. RUDOLF LANG (*Z. anorg. Chem.*, 1922, **122**, 332—348).—A volumetric method for the estimation of iodide is given, based on the fact that an iodide in hydrochloric or sulphuric acid solution is oxidised by an iodate or permanganate in the presence of hydrocyanic acid to cyanogen iodide, the end-point being indicated by starch solution. This can be controlled by estimating the cyanogen iodide with thio-sulphate $\text{ICN} + 2\text{S}_2\text{O}_3^{''} + \text{H}^+ = \text{I}^+ + \text{HCN} + \text{S}_4\text{O}_6^{''}$. The method is found to be applicable in the presence of bromides and nitrates. Different stages of oxidation of iodine can also be estimated in mixtures.

W. T.

The Estimation of Sulphur in Vulcanised Rubber. J. W. W. DYER and AMY R. WATSON (*J. Soc. Chem. Ind.*, 1922, **41**, 332T).—With reference to the method described for the estimation of combined sulphur in vulcanised rubber (this vol., ii, 656), the authors acknowledge priority of publication to A. R. Pearson (*Analyst*, 1920, **45**, 405). They prefer to use the method for combined sulphur only, however, and not for total sulphur, unless the amount of free sulphur is small.

G. F. M.

Estimation of Sulphides by Oxidation with Ferric Salts. P. P. BUDNIKOFF and K. E. KRAUSE (*Z. anorg. Chem.*, 1922, **122**, 171—174).—The estimation is based on the reaction $3\text{Na}_2\text{S} + 3\text{Fe}_2(\text{SO}_4)_3 = 3\text{Na}_2\text{SO}_4 + 6\text{FeSO}_4 + 3\text{S}$. The amount of ferrous salt is found by permanganate. The acidity of ferrous sulphate is neutralised by the addition of alkali carbonate. The method is only applicable to sulphides which are soluble in water and acids.

W. T.

The Estimation of Sulphuric Acid as Barium Sulphate in the Presence of Aluminium. L. MOSER and P. KOHN (*Z. anorg. Chem.*, 1922, **122**, 299—310).—The results of the estimation of sulphuric acid in the presence of aluminium are too low, these low results being due to the presence of aluminium sulphate in the precipitate. The amount of this impurity increases up to a maximum with an increase in the concentration of the aluminium salt. Precipitated barium sulphate takes up aluminium sulphate from solution—a solid solution is thus indicated. The best results are obtained by working in hydrochloric acid solution when the maximum error is -0.15% . The errors observed in the presence of the aluminium-ion are only one-tenth those obtained in the presence of the ferric-ion.

W. T.

A New Accelerator for the Destruction of Organic Matter in the Kjeldahl Method for the Estimation of Nitrogen.

M. SBOROWSKY and I. SBOROWSKY (*Ann. Chim. Analyt.*, 1922, **4**, 266—267).—Mercurous iodide accelerates the destruction of organic matter in the digestion with sulphuric acid much more effectively than metallic mercury or other mercury salts. In two experiments carried out with 10 c.c. of sulphuric acid, with mercurous iodide 0.7 gram of sugar was destroyed in the time required for the destruction of only 0.1 gram with metallic mercury. A digestion was completed in fifty to sixty minutes which with metallic mercury required four to eight hours.

H. C. R.

Estimation of Total Nitrogen in Fertilisers containing Nitrites and of Nitrite Nitrogen in the Presence of Nitrates.

F. MACH and F. SINDLINGER (*Z. angew. Chem.*, 1922, **35**, 473—474).—To estimate the total nitrite and nitrate nitrogen, 25 c.c. of an aqueous solution of the sample (this quantity of solution should contain not more than 0.05 gram of nitrogen) are added gradually to a boiling mixture of 30 c.c. of saturated potassium permanganate solution and 5 c.c. of dilute sulphuric acid (1 : 2); a further quantity of 10 c.c. of the acid is then added, the mixture is cooled, treated with 10 grams of ferrum redactum, and again boiled for about ten minutes. The resulting ammonia is estimated by distillation in the usual way. The nitrate nitrogen is then estimated in another portion of 25 c.c. of the solution by boiling this quantity for ten minutes with 30 c.c. of *N*/3-sulphuric acid and 10 c.c. of methyl alcohol (the whole of the nitrous acid is thus expelled in the form of its methyl ester), neutralising the cooled mixture, and reducing the remaining nitrate with ferrum redactum in sulphuric acid solution. The nitrite nitrogen is found by subtracting the nitrate nitrogen from the total nitrogen. If ammonium salts are present, the ammonia nitrogen must be estimated separately and an allowance made for its quantity.

W. P. S.

Comparison of the Methods for the Estimation of Nitric Oxide.

ALFONS KLEMENC and CORNELIE BUNZL (*Z. anorg. Chem.*, 1922, **122**, 315—331).—Nitric oxide was prepared according to the method of Emich (A., 1892, ii, 939); this, however, contained 1% of impurity and was purified by fractionation, using liquid air. The estimation of the gas by passing it over heated copper was found to give accurate results. Estimations (1) with hydrogen in the Drehschmidt platinum capillary (Knorre and Arndt, A., 1899, ii, 806), (2) by the method of Baudisch and Klinger (*Ber.*, 1918, **45**, 3231), and (3) by absorption with ferrous sulphate were found to give untrustworthy results. Good results were obtained by absorbing the gas by acidified bromate or *N*/5-potassium permanganate and estimating the excess. The latter method can also be used in the presence of carbon dioxide and other gases.

W. T.

Detection of the Nitrous Anion. P. FALCIOLA (*Gazzetta*, 1922, **52**, ii, 87—89).—Small proportions of nitrite may be detected : (1) By the transitory yellow coloration obtained by acidification

with sulphuric acid and gradual addition of sodium thiosulphate solution. (2) By the orange colour developed on addition, to a litre of the solution, of about 2 c.c. of sulphuric acid, excess of thiocyanate, and about 0.1 gram of ferrous sulphate (cf. Horst, A., 1921, ii, 461). (3) By the yellow coloration formed on addition of excess of aniline phosphate. [Cf. *J. Soc. Chem. Ind.*, 1922, 856A.]

T. H. P.

Separation of Phosphoric Acid in Qualitative Analysis.

N. TARUGI (*Boll. Chim. Farm.*, 1922, **61**, 545—552).—The author's investigation of Gattermann and Schindhelm's proposal to eliminate phosphoric acid by means of stannic chloride (A., 1917, ii, 41) shows that, even under the best conditions, 15.4% of the total phosphoric acid passes into the filtrate from the stannic precipitate, and that the latter contains part of the iron, chromium, calcium, barium, etc., present. Further, when the proportion of phosphoric acid in the solution to be examined is unknown, it is impossible to add the exact quantity of ammonium phosphate to give a definite ratio between phosphate and stannic chloride.

T. H. P.

Effect of Iron on the Iodine Titration of Arsenite.

F. L. MELVILL (*J. S. African Chem. Inst.*, 1922, **5**, 3—5).—The interference of ferric salts in the titration of arsenite solution by iodine solution may be prevented by the following procedure. The slightly acid arsenite solution, containing not more than 0.1% of iron (expressed as Fe_2O_3), is treated with about one-half the quantity of iodine solution required to oxidise all the arsenite, 10 c.c. of saturated sodium hydrogen carbonate solution are then added, and the titration is completed. In this way the whole of the iron is precipitated as ferric arsenate and no longer interferes with the titration.

W. P. S.

Estimation of Boric Acid.

WILHELM STRECKER and ERNST KANNAPPEL (*Z. anal. Chem.*, 1922, **61**, 378—397).—The substance containing boric acid or its salts is mixed with 40% phosphoric acid and methyl alcohol and the mixture is distilled in a current of air saturated with methyl alcohol (the air is passed previously through a flask containing methyl alcohol) until all the methyl borate has been collected in a receiver containing sodium hydroxide solution. The distillate is then heated to expel methyl alcohol, treated with a slight excess of hydrochloric acid, using methyl-orange as indicator, boiled to expel carbon dioxide, and neutralised with sodium hydroxide solution. After the addition of mannitol in the proportion of 1 gram for each 10 c.c. of solution, the mixture is titrated with *N*/10-barium hydroxide solution, using α -naphtholphthalein solution as indicator.

W. P. S.

Sulphonated Derivatives of the Naturally Occurring Sulphidic Hydrocarbons.

C. PÉPIN and G. REAUBOURG (*J. Pharm. Chim.*, 1922, [vii], **26**, 258—261).—As the therapeutic value of ichthyol is largely dependent on the amount of "sulphidic" sulphur it contains as distinguished from total sulphur which

comprises in addition sulphonic and sometimes sulphatic sulphur, it is desirable that more precise standards should be laid down to which commercial ichthyol preparations should conform. Ammonium or other sulphates should be almost completely absent, as indicated by the formation of nothing more than an opalescence on the addition of barium chloride to the filtrate after precipitation of an ichthyol solution by albumin and hydrochloric acid. Sulphidic sulphur can only be estimated by difference by Thal's method, which consists in an estimation of total sulphur, by Carius's method, for example, and subtracting from this the sulphur present as sulphate, if any, determined by weighing the above barium sulphate precipitate, and the sulphonc sulphur determined by an ammonia estimation, and calculating on the basis of one sulphonc group for each molecule of ammonia after making allowance for the ammonia combined as sulphate. As thus estimated, "sulphidic" sulphur should represent at least 15% of the weight of the dried ichthyol. The conservation of ethylenic linkings in the preparation of the ichthyol should be confirmed by the decolorisation of bromine water.

G. F. M.

Radioactive Indicators. FRITZ PANETH (*Z. angew. Chem.*, 1922, **35**, 549—552).—Use has been made of radioactive isotopes of metals such as lead and bismuth for indicating the presence of minute and unweighable quantities of these elements or their compounds. Quantities of the radioactive isotopes of the order of a millionth of a milligram are easily detected by the electroscope. Once mixed with the inactive isotope, they cannot be separated by chemical means, so that the presence of the radioactive isotope indicates the presence of the inactive one also. Practical applications have been made in analytical chemistry in determining the solubility of very sparingly soluble substances and in the study of adsorption phenomena. In electrochemistry it has been established by this means that an interchange of the metallic portion of the molecule actually occurs on mixing solutions of two salts of the same metal and subsequently recovering them from solution, but that no such interchange occurs when one or both the substances are non-ionised. The actual deposition of an unweighable quantity of metal on the electrode before the minimum potential of electrolysis is reached has also been established. In colloid chemistry, the active surface of powders has been measured for the first time by the use of a radioactive indicator, and the distinction between crystalloid and colloid in the diffusion of the former through parchment membranes has been studied down to a dilution of 10^{-11} mol. per litre. In inorganic chemistry, the conditions for the preparation of bismuth and lead hydrides were studied by this means and the method was successfully applied to the measurement of the gas-tightness of rubber fabrics for gas-masks. The kinetic theory has received further experimental confirmation by the actual proof of the movement of the molecules in molten lead and measurements of the movement of lead ions in lead chloride even below its melting point.

H. C. R.

Estimation of Small Quantities of Calcium. PATRICK PLAYFAIR LAIDLAW and WILFRED WALTER PAYNE (*Biochem. J.*, 1922, 16, 494—498).—The method described is suitable for estimating calcium in amounts of the order of 0.1 mg., and gives results accurate to about 0.002 mg. The calcium is first precipitated as oxalate (in the case of blood serum, this may be done directly from the serum without previous ashing). After separation, the precipitate is dissolved in hydrochloric acid and the calcium reprecipitated in the form of calcium alizarinate by the addition of excess of alizarin in alcoholic solution, and, after warming, of a few drops of strong ammonia. When crystalline, the precipitate is collected in a Gooch crucible, washed with dilute ammonia, and decomposed with a solution of oxalic acid in 50% alcohol. The liberated alizarin is dissolved in 95% alcohol, made just alkaline with ammonia, and estimated colorimetrically by comparison with a standard solution of ammonium alizarinate. E. S.

The Separation of Zinc from Other Metals, especially Nickel. ALOIS LUDWIG (*Z. anorg. Chem.*, 1922, 122, 239—261).—Zinc can be separated from nickel by precipitation with hydrogen sulphide in the presence of ammonium tartrate. The latter salt forms stable complex compounds with nickel, which may perhaps explain its action; the latter might, however, be due to the replacement of the freed mineral acid by the weaker tartaric acid. Results are also given of attempts to effect the separation by precipitation of zinc from zinc ammonium phosphate in neutral solution in the presence of neutral tartrates and thiocyanates. These investigations are being continued. W. T.

The Influence of the Alkalis on the Titration of some Metals with Ferrocyanide. W. D. TREADWELL and D. CHERVET (*Helv. Chim. Acta*, 1922, 5, 633—639).—The electrometric titration of zinc with potassium ferrocyanide was described by Treadwell and Weiss (*A.*, 1920, ii, 120). The sharpness of the end-point depends on the insolubility of the ferrocyanide of the heavy metal, but it is also dependent on the alkali metal used, since the precipitate is generally a double salt. When cadmium sulphate is titrated with potassium ferrocyanide in neutral or weakly acid solution, the end-point is indicated by a moderately sudden drop in potential, but only in a highly dilute solution has the precipitate the exact composition $\text{CdK}_2\text{Fe}(\text{CN})_6$. In the presence of a rubidium salt or a caesium salt, however, the end-point is much sharper, probably because the alkali metals with higher atomic volumes form less soluble double salts with cadmium ferrocyanide. When sodium ferrocyanide is used for the titration, the precipitate is the simple salt, $\text{Cd}_2\text{Fe}(\text{CN})_6$. When a zinc salt is titrated with potassium ferrocyanide the precipitate is $\text{Zn}_3\text{K}_2[\text{Fe}(\text{CN})_6]_2$, but with sodium ferrocyanide, $\text{Zn}_2\text{Fe}(\text{CN})_6$, is obtained. In presence of a potassium salt, however, sodium ferrocyanide gives the above zinc-potassium salt, whilst in presence of a caesium salt, potassium ferrocyanide gives $\text{ZnCs}_2\text{Fe}(\text{CN})_6$ with a very sharp end-point. Lead nitrate can be titrated with ferrocyanide in neutral solution,

but lead ferrocyanide is very sensitive to acid; consequently zinc can be titrated with ferrocyanide in hot acid solution in presence of lead. The precipitate obtained from lead nitrate and potassium ferrocyanide is $\text{Pb}_2\text{Fe}(\text{CN})_6$, but in presence of a caesium salt the precipitate has the composition $\text{Pb}_3\text{X}_2[\text{Fe}(\text{CN})_6]_2$, where X is probably entirely caesium. The ferrocyanides of the bivalent heavy metals appear to be less soluble the smaller the atomic volume of the heavy metal.

E. H. R.

Estimation of Lead in Lead Amalgam. M. G. MELLON and H. F. REINHARD (*Proc. Indiana Acad. Sci.*, 1921, 189—195).—Existing methods are considered to be unsatisfactory for the estimation of small quantities of lead in the presence of large quantities of mercury. A weighed quantity of the amalgam is covered with 25 c.c. of a 10% solution of cupric nitrate and allowed to remain for fifteen to twenty-four hours; lead enters into solution, but mercury does not. After decantation through a filter, the amalgam is washed, and the filtrate treated with a few drops of acetic acid and sufficient potassium dichromate solution to precipitate the lead as lead chromate, which is washed in a Gooch crucible, dried at 120° , and weighed.

CHEMICAL ABSTRACTS.

The Kastle-Meyer Reagent as a very Sensitive Reagent for Copper. OTTORINO CARLETTI (*Boll. Chim. farm.*, 1922, 61, 449).—A claim for priority (A., 1914, ii, 74) over Thomas and Carpentier (this vol., ii, 86).

T. H. P.

New Method for the Estimation of Manganese. ST. MINOVICI and CONST. KOLLO (*Chim. et Ind.*, 1922, 8, 499—500).—Manganese may be estimated with accuracy, even when present in only small quantities, by precipitation as iodate by means of iodic acid according to the equation $\text{MnSO}_4 + 2\text{HIO}_3 = \text{Mn}(\text{IO}_3)_2 + \text{H}_2\text{SO}_4$. A solution of about twice the theoretical quantity of iodic acid is added to the manganese solution, and after warming for ten minutes on a water-bath twice the volume of alcohol is added. After keeping for a short time, the precipitate is collected on a filter or Gooch crucible and washed with 70% alcohol saturated with manganous iodate. The mother-liquor contains no traces of manganese, the iodate being insoluble in 70% alcohol in presence of iodic acid. In water at the ordinary temperature, its solubility is 0.195%, and in 70% alcohol 0.005%. The precipitate of manganous iodate is finally dried at 100° , and weighed. The absolute percentage error in the examples given varies from 0.16 to 0.63% when quantities of the order of 0.1—0.3 gram of the hydrated sulphate are taken for estimation.

G. F. M.

A New Microchemical Method for the Identification of Tungsten. J. A. M. VAN LIEMPT (*Z. anorg. Chem.*, 1922, 122, 236—238).—A small quantity of sodium nitrite is melted on a platinum spoon and a little tungsten is thrown in; sodium tungstate is formed. This is dissolved in a little water and tungstic acid precipitated by the addition of hydrochloric acid (1:1). This is collected and then mixed with a few drops of concentrated

ammonia and placed on a slide. Ammonium paratungstate soon crystallises in four-cornered plates on the edges of the drop and as long needles in the centre.

W. T.

Glacial Acetic Acid Method for Estimating Uranium in Carnotite. WILFRED W. SCOTT (*J. Ind. Eng. Chem.*, 1922, **14**, 531—532).—Half a gram of the ore is heated with 40 c.c. of dilute (1 : 1) nitric acid, the mixture is evaporated to dryness, the residue ignited, and then boiled for five minutes with a mixture of glacial acetic acid and nitric acid (100 : 5); the insoluble portion is separated by filtration and the filtrate is evaporated to dryness. This residue is ignited until it turns black and the extraction with the acetic acid-nitric acid mixture repeated; the filtrate obtained is evaporated, the residue dissolved in 10 c.c. of nitric acid and 40 c.c. of water, the solution neutralised partly with ammonia and ammonium carbonate is added in quantity sufficient to dissolve the precipitate of uranium carbonate which first forms. After the addition of an excess of 3 grams of ammonium carbonate and 5 c.c. of ammonia, the mixture is filtered, the filtrate is acidified with nitric acid, and heated to expel carbon dioxide. An excess of ammonia is then added and the boiling is continued until all the uranium has been precipitated, which is denoted by the yellow solution becoming colourless. The precipitate is collected, washed with 2% ammonium nitrate solution, ignited, and weighed as U_3O_8 .

W. P. S.

Reductions with Cadmium in Volumetric Analysis. II. W. D. TREADWELL (*Helv. Chim. Acta*, 1922, **5**, 732—743).—[With M. BLUMENTHAL.]—Uranyl salts can be titrated by first reducing to the uranous stage and titrating back with potassium permanganate (cf. A., 1921, ii, 523). When zinc is used for the reduction, the reaction tends to go beyond the uranous stage to the U''' stage and the same occurs, although to a less extent, when cadmium is used. Owing to the ease with which tervalent uranium is oxidised by air to the uranous stage, any over-reduction can be corrected by allowing the reduced solution to run from the reduction tube drop by drop into a vessel open to the air. Oxidation from the uranous to the uranyl stage by means of air depends on the degree of acidity of the solution. To prevent such oxidation, the reduction is carried out in a 3.0*N*-sulphuric acid solution. When the electrometric method of titration is used over-reduction can be ignored, as the titre is given by the distance between the two breaks in the potential curve. Titanium and uranium may be estimated together by reducing in very dilute solution and titrating electrometrically with permanganate in an atmosphere of carbon dioxide, the two breaks in the curve representing the completion of oxidation of titanous and uranous ions respectively.

[With M. STÄRKLE.]—The accuracy of the electrometric method for titrating titanium after reduction with cadmium (*loc. cit.*) was confirmed by comparison with a gravimetric method. It is shown that small quantities of titanium can be estimated accurately by this method in presence of large quantities of iron, using potassium dichromate for the titration.

[With M. HOOFT.]—Careful experiments in which every precaution was taken to exclude air during the reduction and titration with permanganate show that vanadic acid is reduced quantitatively to the V'' stage by cadmium.

[With M. DREIFUSS and A. BOSSI.]—Indigotinsulphonic acid is reduced by finely divided cadmium in 0.2 to 0.5*N*-sulphuric acid solution to the leuco-stage, and can then be accurately titrated by means of ferric chloride by the electrometric method in an atmosphere of carbon dioxide. The course of the potential curve indicates that the oxidation proceeds in two stages, probably through a quinhydrone stage. Thioindigotin and methylene-blue can be estimated in the same way. [Cf. *J. Soc. Chem. Ind.*, 1922, Nov.] E. H. R.

A Micro-method for the Estimation of Ethyl Alcohol in Blood. ERIK M. P. WIDMARK (*Biochem. Z.*, 1922, **131**, 473—484).—A method is described suitable for estimating the alcohol in a drop of blood or in larger quantities. It depends on the absorptive power for alcohol of concentrated sulphuric acid containing a known amount of dichromate. The operations are conducted in a specially designed flask to avoid mixing and contamination of the standard dichromate by organic matter, and at a temperature of 50—60°. Absorption of the alcohol is complete within two hours. The excess of dichromate is estimated, after dilution with water, by potassium iodide and thiosulphate. Blank estimations are essential features. H. K.

The Estimation of the Methyl Group in Methylated Thiolbenzenes. J. POLLAK and ANNA SPITZER (*Monatsh.*, 1922, **43**, 113—120).—The estimation of the methylthiol group by a method analogous to Zeisel's process for estimating the methoxyl group is complicated by the fact that hydrogen sulphide and methylthiol are evolved along with methyl iodide during the decomposition by hydriodic acid. The process now described consists in decomposing the substance with hydriodic acid (*d* 1.7), and passing the volatile products through a paste of red phosphorus and weakly acidified cadmium sulphate solution, to remove hydrogen sulphide, and thence into alcoholic silver nitrate. The precipitate is ignited, and the mixture of silver and silver iodide completely converted into the iodide for weighing. C. K. I.

Identification of Small Quantities of Terpeneol Hydrate in Complex Mixtures. G. DENIGÈS (*Bull. soc. pharm. Bordeaux*, 1922, **60**, 49—54).—The sample is moistened with a drop of ethyl alcohol on a glass slide, terpeneol being deposited on the edge in tufts of prismatic needles; previous sublimation between two slides may be desirable. On addition of a drop of sulphuric acid, a yellow colour is produced, passing to orange on heating. Finally, on addition of a drop of a solution containing 0.5 gram of lævulose in 25 c.c. of ethyl alcohol and 75 c.c. of water, a carmine-red coloration is developed.

CHEMICAL ABSTRACTS.

Estimation of the so-called Total Geraniol Content of Citronella Oil. A. W. K. DE JONG and A. RECLAIRE (*Perf. Essent. Oil Rec.*, 1922, **13**, 319—321).—Numerous samples of citronella oil were analysed by slightly varying methods in order to ascertain the reason for the different results often obtained by different operators. The maximum difference observed was 2·8%, the average difference 0·7%. The influence of acetic anhydride of higher percentage strength than usual (80%) was negligible, and sodium acetate dried over sulphuric acid did not give better results than the usual fused article. The method recommended is to heat 10 grams of the dry oil with 10 c.c. of 80% acetic anhydride and 2 grams of freshly fused sodium acetate for two hours. After cooling, 50 c.c. of water are added and the excess of anhydride is decomposed by warming and shaking. The acetylated oil is separated, washed with brine until neutral, and dried. About 1·5 grams are then saponified with $N/2$ -alcoholic potassium hydroxide after neutralising any residual acidity. After two hours' boiling under reflux the excess of alkali is titrated back with $N/2$ -sulphuric acid.
G. F. M.

Causse and Bonnan's Method for the Estimation of Dextrose. R. KRULL (*Pharm. Weekblad*, 1922, **59**, 1035—1039).—The unsatisfactory end-point referred to by Lemkes and Lansberg (this vol., ii, 724) is due to the fact that towards the end of the titration, when most of the cuprous oxide has been removed from the solution, dextrose is being added to a strongly alkaline solution, to which, as is well known, it is very sensitive. The abnormal course of Fehling's reaction with urine may be considered in the light of Benedict's reaction. The iodometric estimation is accurate to 0·1%.
S. I. L.

Apparatus for Facilitating the Estimation of Dextrose by Titration with Permanganate by the Mohr-Bertrand Method. J. VAN DER HAAR (*Arch. Suikerind.*, 1922, **30**, 213—216).—Precipitation is carried out in a 500 c.c. round flask, and the supernatant liquid siphoned slowly through a Soxhlet tube into an 800 c.c. bottle, the neck of which is of the same size as that of the round flask. The precipitate is washed with hot water and the washings are siphoned off. The Soxhlet tube is removed from the bottle and placed on the flask. A little ferrous ammonium sulphate solution is next run through the siphon into the Soxhlet tube and the remainder poured directly into the tube itself; the tube is rinsed, and the contents of the flask are titrated with permanganate after acidification with sulphuric acid.

CHEMICAL ABSTRACTS.

Estimation of Sucrose in Presence of Other Sugars by means of Alkaline-earth Hydroxides. A. BEHRE and A. DÜRING (*Z. Unters. Nahr. Genussm.*, 1922, **44**, 65—70).—Material containing about 20 grams of sucrose is heated with 1·2 grams of freshly burnt lime in about 50 c.c. of water for one hour at 60—80°.

Other sugars are destroyed, and the sucrose can be determined polarimetrically. A. G. P.

Flax and Kindred Fibres. I. Behaviour and Structure of Textile Fibres, and a Convenient Method of Distinguishing Flax from Hemp. C. R. NODDER (*Trans. Text. Inst.*, 1922, **13**, 161—171).—Flax and ramie fibres always twist in a clockwise direction when drying, whereas hemp and jute fibres twist in the reverse way, and cotton usually exhibits different twists in different parts of the same hair. An examination of about 100 fibres in a warm, dry room is sufficiently accurate for determining the proportion of flax and hemp in a mixture. The direction of twist is connected with the spiral, fibrillar structure of these “bast” fibres. This structure is best revealed by mounting the fibre in concentrated calcium chloride solution, tinged with iodine, and carefully compressing it by gentle pressure on the cover-slip. The fibre is easily made ten times its normal width and the spirals show as bright reddish-purple lines (the compressed parts) among brownish-yellow ones. The striations in the outer layer of flax and ramie cells form left-handed spirals, and those of hemp and jute right-handed spirals. It follows, therefore, that wetting of these fibres is accompanied by an untwisting of the fibrils which make up the outer layer of the cell-wall. The phenomena are discussed in the light of the physico-chemical properties of cellulose. J. C. W.

Rapid Estimation of Acetic and Butyric Acids in Mixtures. L. NOTENBAART (*Natuurwetenschapp. Tijdschr.*, 1921, **3**, 131—134).—After previous experimental determination of the distribution of acetic acid and butyric acid between water and toluene, the total quantity of acid present is estimated by titration with 0.04*N*-sodium hydroxide. After extraction of most of the butyric acid and a little of the acetic acid by shaking with an equal volume of toluene, the aqueous solution is again titrated.

CHEMICAL ABSTRACTS.

Adaptation of the Pentabromoacetone Method to the Estimation of Citric Acid in Urine. WILLIAM B. MCCLURE (*J. Biol. Chem.*, 1922, **53**, 357—363).—The pentabromoacetone method for the estimation of citric acid (cf. Kunz, A., 1915, ii, 595) cannot be applied directly to urine owing to the formation of other precipitates. Satisfactory results may, however, be obtained if the urine is first made alkaline with sodium hydroxide and then treated, in the cold, with animal charcoal, and if the pentabromoacetone is finally separated from small quantities of impurities by volatilisation. E. S.

Estimation of Meconic Acid in Opium. H. E. ANNETT and M. N. BOSE (*Analyst*, 1922, **47**, 387—391).—Five grams of opium are triturated with 50 c.c. of water and after keeping over-night 40—45 c.c. of the filtered liquid are treated with 6 c.c. of 50% calcium chloride solution and kept a further twenty-four hours.

The precipitate, which is almost white, consists of calcium meconate and sulphate. It is collected, washed until the washings are colourless, and dissolved in 15 c.c. of 1.25*N*-hydrochloric acid. After keeping for twenty-four hours, pure meconic acid will have separated in white, crystalline scales. It is collected, washed twice with 0.5 c.c. of water, dried over sulphuric acid, and weighed as $C_7H_4O_7 \cdot 3H_2O$. To the weight found 0.0213 gram is added, to correct for the solubility of meconic acid in 15 c.c. of 1.25*N*-hydrochloric acid. The figure obtained is multiplied by the factor depending on the amount of the aliquot portion of the solution taken for analysis, and then by the factor 10/9, to correct for the amount of meconic acid unprecipitated by calcium chloride, in order to arrive at the weight of acid in 5 grams of opium. G. F. M.

Pregl's Solution. M. BACHSTETZ (*Ber. Deut. pharm. Ges.*, 1922, **32**, 216—221).—Discrepancies between the analyses of Pregl's solution made by different observers indicate that its composition is variable in spite of assurances to the contrary given by the makers. A solution prepared by dissolving 0.0165 gram of sodium iodate and 0.65 gram of potassium iodide in 100 c.c. of water with the addition of 10 drops of *N*/10-hydrochloric acid gave very similar results to Pregl's solution when tested quantitatively for total, active, and free iodine. Its physiological and bacteriological properties were also similar to those of Pregl's solution. E. H. R.

The Sulphuric Acid Reaction for Liver Oil. H. D. RICHMOND and E. H. ENGLAND (*Analyst*, 1922, **47**, 431).—Constant results were obtained in testing cod-liver oil by the dilution method (Drummond and Watson, this vol., ii, 665) by adding 1 c.c. of the cod-liver oil to 10 c.c. of liquid paraffin (B.P.), mixing, and transferring 10 drops of the mixture to a white porcelain basin, adding 1 drop of sulphuric acid (B.P.) and stirring with a glass rod. If a transient purple colour developed, liquid paraffin was added in successive quantities of 5 c.c. until no purple coloration was given, and the dilution at which a faint transient purple was seen was recorded. If no purple was seen, successive additions of 1 c.c., 1 c.c., 2 c.c., and 5 c.c. of cod-liver oil were made. H. C. R.

Properties and Preparation of Dutch East Indies Sandal Wood Oil. A. ROJDESTWENSKY (*Perf. Essent. Oil Rec.*, 1922, **13**, 331—332).—The amount of oil obtainable from Dutch Indian sandal wood varies from 3.8—5.8%, and has the following characters: d_{20}^{25} 0.9745—0.9842, α_D^{25} —16.4 to —18.4, santalol content 93.7—98%; n_D^{25} 1.5000—1.5013, soluble in 3—4 vols. of 70% alcohol. The quantity of oil obtainable from a sample may be ascertained by distilling not more than 0.5 kilo. of shavings with water after soaking for forty-eight hours. After ten to fifteen hours, the colour of the oil begins to darken, and in twenty hours the distillation is finished. The first and last runnings do not differ greatly in properties. G. F. M.

Importance of Dimethylhydroresorcinol for Detection of Volatile Aldehydes in Body Fluids. The Identification of Formaldehyde in Urine after Administration of Hexamethylenetetramine. WILHELM STEPP (*Biochem. Z.*, 1922, **130**, 578—581).—After administration of hexamethylenetetramine to a patient with kidney disease, formaldehyde was recognised in quantity in the urine by combination with dimethylhydroresorcinol.
H. K.

A Modified Schiff's Solution. E. WERTHEIM (*J. Amer. Chem. Soc.*, 1922, **44**, 1834—1835).—Rosaniline hydrochloride (0.005 gram) is dissolved in hot water (50—100 c.c.); the solution is filtered if necessary, diluted to 300 c.c. and cooled with running water. Sodium hyposulphite (6 grams) is added to the cooled solution. The salt dissolves completely in a few minutes, after which the solution is ready for use. If it is boiled for one minute (not longer) it first becomes red and subsequently practically colourless. It may now be heated in testing for aldehydes in order to hasten the test. Used in this manner, the solution gives the aldehyde test in about half the time required for the ordinary Schiff's test, although without heating it is usually a little slower than the ordinary Schiff's solution. Special precautions in preserving the solution are unnecessary.
H. W.

Comparative Estimations of Acetone in Urine. KURT KÄDING (*Biochem. Z.*, 1922, **130**, 448—458).—A comparison has been made of various methods, suitable for clinical purposes for the estimation of acetone in urine. Scharf's method (*Med. klin.*, 1921, **36**), like Schall's method, is a modification of Legal's test and is the most suitable.
H. K.

The Characterisation of the Colouring Matter of Saffron : Its Use in Investigations Relating to Laudanum Poisoning. MARCEL GUERBET (*J. Pharm. Chim.*, 1922, **26**, 218—220).—The coloration produced by the action of concentrated sulphuric acid on crocetin may be used for the detection of the colouring matter of saffron which yields crocetin on hydrolysis. This test may be used in the case of poisoning by drugs which are coloured with saffron.
H. J. E.

A Qualitative Test for Tannin. ETHEL ATKINSON and EDITH OLIVE HAZLETON (*Biochem. J.*, 1922, **16**, 516—517).—A piece of gold-beater's skin is pinned on a surface of paraffin wax, soaked in water, and then covered with an aqueous extract of the material to be tested. After about fifteen minutes it is washed, treated with a 1% solution of ferric chloride, and again washed. If the skin is stained, the presence of tannin is indicated.
E. S.

Estimation of Indican in Blood-serum. J. SNAPPER and W. J. VAN BOMMEL VAN VLOTEN (*Klin. Woch.*, 1922, **1**, 718—721; from *Chem. Zentr.*, 1922, ii, 1122).—In the estimation of indican

in serum, a stronger reaction is given after precipitation with trichloroacetic acid than after precipitation with alcohol. The following procedure is recommended. The serum is precipitated with an equal volume of 20% trichloroacetic acid. 2.5 c.c. of the filtrate are diluted to 10 c.c. with water and after addition of 1 c.c. of thymol in alcohol (5%) and 10 c.c. of Obermayer's reagent, left for twenty minutes. The liquid is then extracted with 2 c.c. of chloroform and the reading taken after thirty minutes. With a weak positive reaction a slightly increased indicanæmia is indicated, implying hypofunction of the kidneys (niereninsuffizienz). In acute nephritis, hyperindicanæmia implies a more marked intoxication than does retention of urea alone. The principal precautions to be observed in the estimation are given.

G. W. R.

Detection of Urea in Tissue by Means of Xanthidrol.

M. BONNET and J. HAUSHALTER (*Compt. rend. Soc. Biol.*, 1922, **86**, 395—397; from *Chem. Zentr.*, 1922, ii, 922).—For the micro-chemical detection of urea, the fixation of the tissue in a 10% solution of xanthidrol in ethyl alcohol and pure acetic acid in the ratio 1 : 7 is recommended.

G. W. R.

A Reaction of Urea with *p*-Dimethylaminobenzaldehyde.

H. K. BARRENSCHEEN and O. WELTMANN (*Biochem. Z.*, 1922, **131**, 591—595).—The yellowish-green coloration obtained in dilute urine on addition of Ehrlich's aldehyde reagent is due to urea. The reaction can be used for the recognition of residual nitrogen in serum freed from proteins by trichloroacetic acid when it exceeds 36—40 mg. %.

H. K.

Accurate Ureometer. ANTONIO SCIORTINO (*Arch. Farm. speriment. Sci. aff.*, 1922, **33**, 186—189).—The modified apparatus for the estimation of carbamide described allows of the use of varying quantities of the urine, blood, etc., and of arbitrary amounts of the sodium hypobromite. Equilibrium may be established between the external and internal pressures prior to the reaction and completion of the latter assured by shaking the reaction bottle under diminished pressure. The volume of the nitrogen formed is read in a burette graduated to 0.05 c.c.

T. H. P.

The Estimation of Urea in Urine by the Hypobromite Method with Complete Yield.

(MLLE) M. JANET (*J. Pharm. Chim.*, 1922, **26**, 161—170).—Sodium hypobromite, under the usual experimental conditions, gives results which indicate only 90—92% of the actual urea present. The method described is said to be accurate within 1% when compared with results obtained by standard gravimetric methods. The solution containing urea is diluted, if necessary, so that the concentration is not much above 1% and a considerable excess of sodium hydroxide is added followed by the hypobromite. The presence of creatinine introduces a slight error; this is stated to be negligible. If ammoniacal com-

pounds are present, the whole of their combined nitrogen is liberated by the action of sodium hypobromite and sodium hydroxide so that the nitrogen due to urea is found by difference after estimating the ammonia.

H. J. E.

Electrometric Titration of Ferrocyanides. ERICH MÜLLER and HANS LAUTERBACH (*Z. anal. Chem.*, 1922, **61**, 398—403).—The end-point of the titration of ferrocyanides in sulphuric acid solution with permanganate solution may be determined accurately electrometrically in cases where the titration has to be made under artificial light; the results obtained agree with those found where the end-point is denoted by the pink coloration of the slight excess of added permanganate.

W. P. S.

A Test for Pyridine. FRIEDRICH LEHNER (*Chem. Z.*, 1922, **46**, 877).—If a few drops of aniline are added to a solution of pyridine containing water and a trace of cyanogen bromide, a red colour is immediately obtained and crystals of 2-anilinodihydropyridine phenyl bromide separate. One part of pyridine in 350,000 parts can be detected in this way.

H. C. R.

Detection of Small Quantities of Pyridine. A. GORIS and A. LARSONNEAU (*Bull. Sci. Pharmacol.*, 1921, **28**, 497—498; from *Chem. Zentr.*, 1922, ii, 731).—By addition of aniline to a solution of pyridine in the presence of cyanogen bromide, 1-anilinodihydropyridinium phenyl bromide, a red substance, is formed. The coloration is noticeable even with one drop of pyridine in 10,000 c.c. of water. This reaction takes place even in the presence of pyrrole derivatives.

G. W. R.

A Reaction of Veronal and of the Hypnotics Derived from Barbituric Acid. RENÉ FABRE (*J. Pharm. Chim.*, 1922, [vii], **26**, 241—249).—Veronal and other hypnotics of the barbituric acid series are readily condensed with xanthydrol to form crystalline dioxanthyl derivatives by heating at 100° for about one minute an approximately 10% solution of the hypnotic in acetic acid with twice its weight of xanthydrol. After keeping for a few hours, the product is separated and washed with a little boiling alcohol, and is then sufficiently pure for melting-point determination. The m. p. of the principal dioxanthylbarbituric acids are as follows: dioxanthylveronal 245—246°, dioxanthylphenylethylbarbituric acid 218—219°, and dioxanthylallylbarbituric acid 242—243°. Similar derivatives are not formed by other hypnotics, and the reaction is therefore valuable for the characterisation and identification of the barbituric acids for both pharmaceutical and toxicological purposes, as it can easily be carried out with as little as 0.01 gram of the substance, or with the crude product obtained by the usual methods in toxicological investigations from the viscera, etc.

G. F. M.

The Estimation of Uric Acid. HENRY JACKSON, jun., and WALTER W. PALMER (*J. Biol. Chem.*, 1922, **53**, 373).—A simplified

method for the preparation of the modified phosphotungstic acid reagent (this vol., ii, 328) is described. E. S.

Estimation of Uric Acid in Blood. L. BAUMAN and L. M. KEELER (*J. Lab. Clin. Med.*, 1922, 7, 551—552).—A modification of Folin and Wu's method in which calibrated Lovibond tintometer glasses replace standard uric acid solution. A red glass (0.4) is placed over the unknown solution and a blue glass (2.9) over the opposite prism in a Duboscq colorimeter; the blue compound is developed without the use of sodium sulphite. The glasses may also be used with the Bock-Benedict colorimeter if the red glass is placed over the immersion cylinder and the blue in front of and parallel to the standard cell. The method is of general application; the use of glasses shortens the time of procedure and removes uncertainty arising from the possible decomposition of the standard uric acid solution. Precipitation may be avoided by addition of three drops of a solution of gum acacia preserved with thymol.

CHEMICAL ABSTRACTS.

Estimation of Uric Acid and Urates in Blood. CH. O. GUILLAUMIN (*Compt. rend. Soc. biol.*, 1922, 86, 194—196; from *Chem. Zentr.*, 1922, iv, 111; cf. this vol., ii, 170—171).—Blood is freed from albuminous substances and a volume of the filtrate corresponding with 2 c.c. of plasma, clot, or total blood is treated with 1—2 c.c. of 0.9—1.0% sodium chloride solution and sufficient 40% sodium carbonate solution to give an alkaline reaction to litmus. Five c.c. of Folin's silver reagent are added, and, after mixing, the liquid is centrifuged. The clear liquid is removed and the precipitate treated with 2 c.c. of a solution of sodium chloride containing hydrochloric acid and 7—8 c.c. of water, and again centrifuged. The clear liquid obtained is treated with 0.5 c.c. of a solution of 2.5 grams of sodium cyanide and 5 grams of sodium sulphite in 100 c.c. of water, 1.5 c.c. of sodium carbonate solution, made up to 12.5 c.c., and, after addition of Folin and Denis's phosphotungstic acid reagent, compared with a standard uric acid solution. G. W. R.

Estimation and Constitution of a Fraction of the Uric Acid in Blood. CH. O. GUILLAUMIN (*Compt. rend. Soc. biol.*, 1922, 86, 258—260; from *Chem. Zentr.*, 1922, iv, 111; cf. preceding abstract).—Direct estimation of uric acid in serum freed from albuminous substances gives higher results than those obtained by the Folin and Denis phosphotungstate method. The difference corresponds with a portion of the uric acid of the blood which is associated with fractions of the original nuclein complex. For its estimation (by difference) the preliminary removal of albuminous substances is preferably effected by using metaphosphoric acid.

G. W. R.

The Volatilisation and Hydrolysis of Atropine in Toxicology. PAUL HARDY (*J. Pharm. Chim.*, 1922, 26, 220—226).—The author has investigated the error in estimations of atropine

due to losses by reason of volatility and hydrolysis, and finds that no loss occurs in extraction of the alkaloid, as it is not volatile in alcohol, ether, or chloroform vapour. In the case of water, atropine was detected in the distillate on boiling. Hydrolysis occurs readily in aqueous solution, increasing considerably with temperature; it is more rapid in alkaline than in neutral solution, but ammonia is not such an active hydrolytic agent as sodium hydroxide. H. J. E.

The Estimation of Creatinine. K. PFIZENMAIER and S. GALANOS (*Z. Unters. Nahr. Genussm.*, 1922, **44**, 29—41).—The method given in the *Schweizerisches Lebensmittelbuch* (3rd ed., p. 72) for the estimation of creatinine is rapid and simple, but can be successfully used only when light-coloured solutions are available for colorimetric comparison and a colorimeter of the Dubosecq type is used. If the solutions are dark in colour or contain sugar, the method fails, as animal charcoal cannot be used because it adsorbs creatinine. The colorimetric comparison in cylinders as specified in the book was found to be unsatisfactory. The method of Sudendorf and Lahrmann (*Z. Unters. Nahr. Genussm.*, 1915, **29**, 1) can always be used and is the only one available for use with dark-coloured solutions. If the authors' instructions are exactly followed and too great an excess of potassium permanganate—especially with very dark-coloured solutions—is avoided, accurate results are always obtained. The methods referred to are given in detail. H. C. R.

An Apparatus for the Extraction of Theobromine and Caffeine by means of boiling Chloroform. O. P. A. H. SCHAAF (*Pharm. Weekblad*, 1922, **59**, 920—923).—The Soxhlet extractor is modified to allow of heating by means of a water-bath. Exact dimensions and procedure are laid down (cf. *J. Soc. Chem. Ind.*, 1922, 781A). S. I. L.

Estimation of Yohimbine in Yohimba Bark. ARNOLD SCHOMER (*Pharm. Zentr.-h.*, 1922, **63**, 385—386).—In applying a method described previously (A., 1921, ii, 360) to barks containing but little yohimbine, the results obtained are more trustworthy when the crystallisation of the yohimbine hydrochloride is made in the cold. The impure hydrochloride, after treatment with 5 c.c. of ether and evaporation of this solvent, is dissolved in 3 c.c. of absolute alcohol and the solution is kept at 0° for eighteen hours. The crystals which form are collected, washed with a small quantity of chloroform, then with ether, dried at 100°, and weighed. W. P. S.

Identification of Traces of True Albumin in Urine. Separation of pseudoAlbumins. M. RENOUX (*J. pharm. Belg.*, 1922, **4**, 381—382).—As a result of tests with a solution of egg-albumin, the author concludes that either neutral crystals of sodium sulphate or magnesium sulphate may be used for the defecation of urine

(after being made alkaline), preparatory to testing for traces of true albumin.

CHEMICAL ABSTRACTS.

The Estimation of Total Albumin in the Spinal Fluid.

J. B. AYER and H. E. FOSTER (*Repert. pharm.*, 1922, **34**, 114—115).—The albumin is precipitated with thiosalicylic acid and compared with the precipitate obtained from blood serum of known albumin content. The method is very exact. The normal quantity of albumin in 100 c.c. of fluid varies between 16 and 40 mg. (average 25 mg.). It is usually increased in pathological conditions. The authors give the albumin content found in a number of cerebrospinal diseases.

CHEMICAL ABSTRACTS.

The Estimation of Albumose-Silver.

J. HERZOG (*Pharm. Z.*, 1922, **67**, 802—803).—One gram of the silver-protein is dissolved in 10 c.c. of water and 10 c.c. of concentrated sulphuric acid added in a thin stream. Two grams of finely powdered potassium permanganate are added in small portions with vigorous shaking. After fifteen minutes, the solution is diluted with 50 c.c. of water and ferrous sulphate added in small portions to decolorise the solution. The silver is then titrated with *N*/10-ammonium thiocyanate solution, the oxidised iron acting as indicator.

H. K.

The Estimation of Fibrinogen. Protein Estimations in Salt Plasma. Question of the Utility of Serum for the Quantitative Investigation of Blood.

G. LEENDERTZ and B. GROMELSKI (*Arch. exp. Path. Pharm.*, 1922, **94**, 114—123).—Indirect methods for the estimation of fibrinogen in blood are based on the fact that the fibrinogen content is equal to the difference between plasma- and serum-proteins. Since, however, serum formed by the spontaneous coagulation of blood contains water and chlorides emanating from the corpuscles, this relation only holds when the serum is obtained from separated plasma. Applications of the refractometric method to the indirect estimation of fibrinogen have not hitherto been successful when oxalate plasma has been used. Such failures have been due to two causes—the formation of a precipitate and the production of hypertonic plasma by the addition of sodium oxalate to blood. By using a 3.55% solution of sodium citrate, which is isotonic with blood and does not produce a precipitate, as anti-coagulant, the refractometric method may be readily applied. Two such methods, based on the above considerations, are described.

E. S.

Estimation of Hæmoglobin.

E. MEULENGRACHT (*Fol. hæmatol. I. Archiv*, 1921, **27**, 1—9; from *Chem. Zentr.*, 1922, ii, 849).—Observations on the working details of hæmoglobin estimations by Sahli's and by Autenrieth's methods. It is held that the former is superior to the latter for clinical work.

G. W. R.

The Colorimetric Estimation of Hæmoglobin with Especial Reference to the Production of Stable Standards. EDWIN H. TERRILL (*J. Biol. Chem.*, 1922, 53, 179—191).—Stock solutions of acid hæmatin such as those of Cohen and Smith (A., 1919, ii, 532) and Robscheit (A., 1920, ii, 339) suffer from the disadvantages that the colour both changes and fades on keeping, whilst a turbidity is produced on dilution. Two modified methods for the preparation of acid hæmatin standards are therefore described. The first results in the formation of a concentrated stock solution which may be diluted, especially when the diluting fluid contains glycerol, without the production of a turbidity; although it fades slowly, it does not change qualitatively in colour. The second gives an acid hæmatin protein powder which is quite stable in the dry state and forms clear solutions in water and in 0.1N-hydrochloric acid. After standardisation, weighed quantities may be used for the preparation of standard solutions. A method is also described for the preparation from the powder of gelatin films of acid hæmatin which may be used with advantage in place of the glass plates of Newcomer (A., 1919, ii, 179).

In estimating hæmoglobin, the laking of the blood with water prior to acidification is recommended. Direct acidification produces a turbidity which leads to high results when a clear standard is used. Heat should not be employed to develop maximum colour as this again produces a turbidity. E. S.

Estimation of Bilirubin in Blood. PAUL HOLZER and HEINZ MEHNER (*Klin. Woch.*, 1922, 1, 66).—Meulengracht's (*J. Amer. Med. Assoc.*, 1920, 74, 68) method is worthless for the estimation of small amounts of bilirubin, and untrustworthy for the estimation of large amounts. To obtain accurate results it is necessary to enhance the bilirubin colour by diazotisation; Bergh's ("Der Gallenfarbstoff im Blute," 1918) method is the most trustworthy, whilst that of Haselhorst (A., 1921, ii, 472) gives inaccurate results for small concentrations of bilirubin.

CHEMICAL ABSTRACTS.

[Detection of Bile Pigments in] Gastric Juice. FRANZ UTZ (*Süddeutsch. Apoth.-Ztg.*, 1922, 62, 77—78; from *Chem. Zentr.*, 1922, ii, 921—922).—In examination of the contents of the stomach for bile pigments, the filtrate should not be used, as the pigments are retained by the filter. Directions are given for the use of the Gmelin and Plesch tests for bile pigments and for the detection of rennin. G. W. R.

Modification of the Iodine Test for Bile Pigments in Urine. ERNST SILBERSTERN (*Zentr. inn. Med.*, 1922, 43, 185—187; from *Chem. Zentr.*, 1922, ii, 850).—The ordinary reaction is modified, whereby the urine under examination is shaken with a solution of 0.5 gram of iodine in 36 grams of ether or 76.5 grams of chloroform (1 c.c. of this solution to 2—4 c.c. of the liquid to be tested). The excess of iodine remains in its original solvent whilst the

biliverdin colours the aqueous phase. In neutral solution, the reaction is more sensitive than the Gmelin test, although less sensitive in alkaline solution. The chloroform solution is preferable to the ethereal solution.

G. W. R.

Tests for Liver Function. LEPEHNE (*Münch. Med. Woch.*, 1922, 69, 342—344; from *Chem. Zentr.*, 1922, ii, 921).—Hay's flowers of sulphur test for bile acids in duodenal juice and urine is described in application to certain pathological conditions.

G. W. R.

Estimation of the Activity of Invertase. T. SWANN HARDING (*Sugar*, 1922, 24, 89—90; from *Chem. Zentr.*, 1922, ii, 1032).—A solution of sucrose, approximately 10%, is prepared so that on addition of 5 c.c. of water to 50 c.c. of the solution a reading of $+33.5^\circ V \pm 1^\circ$ is given in Schmidt and Haensch's polarimeter. The reading being accurately determined after acidifying with acetic acid, 5 c.c. of invertase solution are added and, after keeping at 30° for ten minutes, the solution is rendered alkaline by addition of sodium carbonate solution. The change in polarimeter reading is taken as a measure of the activity of the invertase solution. Ordinary invertase solutions change the polarimeter reading from $+33.5^\circ V$ to $+23-10^\circ V$, the most active invertases giving $10^\circ V$. Invertases which diminish the reading to $+18-20^\circ V$ invert a 10% sucrose solution within half an hour.

G. W. R.

Analysis of Blood. F. UTZ (*Pharm. Zentr.-h.*, 1922, 63, 425—430).—A procedure is given for a complete examination of blood, and the methods used are described in detail. The following estimations should be made, the figures in brackets being the values obtained for normal blood: *Blood*, sp. gr. (1.050 to 1.060) and total solids (21 to 22%). *Blood-serum*, sp. gr. (1.027 to 1.032), refractive index (n_D 1.343 to 1.350), freezing point (-56°), total solids (6 to 10%), total nitrogen (1.04 to 1.2%). *Blood-serum after removal of proteins by uranium acetate*, nitrogen (0.02 to 0.035%), urea (0.02 to 0.04%), uric acid (0.0025 to 0.0035%), creatinine (0.001%), reducing sugars (0.06 to 0.12%), sodium chloride (0.56 to 0.60%), and indican (0.045 mg. per 100 c.c.).

W. P. S.

General and Physical Chemistry.

The Refractive Indices of Phosphorescent Sulphides. MAURICE CURIE (*Compt. rend.*, 1922, **175**, 617—619).—Direct determination of the refractive indices of phosphorescent sulphides gives, for yellow light, values between 2.10 and 2.15. An appreciable fraction of each substance gives figures ranging to a lower limit of 1.6, whilst for no portion did the refractive index exceed 2.20. According to the work of Lenard (*A.*, 1910, ii, 369) and Schmidt (*Ann. Physik*, 1922) the values should lie between 2.70 and 3.16, so that Lenard's interpretation of the constancy of the ratio λ/\sqrt{K} does not appear to be well founded. H. J. E.

Quantum Theory of Line Spectra. N. BOHR (*Danske Vid. Selsk. Skrifter, nat. mat. Afd.*, 1918, **4**, [8], 1—100; from *Chem. Zentr.*, 1922, iii, 221—223).—Theoretical. The author develops his quantum theory of line spectra with special reference to the hydrogen spectrum, and to the Stark and Zeeman effects.

G. W. R.

The Intensities of the Lines in the Balmer Series of Hydrogen. MASAMICHI KIMURA and MITSUHARA FUKUDA (*Mem. Coll. Sci. Kyoto*, 1922, **5**, 165—168).—The intensity distribution of the hydrogen lines in the Balmer series is greatly affected by the pressure of hydrogen. The addition of the vapours of hydriodic acid, iodine, sulphur, mercury, or sodium exerts an effect similar to that obtained on increased pressure. These gases suppress the higher members of the Balmer series and appear to exert a specific effect on the hydrogen atoms. The results on the action of iodine vapour are in disagreement with those of Holtzmark (*A.*, 1918, ii, 283).

W. E. G.

The Broadening of the Balmer Lines of Hydrogen with Pressure. E. O. HULBERT (*Astrophys. J.*, 1922, **55**, 399—405).—Experimental evidence is adduced for abandoning, as a cause which interferes with the absolute homogeneity of spectrum lines, the consideration of disturbance depending on collision with other particles, and suggesting that the principal cause of the widening of the lines is the influence of an electric field on the radiating particle (cf. Merton, *Proc. Roy. Soc.*, 1915, **92**, 322).

A. A. E.

Influence of Gases and Vapours on the Intensities of the Lines of the Secondary Spectrum of Hydrogen. MASAMICHI KIMURA and MITSUHARA FUKUDA (*Mem. Coll. Sci. Kyoto*, 1922, **5**, 153—163).—The intensities of the lines in the hydrogen secondary spectrum are modified by pressure, and the addition of gases and vapours. Increase in pressure weakens those lines in the secondary spectrum on the long wave-length side of λ 6240, and in the region

between λ 5690 and H_{β} . Between these two regions, the lines undergo selective changes in intensity. The Fulcher group I lines are relatively intense at low pressures, whilst those belonging to group II are weak. The addition of helium, mercury, or bromine to the spectrum tube produces similar changes in the intensities of the lines to those obtained on increase of pressure, although helium exerts a specific effect on some of the hydrogen lines. The suggestion is made that the hydrogen molecule can be reformed either by the combination of a positively charged molecule and an electron, or by the association of two neutral atoms, and that the two groups of lines owe their existence to the occurrence of these two distinct processes.

W. E. G.

The Continuous Spectrum of Hydrogen in the Schumann Region. E. P. LEWIS (*Physical Rev.*, 1920, **16**, 367—368; cf. *Science*, 1915, **41**, 947).—By the use of a fluorite vacuum spectrograph it has been found that the continuous spectrum of hydrogen extends with undiminished intensity well into the Schumann region. At λ 1800 it begins rather suddenly to diminish in intensity, and disappears at about λ 1750. Slightly below λ 1700, the line spectrum of hydrogen reappears, with no trace of a continuous background. Attention is directed to the fact that the continuous spectrum completely fills the region between the Balmer series and the Schumann line spectrum, with no lines whatever superimposed on it. The perfect uniformity and continuity of this spectrum make it the best background for the examination of absorption spectra (for example, of benzene) in the ultra-violet. Helium and neon give similar, although less intense, continuous spectra extending far into the ultra-violet.

A. A. E.

Identification of Air Lines in Spark Spectra from λ 5927 to λ 8683. PAUL W. MERRILL, F. L. HOPPER, and CLYDE R. KEITH (*Astrophys. J.*, 1921, **54**, 76—77).—Data have been secured (cf. *ibid.*, 1920, **51**, 211) for the chemical identification of the air lines from λ 5927 to λ 8683 in spark spectra. The spark was operated alternately in oxygen and air, and the lines due to oxygen identified. The remaining air lines, except a few argon lines, are ascribed to nitrogen.

A. A. E.

The Intensity Distribution in the β -Ray Spectra of Radium-*B* and -*C*. J. CHADWICK and C. D. ELLIS (*Proc. Camb. Phil. Soc.*, 1922, **21**, 274—280).—Two radically different views of β -ray disintegration have been put forward. That of Meitner (this vol., ii, 416) in which the entire β -ray emission of a radioactive substance consists of a series of homogeneous groups of electrons, and that of Ellis (this vol., ii, 466) according to which the disintegration electrons form a continuous spectrum. In the present paper, measurements are made of the intensity distribution in the β -ray emission of radium-*B* and -*C*, and it is shown that the continuous spectrum has a real existence, and is independent of the experimental arrangement. The five strong lines in the radium-*B* β -ray spectrum formed only one-fifth of the total emission,

the main feature of which was the continuous spectrum. The number of electrons received per second in the ionisation chamber, calculated from the observed ionisation currents, was in agreement with the number of atoms disintegrating per second at the source.

W. E. G.

The Spectrum of Radium Emanation. R. E. NYSWANDER, S. C. LIND, and R. B. MOORE (*Astrophys. J.*, 1921, **54**, 285—292).—Photographic and visual measurements were made of the spectrum of radium emanation, $\lambda\lambda$ 3982 to 7450. The relative intensities of the lines differed markedly, as a rule, from the previous observations of Watson and Royds and Rutherford; many strong lines of the one hundred and twenty previously measured were not found; of the forty-four lines obtained, nine were new. Changes of intensity with duration of the discharge were observed, some lines decreasing and some increasing in strength, whilst the colour of the discharge changed from a bright glow to violet. A modification is described of Duane's apparatus for the purification of radium emanation.

A. A. E.

The Spectrum of Neutral Helium. C. V. RAMAN (*Nature*, 1922, **110**, 700—701).—A criticism of Silberstein's attempt (this vol., ii, 674) to explain the spectrum of neutral helium on the assumption of the independence of the electrons. The view is expressed that the approximate agreements between the calculated and actual frequencies are merely fortuitous arithmetical coincidences, and a number of statements are made, based on a survey of the figures and a series of computations, in its support. The same considerations apply with even greater force in the case of lithium, when a choice of six numbers, compared with four in the case of helium, is permitted. Further, it is held that the Rydberg constant 109723 is appropriate only to the case of the ionised helium atom in which only one electron is coupled to the nucleus.

A. A. E.

The Structure of the Red Lithium Line. T. R. MERTON (*Nature*, 1922, **110**, 632).—A criticism of the views of McLennan and Ainslie (this vol., ii, 541; cf. Zeeman, A., 1913, ii, 812; *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1130; Kent, *Astrophys. J.*, 1914, **40**, 337; King, *ibid.*, 1916, **44**, 169; Takamine and Yamada, *Proc. Tokio Math. Phys. Soc.*, 1914, **7**, 339; Merton, *Proc. Roy. Soc.*, 1921, [A], **99**, 101) on the structure of the lithium line $\lambda=6708$. Under the appropriate conditions, the line appears to be a simple pair; if the four components were really two pairs due to the two isotopes, they should always appear together with an invariable intensity ratio of 1 : 16. This is not in accordance with the experimental results. Theoretical objections are also raised.

A. A. E.

The Exploded-wire Spectrum of Calcium. R. A. SAWYER and A. L. BECKER (*Physical Rev.*, 1921, **18**, 164).—By expending constant power on wires of varying mass of calcium and other elements, or varying power on wires of constant mass, spectra

have been obtained in which the relative intensities of the three calcium lines, H , K , and $\lambda 4227$, vary as in the spectra of stars of different classes. The calcium lines, particularly H and K , appear to be tremendously enhanced by the very high temperature of the explosion, since they appear more prominently in the spectra of exploded wires of other metals (in which the amount of calcium present must be very minute) than the spectra of the metals themselves.

A. A. E.

Excitation of Atoms to Light Emission by Electron Collisions. R. SEELIGER (*Z. Physik*, 1922, **11**, 197—200).—According to the Bohr theory, the passage of an electron from an initial to a final orbit is determined by the two probabilities, W and w , where W is the probability that the electron shall be raised from the normal to the initial orbit, and w is the probability of the transition from the initial to the final state. The former (W) is affected by the conditions of excitation, and according to Franck, the latter (w) should be also dependent on the external conditions. To test this point, the effect of the velocity of the exciting electrons on the intensity of certain related mercury lines has been examined. Two pairs of lines, 4916 ($3\cdot5S-2\bar{P}$) and 2857 ($3\cdot5S-2p_2$), and 2652 ($4d'-2p_2$) and 4339 ($4d'-2P$) were chosen, and the intensities of these measured in different parts of the glow-discharge. The form of the intensity curves were widely different for the individuals of both pairs, and the maxima occurred at different distances from the mercury electrode. Thus, in these cases, the probability of transition from one orbit to another is dependent on the external electric field.

W. E. G.

Mass-absorption Coefficients as a Function of Wave-length Above and Below the K X-Ray Limit of the Absorber. F. K. RICHTMYER (*Physical Rev.*, 1921, **17**, 264—265).—An extension to silver and lead, and to longer wave-lengths, of the relation between X-ray wave-lengths and the mass-absorption coefficient μ/ρ (for aluminium, copper, and molybdenum, cf. this vol., ii, 105).

A. A. E.

The Evidence Regarding the so-called “ J ” Radiation in the Characteristic X-Ray Spectra of the Elements. F. K. RICHTMYER (*Physical Rev.*, 1921, **17**, 433—434).—From an examination of the absorption of water, aluminium, copper, boron, silver, and molybdenum, the author concludes that, within 1%, there are no discontinuities in absorption suggestive of J -radiations.

A. A. E.

Absorption of X-Rays by Chromium, Manganese, and Iron. WILLIAM DUANE and HUGO FRICKE (*Physical Rev.*, 1921, **17**, 529—531).—The K critical absorption wave-lengths ($\lambda \times 10^8$ cm.) of chromium, manganese, and iron are 2.0623, 1.8893, and 1.7377, respectively. The energy changes corresponding with the critical absorption appear to be the same for iron atoms in the bi- and ter-valent conditions.

A. A. E.

The Tungsten X-Ray Spectrum with a Mica Spectrometer.

USABURO YOSHIDA and SHINSUKE TANAKA (*Mem. Coll. Sci. Kyoto*, 1922, 5, 173—178).—The arrangement is essentially that used previously (*ibid.*, 1921, 4, 343) and the grating constant was calculated from the wave-lengths of the prominent lines of the *L*-series of tungsten. With the mica spectrometer the X-ray spectrum of tungsten may be obtained up to the seventh and even to the tenth order. Eleven lines of unknown origin were detected on the photographs, but these might be due to reflection from the mica in an unknown manner. The wave-lengths of the known lines are in agreement with those given by Siegbahn within the limit of the experimental error. The existence of the line found by Overn at 1070 Å. has been confirmed. W. E. G.

Critical Potentials of the *L*-Series of Platinum.

DAVID L. WEBSTER (*Physical Rev.*, 1920, 15, 238).—The *L*-series must be regarded as consisting of three sub-series, L_1 (containing the lines l , α_2 , α_1 , β_2 , β_5 , and β_6), L_2 (containing the lines η , β_4 , β_1 , γ_1 , γ_2 , and possibly β_3), and L_3 (containing the lines γ_4 , γ_3 , and possibly β_3). A. A. E.

Temperature Shift in Near Ultra-red Bands.

H. M. RANDALL, W. F. COLBY, and R. F. PATON (*Physical Rev.*, 1920, 15, 541—543; cf. Randall and Imes, A., 1920, ii, 570; Colby, A., 1920, ii, 655).—Curves are given showing the absorption of hydrogen chloride in the neighbourhood of $3.4\ \mu$ at 20° , 105° , and 250° . It appears that in spite of the outward shift of intensity to higher velocity values, no shift takes place in the fine structure. Further investigations at higher temperatures are in progress. A. A. E.

The Labile Nature of the Halogen Atom in Organic Compounds. VII. Absorption Spectra of the Halogen Derivatives of some Cyclic Compounds, and their Bearing on the Question of an Oxygen-Halogen Linking. HUGH GRAHAM and ALEXANDER KILLEN MACBETH (*T.*, 1922, 121, 2601—2608).

Carbon Dioxide Absorption in the near Ultra-red.

E. F. BARKER (*Astrophys. J.*, 1922, 55, 391—398).—New absorption curves have been obtained. The $2.7\ \mu$ region, previously considered to be a doublet, proves to be a pair of doublets, with centres at $2.694\ \mu$ and $2.767\ \mu$ (approx.). The $4.3\ \mu$ band appears as a single doublet with centre at $4.253\ \mu$. The frequency difference between maxima is nearly the same for each of the three doublets, and equal to 4.5×10^{11} . Complete resolution of the band series was not effected, but there is evidently a complicated structure, with a "head" in each case on the side of shorter wave-lengths. If a linear configuration of the three atoms in the molecule of carbon dioxide is assumed, the moment of inertia of the molecule, computed from the doublet frequency difference, is 50×10^{-40} . This gives the distance of the central carbon atom from each oxygen atom as 0.97×10^{-8} cm. Since the linear molecule could have only three modes of vibration, it is suggested that the two doublets

at $2.7\ \mu$ may correspond with two successive changes in stationary state for the same vibration. A. A. E.

Absorption of Light by Inorganic Salts. E. F. GEORGE (*Diss., Ohio*, 1920).—The change in absorption produced by mixing sulphates in solution with other sulphates is small in comparison with corresponding changes in nitrates, and still smaller than in the case of chlorides. The influence of temperature on the absorption of solutions of mixed salts is greatest with chlorides. It therefore appears that Ostwald's view that the coloured ion alone is effective in the absorption of light is not well founded. When the ratio of the absorption of the mixture to the sum of the absorptions of the component parts is plotted as a function of the wavelength, the resulting curve generally shows a minimum near the middle of the spectrum. Many of the curves are shown to be exponential in form. CHEMICAL ABSTRACTS.

The Absorption Spectra of *o*-Cresolsulphonphthalein. W. R. ORNDORFF, R. C. GIBBS, M. SCOTT, and S. D. JACKSON (*Physical Rev.*, 1921, **17**, 437).—*o*-Cresolsulphonphthalein and other related compounds have in neutral aqueous solutions two absorption bands which are modified or replaced by new bands on the addition of acid or alkali. In the case of a dilute alkaline solution, the new type of absorption is not stable, but reverts to the two band absorption found in the corresponding neutral solution. It is considered that in neutral aqueous solutions the carbinol and hydrate forms of the phthalein are present and that on the addition of either acid or alkali a salt having a quinoid structure is formed. A. A. E.

Flame Excitation of Luminescence. E. L. NICHOLS and D. T. WILBER (*Physical Rev.*, 1921, **17**, 453—468).—The fluorescence developed by certain substances, notably lime, zirconia, magnesia, silica, alumina, zinc oxide, some phosphorescent sulphides, and a number of other compounds, by contact with a hydrogen flame, differs from photoluminescence and from mere temperature radiation. A definite temperature-range exists for each substance, and the effect does not appear to depend on the presence of traces of activating elements. Many substances which are strongly luminescent under the action of light do not respond to flame excitation. Excitation does not occur by heating in air or hydrogen or in a vacuum, or by contact with a jet of hydrogen while hot unless the hydrogen is ignited and conditions are favourable for free oxidation. The effect probably cannot be ascribed to the presence of H or H_3 molecules. The spectra obtained by flame excitation have been examined. A. A. E.

Chemoluminescence. I. A. A. GRINBERG (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 151—185).—A summary is given of previous work on this subject, particularly on bioluminescence (cf. Radziszewski, A., 1877, ii, 345; Lenard and Wolf, A., 1888, 1000; Trautz, A., 1905, ii, 662; Trautz and Schorigin, A., 1905, ii, 494; Dubois, A., 1913, i, 1021; Harvey, A., 1917, i, 365; ii, 436; Goss, A., 1917, ii, 436). The light effect obtained with the system, pyro-

gallol-hydrogen peroxide-potassium permanganate under various conditions has been investigated, the intensity of the light being measured photographically. At 16–17° the greatest intensity was obtained with a mixture of 4 c.c. of 0.005*M*-potassium permanganate, 2 c.c. of 0.01*M*-pyrogallol, and 2 c.c. of 3–12% hydrogen peroxide solutions. Sulphuric acid in the concentration 0.018–0.04% weakens the effect considerably, whilst 0.0046–0.026% of potassium hydroxide enhances it to a slight extent. T. H. P.

Mutarotation. I. C. N. RIIBER (*Ber.*, 1922, 55, [B], 3132–3143).—The data with regard to the relationship of mutarotation to other physical changes in solution are very scanty and exhibit considerable discrepancies among themselves. The changes in refractive index and volume of a solution containing a substance undergoing mutarotation have now been studied.

The index of refraction of an aqueous solution of dextrose does not appear to vary when the ordinary Pulfrich refractometer is used, but the instrument is scarcely suitable for the purpose owing to the impossibility of maintaining the requisite degree of constancy in temperature. By means of a Hallwachs's prism, it can, however, be shown that the refractive index increases slightly with age in the case of dextrose solutions and that the change occurs with immeasurably greater rapidity when a little ammonia is added to the solution. The method, however, does not lend itself to the periodical observation of the action and attention has therefore been directed to the measurements of alteration of volume in the solution. The dilatometer employed resembles essentially a Sprengel pycnometer. One tube is firmly closed by a small rubber plate and the change in volume of the solution is indicated by the movement of the meniscus in the other limb and measured by means of a microscope. A movement of 0.005 mm. can be detected with certainty; this corresponds with an alteration in volume of less than 0.0000001. The capacity of the instrument is 66.7 c.c. The temperature is maintained constant to within 0.001°. It is thus shown that solutions of dextrose in water increase in volume during the process of mutarotation at a rate corresponding with that required for a unimolecular, irreversible reaction but subsequent observations prove that in reality a state of equilibrium is finally attained and indicate that water possibly takes some part in the change. The quantitative parallelism between mutarotation and change of volume makes it certain that the two phenomena have a common cause.

A solution of lactose the optical activity of which diminishes progressively shows a gradual expansion, whereas a contraction is observed with a solution of maltose with increase of specific rotation. Galactose solution suffers a primary expansion and a subsequent contraction. Solutions of sucrose and mannitol which do not exhibit mutarotation are constant in volume. Solutions of the optically inactive dulcitol do not undergo change in volume. Acetaldehyde, in 30 per cent. aqueous solution, exhibits a considerable expansion, whereas acetone under similar conditions gives

a marked and rapid contraction. Ethyl alcohol gives a slight expansion.

The applicability of the dilatometer just described is not restricted to reactions involving mutarotation, but since changes in volume are probably involved in all chemical reactions, it can be used for the investigation of processes taking place at the ordinary temperature. The accuracy of the procedure is at least as great as that of the polarimetric or refractometric method and it has the great advantage that it does not necessitate the use of transparent and colourless solution. It has been found very useful in the study of the inversion of sugar by invertin and the saccharification of starch by ptyalin; in each case a marked contraction takes place as is to be expected.

H. W.

Photochemistry of Chlorine Detonating Gas. FRITZ WEIGERT and KARL KELLERMANN (*Sitzungsber. Preuss. Akad. Wiss. Berlin*, 1922, **24**, 315—320).—The early stages of the combination of hydrogen and chlorine have been investigated. It is shown that a characteristic streaky appearance is visible in the gas mixture during the time $1/100$ — $1/20$ second from the moment of excitation. A vanishingly small quantity of hydrogen chloride only is formed directly by the radiation, but this is followed by a large subsequent formation. From this result, the authors show that the primary reaction, contrary to many previous assertions, in all probability is in keeping with Einstein's photochemical equivalent law.

J. F. S.

Photochemical Oxidation of Hydriodic Acid. CHR. WINTHER (*K. Danske Vid. Medd. Math.-fys. Medd.*, 1920, **2**, No. 2, 1—28; from *Chem. Zentr.*, 1922, iii, 592).—In the oxidation of hydriodic acid solutions in thin films, the velocity of reaction was measured at the beginning and also in the course of the reaction. The effect of shaking, oxygen concentration, and wave-length of light was also investigated. With vigorous shaking, the reaction shows an increase in velocity during an induction period and then remains constant. The sensitiveness of the oxidative process to light is proportional to the absorption of tri-iodide-ion which acts as an optical catalyst. This is an example of "optical autosensibilisation" where the catalyst is actually formed by the reaction which it catalyses. The oxidation of leuco-compounds to dyes, the oxidation of pyrogallol in alkaline solution, and the oxidation of sodium sulphide in aqueous solution are similarly catalysed.

G. W. R.

Photochemical Efficiency of Absorbed Radiation. CHR. WINTHER (*K. Danske Vid. Medd. Math.-fys. Medd.*, 1920, **2**, No. 3, 1—35; from *Chem. Zentr.*, 1922, iii, 592—593).—The amount of energy absorbed in the photochemical oxidation of a certain amount of hydrogen iodide was found to be identical with the amount calculated as necessary for its activation. The absorbed energy is thus used exclusively for the activation of the hydrogen iodide molecule. The equivalence of absorbed energy and energy required

for activation is enunciated as a general principle in photochemical reactions. Certain consequences of this principle are discussed. Discrepancies are attributed to experimental errors or to the conversion of the absorbed radiation into radiation of shorter wave-length.

G. W. R.

The Decomposition of Hydrogen Molecules by Excited Mercury Atoms. G. CARIO and J. FRANCK (*Z. Physik*, 1922, **21**, 161—166).—On the collision of excited atoms with other atoms, the quantum energy may be given up without light emission (cf. Franck, this vol., ii, 464), and chemical change may take place. On exposing a mixture of hydrogen and mercury to the mercury line $2536\cdot7 \text{ \AA.}$, the radiation was strongly absorbed, and the hydrogen dissociated. Powdered copper oxide was reduced, and the pressure of the hydrogen continuously decreased at a temperature of 45° . In the absence of hydrogen and mercury, no reduction occurred. The mercury is acting as a sensitiser. In the absence of copper oxide, the atomic hydrogen is adsorbed by the walls. At low pressures, the velocity of dissociation was very slow, and this behaviour indicates a short period of activity of the mercury atoms. The velocity of reaction increases up to 15 mm. pressure and then remains constant. Tungsten trioxide is also reduced, and the reduction is not in any way due to illumination by the light. Since tungsten oxide is not reduced by hydrogen below a red heat, it is unlikely that the phenomenon is caused by rapidly moving hydrogen molecules.

The hydrogen is dissociated by mercury atoms which are in the $2p_2$ condition. Calculations show that the upper limit for the heat of dissociation of hydrogen is 112 Cal.

W. E. G.

Photoelectric Effect of Alkali [Metal] Vapours and a New Determination of h . E. H. WILLIAMS and JAKOB KUNZ (*Physical Rev.*, 1920, **15**, 550).—The resonance potential of caesium vapour is 1.48 volts, whilst the ionisation potential is 3.9 volts. If the same amount of work is required for the breaking up of a neutral caesium atom by light as by moving electrons, then the long wave-length limit of the photoelectric effect of caesium vapour should be $l=318\cdot4 \mu\mu$, according to the equation $hn=eV$. If this is found to be the case, then (1) the long wave-length limit is quite different for caesium metal and for caesium vapour, and (2) a new photoelectric method for the determination of h is available. Experimentally, there is no photoelectric effect in caesium vapour down to $313 \mu\mu$, but the effect at $253 \mu\mu$ is very marked.

A. A. E.

The Photoelectric Long Wave-length Limit of Platinum and Silver. OTTO STUHLMAN, jun. (*Physical Rev.*, 1920, **15**, 549—550; cf. *ibid.*, 1919, **13**, 109).—The photoelectric long wave-length limits of platinum and silver are $\lambda_0=284 \mu\mu$ and $\lambda_0=325 \mu\mu$, respectively.

A. A. E.

Soft X-Rays of Characteristic Type. E. H. KURTH (*Physical Rev.*, 1921, **17**, 528—529; **18**, 99—100).—The radiation curve of

aluminium shows breaks at 38 and 120 volts, corresponding with 326 Å.U. (possibly the *M*-series) and 103 Å.U. (possibly the *L*-series), respectively. For iron, 62.8 Å.U. and 48.4 Å.U. appear to represent the extremes of the *M*-series, whilst 16.3 Å.U. probably corresponds with the *L*-series. There was also some indication of a break in the curve at 50 volts, corresponding with 247 Å.U. Carbon yields a pronounced break at 43.6 Å.U., agreeing with the extrapolated value for the *K* series. The following approximate figures (Å.U.) are also recorded: *K*-series: carbon, 42.6; oxygen, 23.8. *L*-series: carbon, 375; oxygen, 248; iron, 16.3; copper, 12.3. *M*-series: iron, 54.3; copper, 41.6. *N*-series: iron, 247; copper, 119. A. A. E.

Absorption of X-Rays in Crystals. TYCHO E:SON AURÉN (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, 4, No. 10, 1—6).—It has been shown in a previous paper (A., 1921, ii, 367) that, in the case of amorphous substances, the molecular absorption coefficient can be calculated as a sum of the atomic absorption coefficients for X-rays of the constituent elements. It is now shown that the same holds true for a number of crystalline substances, including alum, calcite, and gypsum. The observed absorption coefficients agreed with considerable accuracy with those calculated from the atomic absorption coefficients derived from a study of amorphous substances, and the absorption showed no variation in different directions in the crystals. In the cases of rock salt and sylvine an abnormally low absorption was observed when the incident rays were parallel to the principal planes of the crystal. This effect, which is probably due to scattering, becomes less marked as the angle between the direction of the incident rays and the principal structural planes is increased. E. H. R.

The Durability of Radium Solutions. AUG. BECKER (*Z. anorg. Chem.*, 1922, 124, 143—152).—The permanency of the radium solution is defined as its constancy in emitting emanation. The author found that solutions containing from 0.02 to 0.0000005 mg. radium per gram solvent did not show any decay in eight years. The possible experimental error was 1%. W. T.

Electric Furnace Experiments involving Ionisation Phenomena. ARTHUR S. KING (*Astrophys. J.*, 1922, 55, 380—390; cf. Saha, A., 1920, ii, 457, 659; 1921, ii, 4, 162; *Proc. Roy. Soc.*, 1921, [A], 99, 135).—Results are obtained which verify certain predictions due to Saha. It is shown that the intensity of the enhanced lines of alkaline-earth metals is decreased by the presence of the more easily ionised potassium and caesium. The results with mixed gases are such as would be expected if it is assumed, with Saha, that flame and enhanced lines are associated with neutral and ionised atoms, respectively. A. A. E.

Thermal Ionisation of Gaseous Elements at High Temperatures. Confirmation of Saha's Theory. ARTHUR A. NOYES and H. A. WILSON (*Proc. Nat. Acad. Sci.*, 1922, 8, 303—307).—On the basis of Saha's hypothesis (A., 1920, ii, 659; 1921,

ii, 162), the authors show that the constant, K , of the reaction $M = M^+ + e^-$ can be calculated by means of the formula $\log k = -5048V/T + 2.5 \log T - 6.56$, where V is the ionisation potential and T the absolute temperature. From some earlier experiments of Wilson on the conductivity of salts in flames, it is possible to calculate approximately the value of K (A., 1916, ii, 72). These values have been calculated for the case of salts of the alkali metals and the value of $K \times 10^{12}$ obtained both by means of the above formula and Wilson's experiments. The values in brackets are obtained by the formula, caesium 3500 (8200), rubidium 780 (1600), potassium 430 (620), sodium 5.6 (6.2), and lithium 0.8 (1.4). The two sets of values are comparable and of the same order, and this is taken as a confirmation of Saha's hypothesis. From these ionisation constants, it is possible to calculate the degree of ionisation of an element into an electron and an ion. J. F. S.

Resonance and Ionisation Potentials of Helium. J. FRANCK (*Z. Physik.*, 1922, **11**, 155—160).—A theoretical paper. The lines in the parhelium spectrum discovered by Lyman (this vol., ii, 674) throw light on the relationship between the resonance and ionisation potentials, and the structure of the helium atom. The potentials calculated from the lines in this spectrum are in agreement with the experimental results of Franck and Knipping (A., 1920, ii, 72) and Horton and Davies (A., 1921, ii, 672), if 0.8 volt be subtracted from these values. It is not possible that this divergence is due to error of observation. Reasons are advanced to show that the first break in the curve corresponds with the change 0.5S—1.5s, and the second with two successive changes, 0.5S—1.5S+0.5S—1.5s. The difference is 0.5S—1.5S, and not 0.5S—1.5s as has been assumed. This accounts for the difference of 0.8 volt.

The resonance and ionisation potentials of other gases, which are based on those of helium, must be reduced by this amount, and the following ionisation potentials are obtained after making this correction: H_2 , 16.4 ± 0.25 , 29.7 ± 0.4 ; N_2 , 17.05 ± 0.3 , 24.7 , 30.0 ; HI , 12.7 ; HBr , 13.3 ; HCl , 13.7 ; HCN , 14.8 . W. E. G.

Spectroscopic Investigation of the Ionisation of Argon by Electron Collisions. F. HORTON and ANN CATHERINE DAVIES (*Proc. Roy. Soc.*, 1922, [A], **102**, 131—150).—The authors' previous determinations of the resonance radiation, 11.5 volts, and ionisation, 15.1 volts, of argon (cf. A., 1920, ii, 215) have been confirmed by both spectroscopic investigation and current-voltage curves. The apparatus used resembles that developed in their experiments with neon (cf. A., 1921, ii, 422). The brighter red lines of the argon spectrum appeared simultaneously, at a point a few volts higher than the ionisation voltage. The first visibility of the lines is accompanied by a sharp increase in the current which is due to the neutralisation of the space charge of the emitted electrons near the filament. On reducing the voltage the lines persist to an extent which depends on the electron current. At moderate gas pressures, the difference between the voltages of

appearance and disappearance of the lines sometimes amounted to 11 volts. On decreasing the voltage from about 25 volts, the lines in the "red spectrum," λ 4510.9, λ 4345.3, λ 4272.3, undergo a marked enhancement in the region of 19 to 16 volts. The intensity of the bright lines λ 7067.5 and λ 6965.8 decreases continuously in brightness as the voltage is lowered. The "blue spectrum" requires for its stimulation higher potential differences across the tube. At 19 volts, the lines λ 4430.4 and λ 4426.2 become visible, and with increasing voltage the intensity increases up to 24 volts and remains stationary until 34 volts, when the intensity again rapidly increases. The break at 19 volts corresponds with the removal of a second electron from an already ionised atom, and that at 34 volts with the double ionising voltage of the argon atom. The difference between the two values gives the normal ionising voltage. From a consideration of the minimum voltages at which the "blue spectrum" lines could be detected, it is shown that the Stark classification of the helium lines into "bivalent" and "tervalent" is inaccurate. The ionisation voltage is related to one of the *M* X-ray absorption limits of the elements in a manner analogous to that in which the helium ionisation voltage is related to the *K* absorption limits, and the neon ionisation voltage to the *L* absorption limits.

W. E. G.

Luminous Discharge in Hydrogen and Mercury and a New Method of Measuring Ionisation Potentials. GEORGE E. GIBSON and W. ALBERT NOYES, jun. (*J. Amer. Chem. Soc.*, 1922, **44**, 2091—2106).—The authors have examined the conditions of stability of the luminous discharge in hydrogen and mercury, and the variation of the potential, E_a , at which the luminous discharge vanishes, with changes of pressure. To explain the phenomena observed, they put forward the hypothesis that the potential gradient in the portion of the tube between the cathode and the place where ionisation first occurs diminishes as the pressure is decreased until at the minimum of E_a the potential drop in this region has fallen to a very low value, not more than a few tenths of a volt in the shorter tubes or more than about a volt in the longest tubes measured. At the higher pressures, ionisation occurs at regions intermediate in position between the anode and cathode, and as the pressure is diminished these regions recede from the cathode until at the minimum of E_a ionisation occurs only in the immediate neighbourhood of the anode. It is shown that the voltage at which the luminous discharge in hydrogen disappears in tubes furnished with heated tungsten cathodes is a function of the pressure for a given tube passing through a minimum value which is usually a simple multiple of the ionisation potential, 30.9 ± 0.4 volts. In mercury vapour the disappearance voltage of the luminous discharge is a simple integral multiple of the ionisation potential, 10.7 ± 0.4 volts.

J. F. S.

Electrical Conductivity of Hydrochloric Acid and Potassium Chloride in Presence of Sucrose. ARTHUR JOSEPH KIERAN (*Trans. Faraday Soc.*, 1922, **18**, 119—125).—Experimental deter-

minations have been made of the electrical conductivities at 25° of solutions of hydrochloric acid of concentrations ranging from 0.05*N* to 0.0005*N* in the presence of 5%, 10%, and 20% of sucrose. Similar determinations were made with potassium chloride solutions ranging from 0.01*N* to 0.0005*N* in the presence of 10% of sucrose. In the latter case, the equivalent conductivity increased normally with increasing dilution, to an asymptotic limit. In the case of hydrochloric acid solutions, however, the behaviour was abnormal, the equivalent conductivity passing through a maximum in the region $N/300$ — $N/500$, dependent on the concentration of the sucrose, and thereafter steadily decreasing with increasing dilution. This abnormality was traced to the presence of minute traces of an electrolytic impurity (probably an organic salt of calcium) in all samples of sucrose. Values of m in the relation $\Lambda = \Lambda' \eta^m$, in which Λ and Λ' are respectively the equivalent conductivities in media of unit viscosity and of viscosity η , have been determined as follows: hydrochloric acid and sucrose, 0.57; hydrochloric acid and dextrose, 0.68; potassium chloride and sucrose, dextrose, and glycerol, respectively, 0.73, 0.77, and 0.92. The results confirm the conclusion of Kraus (A., 1914, ii, 90) that m approaches the value unity as the molecules of the medium become smaller in size and the larger the size of the ions of the electrolyte.

J. S. G. T.

Conductivity of Sodium Iodide in Amyl Alcohol at very Low Concentrations. CHARLES A. KRAUS and J. EGBERT BISHOP (*J. Amer. Chem. Soc.*, 1922, **44**, 2206—2212).—Exceedingly pure amyl alcohol may be prepared, as follows: ordinary amyl alcohol was submitted to an initial fractionation and the portion boiling above 130° dehydrated over quicklime, after which it was redistilled. The product was treated with a small amount of sodium and the resulting solution repeated fractionated. In this way, amyl alcohol with a specific conductivity of 2×10^{-8} was obtained and by effecting the fractionation under reduced pressure the specific conductivity became 1×10^{-8} . Solutions made up in this product were not stable, but if the alcohol was subjected to fractional condensation under reduced pressure and the distillate collected in the conductivity cell a product with specific conductivity 1.4×10^{-9} was obtained and solutions made up in this were very stable; solutions of sodium iodide in this specially prepared amyl alcohol did not vary more than 0.1% in fourteen hours. The electrical conductivity of solutions of sodium iodide in amyl alcohol was measured at 18° for concentrations ranging between $1.0 \times 10^{-5}N$ to $17 \times 10^{-5}N$. The mean variation of the results does not exceed 0.1%. In the more dilute solutions, the points conform to the requirements of the law of mass action within the limits of the experimental error. At the higher concentrations there is a small although constant deviation from the mass action relation. From an extrapolation of the curve to zero concentration the value 11.059 is obtained for Λ_0 and the value 2.933×10^{-4} for K .

J. F. S.

Variation of the Electrical Conductivity among the Ammoniacal Derivatives of Platinous Nitrite. L. A. TSCHUGAEV and N. A. VLADIMIROV (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 135—138).—The values of Λ_{1000} for tetra-amminoplatinous nitrite, $[\text{Pt}4\text{NH}_3](\text{NO}_2)_2$; nitrotri-amminoplatinous nitrite,



cis- and *trans*-dinitrodiamminoplatinum, $[(\text{NO}_2)_2\text{Pt}(\text{NH}_3)_2]$; and potassium platinonitrite are found to be, respectively, 276.5, 96.5, 0.95, 2.42, and 302.4. The observed value of Λ_{2000} for nitrotri-amminoplatinous platinonitrite, $[\text{NO}_2\text{Pt}3\text{NH}_3]_2\text{Pt}(\text{NO}_2)_4$, is 217, the value calculated by summation of the mobilities of the corresponding ions being 197.2 (cf. Tschugaev and Kiltinovitsch, T., 1916, **109**, 1286). T. H. P.

Passivity and Over-potential. ULICK R. EVANS (*Trans. Faraday Soc.*, 1922, **18**, 1—13).—It is suggested that the relative values of the interfacial tensions between the metal, corrosion product, and solution is the factor on which the protection against corrosion of the metal by the solution depends. The activation of passive metals by chlorides is related to the peptising action of metallic hydroxides by chlorides; the rendering passive by chromates is correlated with the flocculating action of these salts. The protective layer probably consists of a layer of oxygen atoms connecting the metal on the one side with solution on the other. Similarly, at a cathodically polarised electrode a layer of hydrogen nuclei connect the metal with the liquid, the hydrogen being probably in a state intermediate between the elementary and ionic forms. The theory is, in some respects, opposed to that of Friend (T., 1922, **119**, 932). J. S. G. T.

Chemical Passivity of Metals. J. GILLIS (*Natuurwetenschapp. Tijdschr.*, 1921, **3**, 66—68).—The phenomena of passivity may not be explained by the formation of an oxide membrane protecting the metal. The most accurate optical methods—which permit estimation of a layer of $0.8\ \mu\mu$ —fail to detect any sign of an oxide membrane. On the other hand, the metals which become passive by anodic polarisation are also those the ions of which do not readily discharge and precipitate on the cathode. There is, therefore, a co-existence of the anodic retardation (passivity) and of the cathodic retardation (slow metallic precipitation); the transformation $\text{M}^+ \rightleftharpoons \text{M} + \oplus$ is slow in both directions.

CHEMICAL ABSTRACTS.

Thermo-electric Force, the Entropy of Electrons and the Specific Heat of Metals at High Temperatures. WENDELL M. LATIMER (*J. Amer. Chem. Soc.*, 1922, **44**, 2136—2147).—A theoretical paper in which the thermo-electric force of a circuit of two metals has been expressed in terms of the entropy of the electrons in the two metals. This expression has the form

$$dE/dT = \int_0^T \sigma_2 \cdot dT/T - \int_0^T \sigma_1 \cdot dT/T$$

where σ_1 and σ_2 are the specific heats of the electrons of the two

metals. It has been postulated that the specific heat of a gram-molecule of electrons in a metal is given by the increase in the specific heat at constant volume of a gram-molecule of the metal above the equipartition value of $6/2R$. On this assumption, the absolute value of the thermo-electric force of the potassium sodium couple has been calculated at 25° from values of the specific heats of these metals. The changes in thermo-electric force of platinum, iron, cobalt, nickel, gold, copper, tungsten, molybdenum, calcium, aluminium, magnesium, and lead against silver have been calculated from specific heat data for temperature differences of 100° to 700° . Satisfactory agreement is obtained between the calculated and observed values. To make these calculations, the existing data on the thermo-electric force have been collected; new data for the thermo-electric force of lead, zinc, magnesium, aluminium, molybdenum, and tungsten against silver have been obtained, and these are summarised in a thermo-electric diagram. The entropy of the metal electrons at low temperatures has been discussed and the possibility of using thermo-electric data as a means of determining C_v for metals at higher temperatures pointed out. The C_v curves for cobalt, iron, calcium, nickel, palladium, aluminium, platinum, lead, magnesium, iridium, gold, copper, silver, molybdenum, and tungsten have been drawn in agreement with existing thermo-electric data. J. F. S.

Thermochemistry and Electromotive Force in Electric Elements. JARL A. WASASTJERNA (*Monograph, Helsingfors, 1918*).—A systematic, mathematical study of representative types of electrolytic cells, the *E.M.F.* being derived from the reaction energy and the affinity. The following results are recorded for the various cells, for the reaction energy, U , the affinity, A , and the electromotive force, E , respectively, the subscript figures representing absolute temperatures: (1) $\text{Cu}|\text{saturated solution CuI}|\text{I crystals}$; U_0 16296; A_{293} 15908; E_{293} 0.69. (2) $\text{Cd}|\text{saturated solution CdI}_2, -\text{Hg}_2\text{I}_2 \text{ paste}|\text{Hg}$; U_0 20856; A_{234} 20485; E 0.45. (3) $\text{Cu amalgam 10\%}|\text{saturated solution CuSO}_4, 5\text{H}_2\text{O}, -\text{Hg}_2\text{SO}_4 \text{ paste}|\text{Hg}$; U_{293} 25745; A_{293} 16560; E_{293} 0.353. (4) $\text{H}_2|0.1N\text{-HCl}|\text{Cl}_2$; E_{298} 1.38. (5) $\text{Pb}|\text{saturated solution PbCl}_2|\text{Cl}_2$; E_{291} 1.58. (6) $\text{H}_2|\text{equivalent weights of FeCl}_3 \text{ and FeCl}_2 \text{ in } 0.1N\text{-HCl}|\text{Pt}$; A 3480 and 5220; E_{293} 0.42 and 0.46. (7) Daniell element with saturated solutions of $\text{CuSO}_4, 5\text{H}_2\text{O}$ and $\text{ZnSO}_4, 7\text{H}_2\text{O}$; U_{291} 52045; A_{291} 49488 (subtract 220 cal. for osmotic work); E_{291} 1.69. (8) Daniell element with water as $100\text{H}_2\text{O}$; U_0 50350; A_{290} 50600; E 1.098. Cells delivering electrical energy, but without thermal changes, are considered, but no data are given. Values obtained for the Clark element are: U_0 67310; A_{288} 66218 (subtract 295 cal. for osmotic work); E_{288} 1.43.

CHEMICAL ABSTRACTS.

Complex Ion Formation in Hydrochloric Acid. RALPH M. HIXON (*Medd. K. Vetenskapsakad. Nobel-Inst., 1922, 4, No. 12, 1—8*).—If complex acids of the type H_2CaCl_4 exist in solutions of metallic chlorides in hydrochloric acid solution, a study of the

migration of the metallic ion when such solutions are electrolysed should reveal their presence. Solutions of magnesium, calcium, barium, and zinc chlorides at different concentrations in concentrated hydrochloric acid were electrolysed for six to eight hours at 12 volts, and samples of anolyte and catholyte were analysed. The solutions of magnesium and calcium chlorides both showed migration of the metal towards the anode at medium concentrations, but towards the cathode at higher and lower concentrations. The migration towards the anode is strong evidence for the existence of complex ions of the type $(\text{CaCl}_2)_y\text{Cl}_x^-$. The observed migration will depend on the relative concentrations of these complex ions and of the simple ions Ca^{++} , as well as on their migration velocities. At low concentrations, Ca^{++} will predominate. At concentrations of $[\text{CaCl}_2]$ approaching saturation, Ca^{++} may again predominate owing either to the decrease in the $[\text{HCl}]$ concentration or to the formation of a more complex acid $(\text{HCl})_x(\text{CaCl}_2)_y$ which would be less dissociated than the simpler acid formed at medium concentrations.

E. H. R.

The Hydration of the Lithium-ion. J. BABOROVSKY and J. VELISEK (*Chem. Listy*, 1922, **16**, 250—256).—A new apparatus suitable for determining the transport numbers and hydration of ions, consists of two membranes of parchment paper separating the central portion of the solution from the anodic and cathodic portions and also of an arrangement whereby the anodic and cathodic vessels can be disconnected and weighed with their contents. The hydration of the lithium-ion was calculated from the change in weights and in concentrations of the solutions around the electrodes. The determination of the hydration of ions by this method is complicated by electro-osmosis. This the authors claim to have measured by replacing the two parchment paper membranes by a single membrane and estimating the differences in the concentration and specific gravity of the central portion after each experiment. The lithium-ion has one more molecule of water of hydration than the chlorine-ion. The transport number of lithium in a decinormal solution of its chloride is 0.3128 ± 0.0048 . The authors propose that the hydration of ions should be expressed in terms relative to that of the hydrogen-ion (the most mobile of all) which would be put equal to zero.

W. T.

Electrolysis with Drops of Mercury as the Electrode. J. HEYROVSKY (*Chem. Listy*, 1922, **16**, 256—264).—To study the electrolysis of aqueous solutions of the alkali and alkaline-earth metals, the author employed drops of mercury as the electrode; the apparatus is figured. This enabled him to determine the exact course of the electrolysis. Electrolysis is produced when a certain *E.M.F.* is applied the value of which is characteristic of each salt and depends on the logarithm of the concentration. The rapid increase of the current is explained by a diffusion towards the interior of the drop of mercury of very dilute amalgams. This diffusion commences because the metal has not sufficient mercury for combination. The author calculated the potential at which

the kations deposit from their normal solutions on a mercury cathode: lithium, -2.023 ; sodium, -1.860 ; potassium, -1.883 ; rubidium, -1.796 ; caesium, -1.837 . The affinity of the metals for mercury is given by the difference between the characteristic potentials of polarised drops and the normal electrolytic potentials of the pure alkali metals. They were found to be lithium, 1.281 ; sodium, 1.138 ; potassium 1.325 ; rubidium, 1.409 ; caesium, (1.50) .
W. T.

Simultaneous Electrodeposition of Lead and Lead Dioxide.

M. G. MELLON and H. F. REINHARD (*Proc. Indiana Acad. Sci.*, 1921, 181—188).—The amounts of lead and lead dioxide deposited simultaneously on the cathode and anode respectively when a solution of lead nitrate is electrolysed under varying conditions are variable when free nitric acid is present, but for neutral solutions a fair constancy exists in the ratios for the amounts of each of the two deposits to that of the quantity of silver deposited in a coulometer in the circuit. The ratios of the anode and cathode deposits respectively to the lead equivalent of the silver were 1.0053 (alternatively, 0.990) and 0.9864 . The cause of the inaccuracy has not been traced.

CHEMICAL ABSTRACTS.

Electrolytic Migration of Sodium through Glass. M. PIRANI and E. LAX (*Z. tech. Physik*, 1922, 3, 232—235).—The film of water which persists inside an exhausted glass tube was removed by the migration of sodium ions through the glass. A tube shaped like a lamp bulb and containing a small tungsten wire was exhausted and immersed in molten sodium nitrate at 450° . The wire was heated to a high temperature and a potential of 200 volts was applied between the wire and the molten bath. Sodium ions migrated through the glass and a yellow luminescence was produced in the tube. The water film was displaced by this process and was attacked by the hot tungsten as evidenced by the formation of a film of blue tungsten trioxide on the tube.

CHEMICAL ABSTRACTS.

Method of Maintaining Small Objects at any Temperature between -180° and $+20^{\circ}$. P. P. CIOFFI and L. S. TAYLOR (*J. Opt. Soc. Amer.*, 1922, 6, 906—909).—The object is placed within a double-walled vacuum tube through which a stream of cold air, produced by the evaporation of liquid air contained in a Dewar vessel, is maintained. The rate of evaporation is controlled by means of an electric heater immersed in the liquid air, and determines the temperature to which the object is subjected. If desired, the object may be placed beyond the splayed-out end of the vacuum tube and an unbroken stream of cold air caused to flow across it by suction across the gap between the end of this tube and the wide mouth of a second tube connected to a vacuum pump. The latter tube should have a diameter about double that of the former and its length should be about twice that of the gap. The Dewar flask is preferably unsilvered, and is charged with liquid air through a funnel extending almost to the bottom and

provided with a plug of glass wool for filtering out ice and solid carbon dioxide. Temperature regulation may be maintained constant to within about 4° for many hours. J. S. G. T.

Heat of Evaporation. W. HERZ (*Z. anorg. Chem.*, 1922, **124**, 56—58).—Employing the values obtained by Young, the author finds that the quotients of heats of evaporation at equal fractions of the critical temperatures (on absolute scale) are fairly constant for the twenty-six organic compounds investigated. The quotient of latent heat of evaporation and absolute temperature is given for pentane at different temperatures, and remains fairly constant, 0.11—0.15, except in the neighbourhood of the critical temperature. The same was found to hold in the case of twenty-eight other organic compounds. Acetic acid is exceptional, this being probably due to association. W. T.

The Form of the Vapour Pressure Curve at High Temperature. I. The Curve for Lead. CHRISTOPHER KELK INGOLD (*T.*, 1922, **121**, 2419—2432).

High Temperature Investigations. XV. The Vapour Pressure of the Alkali Fluorides. OTTO RUFF, GERHARD SCHMIDT, and SUSANNE MUGDAN (*Z. anorg. Chem.*, 1922, **123**, 83—88).—The apparatus used was like that described by Ruff and Mugdan (*A.*, 1921, ii, 485) except that iridium crucibles were employed. The results are given for the fluorides of sodium, lithium, potassium, rubidium, and caesium. The latent heat of evaporation calculated by means of Liempt's equation (*A.*, 1920, ii, 588) was found to be, LiF, 52.2 Cal.; NaF, 51.1 Cal.; KF, 44.7 Cal.; RbF, 40.4 Cal.; CsF, 33.6 Cal. The critical temperatures calculated by the relationship $T_c = 1.55T_{760}^{\circ}$ are LiF, 3010° ; NaF, 3070° ; KF, 2750° ; RbF, 2600° ; CsF, 2370° .

W. T.

Heats of Combustion and Energy of Dissociation. WALTER HÜCKEL (*Ber.*, 1922, **55**, [B], 2839—2843).—A detailed criticism of the publications of von Weinberg on this subject (*A.*, 1920, ii, 668, 669).

In the final tables given by von Weinberg, only the previously known data for HCl, HBr, and HI are independent of hypothesis. The values for the C—C, C—H, C=C, C \equiv C, C—Cl, C—Br, and C—I linkings depend on the equality of Q_{CC} and Q_{CH} which has not been established. All the other data depend also on other unproved assumptions. The value of Weinberg's work lies in the fact that he has established for the first time a series of interesting relationships between the energy content of different organic compounds as illustrated by the scheme: (1) $Q_{(CO)} = Q_{C=O} + Q_{C-C}$, $Q_{(CO)} = Q_{C-O-C} + Q_{C-C}$, $Q_{C=O} = Q_{C-O-C}$ (2) $6Q_{NH} - Q_{N=N} = 6Q_{CH} - 3Q_{CC}$ (3) $Q_{CC} - Q_{CH} = Q_{CCL} - Q_{HCl}$.

H. W.

The Energy of the Atomic Linkings in Diamond and in Aliphatic Hydrocarbons. K. FAJANS (*Ber.*, 1922, **55**, [B], 2826—2838; cf. *A.*, 1920, ii, 354).—A reply to various criticisms

in many of which allowance has not been made for the admitted uncertainty of the author's data (cf. Hückel, A., 1920, i, 603; Polanyi, A., 1921, ii, 179; Swientoslawski, A., 1921, ii, 535; von Weinberg, A., 1920, ii, 668, 669; Thiel, A., 1920, ii, 667).

1. *Heat of sublimation of carbon and the absolute values of the linking energies.*—In the previous paper, the heat of sublimation of carbon was assumed for purposes of numerical illustration to be 287 Cal. Subsequently it has been shown by Kohn (A., 1921, ii, 302) that the heat of sublimation of carbon is 163.5 Cal. as a general mean of all measurements and that of diamond 168 Cal. The values for the most important linking energies have therefore been recalculated on a basis of 150 Cal. as the most probable value, on the supposition that carbon vapour is monatomic at 4200°, and that an equilibrium is established in Lummer's experiments.

2. *The energy of the double and triple linking.*—It is shown by a somewhat modified method that the heat of formation of a double or treble bond is greater than that of a single bond. Arguments are advanced in disproof of the criticism by Thiel (*loc. cit.*) that this conception is contrary to the known instability of substances with unsaturated linkings.

3. *Chemical forces in crystals.*—It has been asserted by Thiel (*loc. cit.*) that the chemical forces which are operative in the formation of a crystal are essentially those of subsidiary valency. This does not appear to be universally true, since the forces which hold the sodium chloride lattice together are identical with those which are operative in the vaporised salt molecule. The lattice is therefore held together by main valencies and the heat of sublimation is of the same order as that of the dissociation of the molecules into the free ions. On the other hand, the lattices of many organic compounds, for example solid hexane, are without doubt held together entirely by subsidiary valencies; this is shown by the fact that the molecular heat of sublimation of solid hexane is only 8 Cal., whereas the energy necessary for the disruption of the vaporised molecule into atoms is calculated to be 1511 Cal. The conception that the valency forces which unite the carbon atoms in the diamond lattice are identical with those uniting the carbon atoms of aliphatic compounds is not new; the advance made by Fajans consists in the exact quantitative demonstration of the correctness of the hypothesis by thermochemical methods.

4. The remainder of the communication is devoted to a question of priority (cf. von Weinberg, *loc. cit.*). H. W.

The Thermochemistry of Carbon Compounds. A. THIEL (*Ber.*, 1922, 55, [B], 2844—2845).—A reply to Fajans (preceding abstract). H. W.

Thermochemistry of Solutions. M. LEVALT-EZERSKY (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 108—113).—Simple reasoning from fundamental principles leads to a number of equations which may be combined in the form: $q'_m = q_m - Bq_i^k = BQ_i - Q_m = \phi_i - \phi_m = BR_i - R_m$, where q'_m represents the heat of dilution of a solution containing $100m/(100-m)$ grams of solute per 100 grams

of water to the concentration $l\%$, and q_m^k and q_l^k have analogous significations; Q_l and Q_m are the heats of solution of $100l/(100-l)$ and $100m/(100-m)$ grams, respectively, of the solute in 100 grams of water; $\phi_m = Q_m$ and $\phi_l = m(100-l)Q_l/l(100-m)$, that is, $\phi_l - \phi_m$, corresponds with the difference between the heats of solution of one and the same quantity of the solute in such different amounts of water that solutions of $l\%$ and $m\%$ concentration, respectively, are obtained; R_l and R_m represent, respectively, the heats of reaction of $100l/(100-l)$ and $100m/(100-m)$ grams of the solute, liquefied at the temperature of the experiment, with 100 grams of water.

The above equation furnishes a convenient means of passing from the heats of solution of different amounts of a substance in one and the same amount of solvent to the heats of solution of one and the same quantity of solute in different quantities of solvent and from these to the heats of dilution. T. H. P.

Effect of Variation in Weight of the Riders and Plummets of the Westphal Balance on the Accuracy of Specific Gravity Determinations. EDWARD A. TSCHUDY (*J. Amer. Chem. Soc.*, 1922, **44**, 2130—2135).—Accurate specific gravity determinations with the Westphal balance are possible only when the weight of water displaced by the plummet at 15° and the weights of the riders possess an exact multiple relationship amongst themselves. Variations in weight of the riders which disturb this relationship produce errors, often of considerable magnitude, in specific gravity determinations. Inaccurate plummet thermometers are also a source of error. The magnitude of ordinary variation in weight of riders and plummets has been ascertained, and equations have been derived for calculating the correction which must be applied to any indicated balance reading to obtain the true specific gravity of liquids lighter or heavier than water. Application of the corrections for any specific system of riders to indicated balance readings is facilitated by the construction and use of correction graphs. J. F. S.

The Degree of Molecular Polymerisation of Substances under Critical Conditions. J. A. MULLER (*Compt. rend.*, 1922, **175**, 760—761).—A table of the calculated values of the degree of polymerisation of a number of elements and compounds under critical conditions is given. All the substances included, with the exception of helium, undergo polymerisation to a certain extent; those which, under normal conditions of pressure and temperature, approximate in their behaviour to perfect gases are least affected, the values of the mean degree of polymerisation ranging from 1.227 in the case of hydrogen to 1.285 in that of nitrogen. Liquid hydrocarbons and monohalogen derivatives of benzene give values from 1.39 to 1.45, whilst those for esters of saturated monobasic fatty acids vary from 1.45 to 1.48. Nitriles, water, and acetic acid yield results in the neighbourhood of 2. H. J. E.

Corresponding States. W. HERZ^F (*Z. anorg. Chem.*, 1922, **123**, 132—136).—A theoretical paper in which the author investigates whether there is a constant relationship between the viscosity of liquids at the same fraction of the critical temperature. The viscosity at one-half the absolute critical temperature is divided by the viscosity at seven-twelfths the absolute critical temperature. In the case of 29 non-associating liquids, the ratio is 1.51—1.91. In the case of liquids which associate, the viscosity decreases more rapidly with increasing temperature and the ratio in the case of six liquids varies from 1.95 to 4.33. The author in the same way finds the ratio of the refractive indices at corresponding temperatures. The refractive index is calculated by equation $n = \sqrt{M + 2dR_L / M - dR_L}$. In the case of 29 liquids the approximate constancy of the ratio showed the validity of the law of corresponding states. W. T.

The Viscosity of Amphoteric Electrolytes in Solution. GUNNAR HEDESTRAND (*Z. anorg. Chem.*, 1922, **124**, 153—184).—Solutions of amino-acids are found to have a minimum viscosity at the isoelectric point. In the case of glycine and alanine, the viscosities of the anions is greater than that of the kations. Mixtures of glycine and alanine solutions have a viscosity which is the arithmetical mean of the corresponding unmixed solutions. The addition of neutral salts increases the viscosity of glycine and alanine solutions; it also displaces the minimum. The minimum viscosity of a gelatin solution is at the isoelectric point; the addition of salts increases the minimum value and at the same time shifts it to a lower hydrogen-ion concentration. On both sides of the minimum, the viscosity is decreased considerably by the salts. The author treated powdered gelatin with hydrochloric acid, and found that, on washing, a large amount of the gelatin went into solution; the same result was obtained by treating the powder with a mixture of hydrochloric acid and a salt. W. T.

Effect of Surface Tension. P. B. GANGULY and B. C. BANERJI (*Z. anorg. Chem.*, 1922, **124**, 140—142).—A stick of sodium hydroxide was held vertically in distilled water so that only one-half was immersed. In the absence of stirring, the part of the stick in contact with the surface dissolved the more rapidly. The same was observed in the case of sticks of potassium hydroxide, sodium nitrite, copper sulphate, and zinc chloride, and also of a zinc rod in dilute sulphuric acid. In the case of an iron rod in hydrochloric acid the reverse was observed and the part further from the surface dissolved the more rapidly. These effects are reduced by lowering the surface tension by a covering of oil, and are therefore assumed to be due to surface tension effects. W. T.

Negative Adsorption. II. Calculation of the Amount of Adsorbed Solvent. M. A. RAKUSIN and TATJANA GÖNKE (*Biochem. Z.*, 1922, **132**, 82—83).—The amount of adsorbed solvent

can be calculated by Gurvitsch's equation for positive adsorption (A., 1914, ii, 435). H. K.

The Sorption of Saturated Vapours by Charcoal. JOHN DRIVER and JAMES BRIERLEY FIRTH (T., 1922, **121**, 2409—2414).

Salt Adsorption on Metal Surfaces. H. VON EULER and G. ZIMMERLUND (*Arkiv Kem. Min. Geol.*, 1922, **8**, No. 14, 1—23).—Measurements have been made of the silver nitrate and potassium chloride adsorbed from aqueous solution by finely divided gold particles and by gold leaf. It has been found that the amount adsorbed increases with the amount of salt in solution, at first linearly and then tending to a maximum. At the maximum there is more adsorbed than would correspond with a unimolecular layer on the gold. Experiments are also described with mercury dropping through a calomel solution in which the amount of mercury in solution was determined by finding its effect as an enzyme poison. W. O. K.

Mordanting of Wool with Potash Alum. W. W. PADDON (*J. Physical Chem.*, 1922, **26**, 790—793).—Experiments are described from which it is concluded that, contrary to the opinion of Knecht, the mordanting of wool with potash alum does not lead to the formation of definite chemical compounds on the fibre, but is strictly an absorption phenomenon in which both alumina and sulphuric acid are involved. J. S. G. T.

Mordants. III. Chrome. WILDER D. BANCROFT (*J. Physical Chem.*, 1922, **26**, 736—772).—The author reviews critically a part of the literature, more especially the work of Liechti and Hummel (*J. Soc. Chem. Ind.*, 1893, **12**, 244) concerned with the use of chromic oxide as a mordant in dyeing wool, cotton, and silk. The following are among the conclusions drawn: from dichromate solutions wool first adsorbs chromic acid and this is reduced to chromic oxide, which is the true mordant; within limits, increasing the acid concentration increases the chromic acid taken up; chromic acid oxidises organic compounds more readily in presence than in absence of wool; when wool is mordanted with chrome alum, a basic sulphate changing later to chromic oxide is first formed; silk adsorbs chromic oxide less strongly than wool does; cotton takes up scarcely any chromic oxide from chrome alum, but adsorbs it from an alkali solution; there is no evidence of the formation of any definite compound when wool is mordanted with chromic oxide. J. S. G. T.

Tungsten Furnace for Experiments on Dissociation and Ionisation. K. T. COMPTON (*J. Opt. Soc. Amer.*, 1922, **6**, 910—912).—Tungsten sheet is bent into the form of a cylindrical tube and clamped by end pieces each consisting of a steel ring fitting in a split rectangular steel block. The blocks are mounted on water-cooled brass tubes serving as leads for the heating current. Short glass tubes surround the leads for purposes of insulation. Loops of fine tungsten wire, drawn tightly round the cylindrical

tube, prevent bulging of the furnace. The central electrode consists of a straight length of "20 mil." tungsten wire welded to heavier molybdenum leads. A furnace 60 mm. overall length and about 5 mm. diameter was raised to a white heat by 100 amperes at 6 volts, and reached its melting point when a current of about 200 amperes was employed.

J. S. G. T.

The Thermal Decomposition of Chlorine. FR. A. HENGLEIN (*Z. anorg. Chem.*, 1922, **123**, 137—165).—A description of the apparatus suitable for a reactive gas at low pressure and high temperature is given in detail (cf. this vol., ii, 441). The apparatus was tested by measuring the dissociation of bromine. The dissociation of chlorine was investigated at a pressure of 1×10^{-5} atmospheres and between the temperatures of 700° and 900°. The following relationship was found to hold $\log K_{(\text{atmos.})} = -(5400/4.571T) + 1.75 \log T - 4.09 \times 10^{-4}T + 4.726 \times 10^{-8}T^2 + 0.93$ (cf. Bodenstein, A., 1916, ii, 554). The chemical constant of monatomic chlorine was calculated in three different ways: (1) by Stern's method (A., 1914, ii, 543), (2) by the reaction $\text{Ag} + \frac{1}{2}\text{Cl}_2 = \text{AgCl}$, the heat effect and electromotive force of which are accurately known, (3) by the reaction $\text{Hg} + \frac{1}{2}\text{Cl}_2 = \text{HgCl}$. The values found were respectively 0.68, 0.93, and 1.50. A linear relationship was found to exist between the heats of dissociation of chlorine, bromine, and iodine and their atomic radii and other spatial and thermal constants. The electroaffinity of chlorine was calculated to be 73 cal.

W. T.

Theory of Solvates. JA. K. SYRKIN (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 267—280).—Solvates in general and hydrates in particular vary in composition and are stable only within narrow limiting conditions, so that they must be regarded as transitory systems of physico-chemical character. The structure of a hydrate may be represented as a molecule of solute surrounded by an envelope of water molecules. Such of the latter as are near to the nucleus are held by a force approximating to chemical force, whereas the more remote, semi-combined water molecules exist under the configurational influences of chemical and kinetic forces, the system being in a condition of stationary thermal equilibrium. Hence it is possible for hydrates of different composition to exist in one and the same solution. This equilibrium of hydrates possesses a macroscopic character. The gradual variation of the thermal effect with the temperature confirms these views and distinguishes the decomposition of a hydrate from the stoichiometric decomposition of an ordinary system. The existence of hydration is shown also by the change in the internal pressure, and the work of the internal forces may be expressed as the mechanical equivalent of chemical affinity (cf. Tammann, "Über die Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," 1907, 34).

T. H. P.

Solubility of Carbon Dioxide and Nitrous Oxide in certain Solvents. WILLIAM KUNERTH (*Physical Rev.*, 1922, **19**, 512—524).—In view of its bearing on the Lewis-Langmuir theory, a

comparison was made between the solubilities of carbon dioxide and of nitrous oxide between 18° and 36° in water, acetone, acetic acid, methyl alcohol, pyridine, ethyl alcohol, benzaldehyde, aniline, amyl acetate, ethylene bromide, *iso*amyl alcohol, and chloroform. In this series, the ratio of the solubility of carbon dioxide to that of nitrous oxide decreases regularly from 1.34 to 0.66. The ratio is nearly constant for each solvent, and the temperature coefficient, ds/dT , which is always negative, is in most cases nearly the same for the two gases. It is found that Raoult's law does not hold for the solubility of gases in liquids, and that there is little, if any, relation between solubility and the difference between internal or cohesion pressures of solvent and solute. Since, however, the ratio of the solubilities of carbon dioxide and nitrous oxide (the former of which is the more active chemically, and therefore has the stronger polarity) varies regularly with the dielectric constant of the solvent, and since this constant may be taken as an index of the polarity of the solvent, it is suggested that polarity may be an important factor in determining the relative solubility of gases in liquids. The following figures, for carbon dioxide and nitrous oxide, respectively, at 20°, are abstracted from a table giving the solubilities expressed in c.c. of the gas under existing barometric pressure per c.c. of solvent: water, 0.900, 0.675; acetone, 6.98, 6.03; acetic acid, 5.23, 4.85; pyridine, 3.85, 3.58; methyl alcohol, 3.57, 3.32; ethyl alcohol, 2.87, 2.99; benzaldehyde, 2.98, 3.15; aniline, 1.38, 1.48; amyl acetate, 4.65, 5.14; ethylene bromide, 2.27, 2.81; *iso*amyl alcohol, 1.91, 2.47; chloroform, 3.71, 5.60.

A. A. E.

Partition of a Substance between two Solvents and the Solution Field of Force. N. A. SCHILOV and L. K. LEPIN [with M. P. JANTSCHAK] (*Nachr. Phys.-Chem. Lomonossow-Ges.*, 1920, 1, 1—103; from *Chem. Zentr.*, 1922, iii, 541—542).—The partition of a dissolved substance between two liquid phases changes with varying concentrations and only remains constant in particular cases owing to the operation of compensating factors. The partition does not in general depend on the solubilities in the individual solvents; this relationship, in fact, only holds at the triple point of the three phases. The isotherms for the changes in concentration are different for each phase and are not linear. The relation $k=c_1^2/c_2$ is only a particular case of the relation $k=c_1^n/c_2=q \cdot c_1^n/c_2^n$, where n is an integer or fraction and given by $n=\log \beta_1/\log \beta_2$, β_1 and β_2 being factors expressing the changes in the solution field of force (Lösungskraftfeld) depending on concentration. The partition coefficient thus obtained is constant for many systems, excepting those where the two solvents have a considerable reciprocal solubility, and where chemical factors may play a part.

G. W. R.

Solubility of Liquids in Liquids. The Partition of the Lower Acids, particularly Formic, between Water and various Organic Solvents. NEIL E. GORDON and E. EMMET REID (*J. Physical Chem.*, 1922, 26, 773—789).—The partition

ratios at 25° of formic acid between water and the following respective solvents: cotton-seed oil, petroleum, benzene, toluene, xylene, carbon tetrachloride, carbon disulphide, and bromoform have been determined. In like manner, the respective partition ratios at 25° of acetic acid between water and either cotton-seed oil or petroleum, of propionic and butyric acids between water and cotton-seed oil have been determined. The results have been employed to determine the so-called solubilities of the acids in the solvents and vice versa.

J. S. G. T.

The Behaviour of Two Metals towards One Another when Dissolved in Mercury. G. TAMMANN and W. JANDER (*Z. anorg. Chem.*, 1922, **124**, 105—122).—The authors investigated the affinity of one metal for another when dissolved in mercury: (1) by measuring the freezing-point depression of the compound crystals and comparing this with that of the components, (2) by measuring the influence of the one metal on the *E.M.F.* concentration-curve of the other dissolved in a third more noble liquid metal. Thus the addition of small amounts of a more noble to a less noble metal has but a very small effect on the *E.M.F.* if the compound of the two metals is very highly dissociated, whereas, if a stable compound is formed, then a sudden change in the *E.M.F.* is caused when the concentrations of the metals correspond with the composition of this compound. The following intermetallic compounds were found to be very stable: AuZn , Mg_2Sn , CeSn_2 , and Ce_4Bi_3 , having very high affinity constants. AuZn $K=3.4 \times 10^7$. Mg_2Sn $K=1 \times 10^{10}$. CeSn_2 $K=1 \times 10^{40}$. Ce_4Bi_3 $K=3 \times 10^{120}$. Cf. water $K=4.6 \times 10^{78}$. Others were very highly dissociated in solution in mercury; for example, compounds of gold with cadmium and lead, of silver with zinc and cadmium, of copper with zinc and cadmium.

W. T.

Systems in which Metals Crystallise. JOHN L. HAUGHTON and G. WINIFRED FORD (*Trans. Faraday Soc.*, 1922, **18**, 112—118).—Of the twenty-nine elements the crystalline structures of which have been determined by X-ray analysis, five only are exceptions to the rule that all elements of the same periodic series crystallise in the same system. In nearly every case, alloys which form a homogeneous series of solid solutions right across the equilibrium diagram, crystallise in the same system. There appears to be no relationship between the changes which occur in the physical properties of metals at the melting point and the crystalline habit of the metals. A possible exception occurs in the case of the electrical resistivity of the metals in the odd series of group 5.

J. S. G. T.

Solutions, Suspensions, Colloids. N. P. PESKOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 73—99).—The theoretical considerations developed by the author lead to the following conclusions. The modern doctrine of colloids deals with a conception of heterogeneity which is totally different from that assumed by the doctrine of phases, but is identical with the molecular-kinetic view of the universe; the latter is termed the generalised conception

of heterogeneity. The notion of dispersion current in the chemistry of colloids must be regarded as composed of two different conceptions, distinguished as qualitative and quantitative dispersion. The former of these is synonymous with the generalised conception of heterogeneity referred to above, and has no special bearing on systems represented by suspensions, colloids, and solutions. The latter, possessing a dimensional character, differs from the idea of a phase only in that the latter is characterised by the spacial magnitudes of its separate elements. Thus all systems to which the term quantitative is applied must be considered to be polyphasic.

Physical theories of colloids in general postulate that: (1) suspensions, colloids, and true solutions are systems, the qualitative differences between which may be regarded as functions of their degrees of dispersion, (2) colloids represent typical polyphase systems, and (3) all the characteristic properties of colloids are merely the results of the magnitudes of the molecules. The logical objection to such theories is that they accept as results of the doctrine of dispersion the hypothetical assumptions on which this doctrine is based.

The author considers that only careful investigation, from all points of view, of the process of coagulation and of the adsorption phenomena accompanying them will decide the question of the heterogeneity of colloids in their normal condition. T. H. P.

Electrical Colloid Synthesis. SVEN BODFORSS and PER FRÖLICH (*Koll. Chem. Beihefte*, 1922, **16**, 301—340).—Svedberg's method of synthesis of colloids has been investigated for the case where the induction coil current is replaced by a high tension symmetrical alternating current and the dependence of the amount of dispersion on the dimensions of the oscillation circuit determined. The dispersion of copper, tin, lead, zinc, antimony, aluminium, silver, magnesium, bismuth, and thallium by Svedberg's method and the present method has been compared, and it is shown that for the more easily dispersed metals the present method is inferior to the original Svedberg method, the yield being about one-half to two-thirds that obtained by the older method. In the case of the harder metals, the dispersion is about the same by both methods. Alloys belonging to the systems lead-tin and antimony-zinc have been dispersed by the present method and the sols produced examined. J. F. S.

Winkelblech's Phenomenon or Pseudo-extraction and its Importance in Colloidal Chemistry. New Methods of Extracting Solids. K. CHARITSCHKOV (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 96—107).—Winkelblech (A., 1907, ii, 17) found that when certain pseudo-solutions are treated with various non-aqueous solvents insoluble in water, the solid disperse phase passes partly or completely into the liquid, non-aqueous phase, throughout which it becomes distributed in the form of a gel. This phenomenon is usually regarded as a special case of adsorption, but the results obtained on examining different combinations of disperse phases and non-aqueous solvents are completely incompatible

with this view. The effect seems to be due rather to mechanical seizure of the molecules of the solid phase by disintegrated liquid drops of lower specific gravity or to attraction of these molecules to the bottom by molecules of a heavier liquid.

From a pseudo-solution of gelatin part of the sol may be drawn to either the surface or the bottom of the liquid by treatment with light petroleum, chloroform, carbon disulphide, etc., and owing to the resemblance of the phenomenon to extraction the author terms it "pseudo-extraction."

For the velocity of transport of the molecules, Lewis's formula, $V = 2r^2S(S - S_1)/9\eta$, should be valid, S and S_1 being the specific gravities of the solid and liquid phases, r the radius of the molecules, and η the coefficient of viscosity, but greater exactitude would be attained by addition of the term, $2r^2S(S - d)/9\eta$, d denoting the specific gravity of air.

The fact that sols of silicic acid, Prussian blue, and almost all metals remain unchanged when treated with light petroleum, benzene, and similar liquids is explained on the assumption that, for certain values of S and S_1 the magnitude of V will be negative, the specifically lighter molecules of air and light petroleum being then not in a condition to draw upwards the heavier molecules of the sols of metals and various oxides.

The results of experiments on the pseudo-extraction of gelatin, agar-agar, and sodium oleate show that the quantity of the colloidal substance thus extracted is not proportional to the concentration; when the latter is very high, no pseudo-extraction takes place. For every disperse phase, the phenomenon appears to exhibit an optimum concentration and an optimum temperature. In no case, however, is it possible to remove by pseudo-extraction the whole amount of a sol occurring in the disperse phase. The excess above the normal proportion of potassium hydrogen tartrate or sodium sulphate present in supersaturated solution is withdrawn instantaneously from the latter by shaking with light petroleum. The same occurs when an aqueous alcoholic solution of sucrose is similarly treated, but in this instance the sucrose withdrawn partly redissolves in the aqueous alcoholic layer on prolonged keeping of the system after being shaken with the light petroleum. T. H. P.

General Method for Obtaining Gels of Inorganic Salts, and its Relation to Theories of the Colloidal State. K. CHARITSCHKOV (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 91—96).—Treatment of a solution of sodium (potassium, etc.) naphthenate in a hydrocarbon containing excess of naphthenic acid with hydrogen chloride or carbon dioxide yields colloidal sodium chloride or carbonate. With heavy metal salts of naphthenic acid, which dissolve readily in benzene, toluene, or light petroleum, excess of naphthenic acid is not required; colloidal cupric and mercuric chlorides, etc., are obtainable in this way. The naphthenic acid may be replaced by oleic acid. The products formed show Brownian movement and the corresponding ultramicroscopic appearance. The sol first formed rapidly undergoes coagulation

but not throughout its entire mass, part remaining in a condition of pseudo-solution detectable ultramicroscopically.

Treatment of ferrous sulphate in the above way results in the formation of a white precipitate which, as oxidation proceeds, is gradually converted first into a black sol of triferric tetroxide and ultimately into a brown sol of ferric oxide. The action of hydrogen chloride on ferric naphthenate yields, not ferric, but ferrous chloride, the hydrogen chloride acting as a reducing agent under these conditions.

These and allied phenomena do not appear to be explicable by any of the existing theories of the colloidal state, or by von Weimarn's crystallisation theory, which is generally accepted. Neither this author's formula for expressing the course of separation of precipitates, nor that given by Nernst to indicate the velocity with which a precipitate forms round centres of crystallisation, takes into account the attraction or affinity between solvent and solute, which constitutes an important factor; in many cases, the whole process of crystallisation is the resultant of the force uniting the molecules and the affinity of the latter for the solvent.

The author regards gels and sols as the extreme and final stages of the interactions between solid and liquid phases, intermediate stages being represented by crystals of various degrees of symmetry.

T. H. P.

Sensitisation of Coagulation Processes: Colloids as Indicators of Photo-electric Effects. N. P. PESKOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 101—104).—Anthracene is found to exert a sensitising action on the coagulation of sols of arsenic trisulphide, platinum, and carbon, but it is not known if this action is exercised towards all sols or if it is limited to those carrying a definite charge. The action does not depend on chemical transformation of the anthracene or on its fluorescence, but lies in the electronic transpositions taking place in the system under the influence of insolation. Hence colloids constitute a new type of indicator for photo-electric effects. Reference is made to the various possible interpretations of the mechanism of the coagulation of colloids under the sensitising action of anthracene.

T. H. P.

Flocculation by Mixtures of Electrolytes. H. FREUNDLICH and P. SCHOLZ (*Koll. Chem. Beihefte*, 1922, **16**, 267—284).—The authors have confirmed the results of Odén, to the effect that the coagulating properties of a salt are diminished or destroyed by the presence of a second salt, but in contradiction to Odén they have also found that the reduction is not due to a diminution of the kation action by the anion but rather to an antagonism between the kations. The antagonistic action is measured by mixing Odén's sulphur sol with a quantity of an electrolyte insufficient to cause flocculation and then determining the quantity of a second electrolyte necessary to effect this change. In the case of ion pairs with strong antagonism such as magnesium—lithium, or magnesium—hydrogen, the coagulation value of the magnesium

is a whole number multiple of the value obtained when the coagulation is effected by magnesium alone. The anions have also an influence in the diminution of the coagulation value in the order citrate''>sulphate''>chloride'. Definitely hydrophobic sols, such as Weimarn's sulphur sol and Donau's gold sol, do not exhibit the above-named phenomena. In these cases the coagulation values of sols containing electrolytes are always less than those of the pure sols; that is, the action of the two electrolytes is additive, as is to be anticipated from the coagulation hypothesis of hydrophobic sols. In these cases also, the coagulum cannot be peptised by electrolytes. The behaviour of Odén's sulphur sol is probably to be connected with its distinct hydrophilic character; that is, with the hydration of the micellæ. In the case of arsenic sulphide sol, a certain antagonism is observed for salts such as lithium chloride and magnesium chloride.

J. F. S.

Coagulation of Manganese Dioxide Sol by Different Electrolytes. PHANI BHUSAN GANGULY and N. R. DHAR (*J. Physical Chem.*, 1922, **26**, 701—714).—The coagulative powers of different electrolytes on manganese dioxide sol do not follow the Schulze-Hardy law, namely, the higher the valency of an ion the greater its precipitating action on a colloid. Changes of concentration of the sol alter the relative order of the electrolytes when arranged according to their coagulative powers. Coagulative power is not purely a function of valency, but is more a specific property of the ions, and is influenced, among other factors, by the time allowed for coagulation and the presence of anions.

J. S. G. T.

Rôle of the Hydrogen-ion Concentration in the Precipitation of Colloids. HERMANN V. TARTAR and ZALIA JENCKS GAILEY (*J. Amer. Chem. Soc.*, 1922, **44**, 2212—2218).—The effect of the hydrogen-ion concentration on the precipitation of mastic and gamboge sols by solutions of acids and salts has been investigated. It is shown that acids cause precipitation at the same hydrogen-ion concentration irrespective of the concentration of the colloid. The negative ion of the acid is without effect. Various potassium and ammonium salts precipitate the sols at the same concentration provided that the hydrogen-ion concentration is kept approximately constant. The precipitating values of the salts vary directly as the concentration of the colloid at the same hydrogen-ion concentration. The stabilising or peptising effect of the ion bearing a charge similar to that of the colloidal particle is shown to be very limited if it exists at all.

J. F. S.

Soaps and Proteins. II. Colloid Chemistry of Soap Manufacture, Analogies in the Colloid Chemistry of Soaps, Albumins, and Tissues. III. Colloid Chemical Behaviour of Fatty Acids and their Derivatives and the Analogous Behaviour of Neutral Proteins and their Derivatives. MARTIN H. FISCHER [with GEORGE D. McLAUGHLIN and MARIAN O. HOOKER] (*Koll. Chem. Beihefte*, 1922, **16**, 99—179; cf. this vol., ii, 430).—A continuation of previous work. The principles of the hot and

cold processes in the soap industry are described. The significance of some of the constants of oils and fats, such as the density, saponification number, the iodine number, and the Reichert-Meissl number, is pointed out. The physical properties of soaps are discussed. An account of experiments on the systems, globulin-water, globulin-sodium hydroxide, globulin-acid, globulin-metallic chloride, gelatin-water, gelatin-alkali hydroxide, gelatin-acid, and gelatin-salt is given and peptisation and coagulation are discussed. The theory of poisoning by ammonium and heavy metal salts is discussed and it is shown that these substances combine with the protoplasm with the formation of compounds which are much less hydrated than the normal protoplasm compounds, and that this constitutes the poisoning. Reproductions of a large number of photographs, illustrating the experiments, are contained in an appendix to the paper.

J. F. S.

Action of Anions, particularly the Hydroxyl-ion, on the Colloidal Condition of Night-blue. S. AKAMATSU (*Kolloid Z.*, 1922, **31**, 209—215).—The effect of various anions on the surface tension of solutions of night-blue has been investigated to ascertain whether or no the position of the hydroxyl-ion in the activity series found by Traube (A., 1912, ii, 740) is correct. This series places the hydroxyl ion after the halogen ions instead of in the most active position as was expected. The surface tension of 0.2% solutions of night-blue containing concentrations varying from $N/10$ to $N/1000000$ of potassium iodide, bromide, chloride, nitrate, thiocyanate, chlorate, sulphate, hydroxide, and dihydrogen phosphate has been measured. It is shown that the addition of the various electrolytes causes the surface tension to rise to a maximum and then to fall to a value approaching the water value with decreasing concentration of the added electrolyte. The measurements showed that the hydroxyl ion is the most active of all anions and that the reason for the position given to it by Traube lies in the fact that he took as his concentration of hydroxyl ions the concentration of the hydroxide added. In the present work the concentration of the hydroxyl ion has been measured electrometrically.

J. F. S.

The Equilibrium between some Organic Substances. H. HAMMERSTEN (*Arkiv Kem. Min. Geol.*, 1922, **8**, No. 16, 1—14).—The equilibrium constant, K , for the reaction between phenylhydrazine and acetone or acetaldehyde has been investigated by the solubility method of Euler and Svanberg (A., 1921, i, 68), and also by the measurement of the refractive indices of the solutions. The various results are not very consistent, but in the case of acetone-phenylhydrazine the value of K appears to be about $7-9 \times 10^{-4}$, and in the case of acetaldehyde-phenylhydrazine about 10^{-3} .

W. O. K.

The Solubility of Calcium Carbonate in Water in Equilibrium with a Gaseous Phase containing Carbon Dioxide. YUKICHI OSAKA (*Mem. Coll. Sci. Kyoto*, 1922, **5**, 131—141).—The solubility of calcium carbonate in water has been calculated

from the data given by McCoy and Smith (A., 1911, ii, 379). It is assumed that carbon dioxide dissolved in water is a much stronger acid than acetic acid (cf. Strohecker, A., 1916, ii, 522, and Pusch, A., 1916, ii, 477, 557) and that the gas is only slightly combined with water. The apparent first dissociation constant and the second dissociation constant of water are taken as 3.50×10^{-7} , and 4.91×10^{-11} , respectively, and the solubility product of calcium carbonate (calcite) at 25° was calculated to be 7.24×10^{-9} . The solubility of calcium carbonate in water, in the presence of carbon dioxide, is given by $C = [Ca^{**}] + 1 - \gamma/2\gamma[HCO_3']$, where γ is the degree of dissociation of calcium hydrogen carbonate, assuming that the solution is ionised to the same extent as that of calcium acetate of the same concentration. Formulae are given for the relationship between $[Ca^{**}]$, and $[HCO_3']$, and the partial pressure of carbon dioxide.

W. E. G.

The Propagation of Explosion Waves in Gases contained in Tubes of Varying Cross-section. COLIN CAMPBELL (T., 1922, 121, 2483—2498).

Limits for the Propagation of Flame in Vapour-Air Mixtures. II. Mixtures of More than One Vapour and Air at the Ordinary Temperature and Pressure. ALBERT GREVILLE WHITE (T., 1922, 121, 2561—2577).

The Velocity of the Action of Oxygen, Hydrogen Sulphide, and the Halogens on Metals. G. TAMMANN and W. KÖSTER (*Z. anorg. Chem.*, 1922, 123, 196—224).—When iodine, chlorine, or air acts on a metal, a variety of surface colours is formed, and these colours give the rate of thickening of the film of compound formed (cf. A., 1920, ii, 248). The rate of chemical action is high but diffusion of the gas through the film of compound is slow. In the case of iodine, the rate is inversely proportional to the thickness of the film and is independent of the temperature. There is in the case of the action of iodine on silver a change in the velocity at 145° which is the transition temperature of silver iodide. In the case of the action of moist air containing chlorine and bromine on copper, silver, and lead there is a parabolic relationship between the time of action and the thickness of film. The same holds in the case of the oxidation of metals. At high temperatures oxidisable metals are almost immediately covered with a thin film of oxide which protects the metals.

Hydrogen sulphide reacts rapidly with copper and manganese, more slowly with silver, and still more slowly with lead. Iron, cobalt, nickel, chromium, antimony, bismuth, tin, aluminium, zinc, and cadmium show no change after several days' contact with the gas. The action of air on copper-zinc alloys was also investigated.

W. T.

The Formation of Oxides of Multivalent Metals from their Hydroxides. HANS VON EULER and ULF VON EULER (*Z. anorg. Chem.*, 1922, 124, 70—80).—The temperature-coefficient of the coagulation of albumin is very high, the rate being doubled

for an increase of temperature of 2° . The rate of dehydration of copper hydroxide was measured at different temperatures. The temperature-coefficient was very high, as in the coagulation of albumin, but was found to decrease with increasing temperature $40-45^{\circ}=3.0$ for 5° , $55-60^{\circ}=1.8$. The results were not in agreement with Arrhenius's formula (A., 1889, 1103), which led the authors to the conclusion that the dehydration consists of several reactions. The rate of dehydration was measured colorimetrically. The isoelectric points for copper hydroxide is 3×10^{-13} as obtained from the equation $I = \sqrt{K_s \cdot K_w / K_b}$. W. T.

Velocity of Hydrolysis of Ethyl Acetate. HERBERT S. HARNED and ROBERT PFANSTIEL (*J. Amer. Chem. Soc.*, 1922, **44**, 2193—2220).—The unimolecular velocity constants of the hydrolysis of ethyl acetate in the presence of hydrochloric acid of many concentrations have been accurately determined at 25° . A solution of the general equation for the velocity of hydrolysis has been obtained and the velocity constants have been calculated by the general equation. In four series of measurements, it has been found that the curve of the velocity constants divided by the molecular concentration of hydrochloric acid against $\log c_1$, where c_1 is the molecular concentration of hydrochloric acid, shows a minimum at $0.07-0.08N$ -acid. This is similar to the curve of the individual hydrogen-ion activity coefficient against $\log c_1$, which has a minimum at $0.15-0.18N$ -acid. It has been shown that the velocity constant divided by the product of the activities of the hydrogen ion and the water molecule is not a constant at different acid concentrations but has a maximum at $0.3N$ -hydrochloric acid. Some factors which may cause this deviation from constancy have been suggested. The kinetics of the hydrolysis of ethyl acetate are very complex, but the authors are of the opinion that the evidence obtained in the present work shows that the method employed is in general the correct method of attacking this problem. J. F. S.

Velocity of Inversion of Sucrose as a Function of the Thermodynamic Concentration of the Hydrogen-ion. HAROLD A. FALES and JACQUE C. MORRELL (*J. Amer. Chem. Soc.*, 1922, **44**, 2071—2091).—The velocity of hydrolysis of sucrose by solutions of sodium hydroxide, acetic acid, and hydrochloric acid of various concentrations has been determined at 35° and the thermodynamic hydrogen-ion concentration has been calculated from *E.M.F.* determinations of the reaction mixtures at the same temperature. It is shown that the addition of sucrose to solutions of hydrochloric acid causes a definite increase in the thermodynamic concentration of hydrogen-ion over the whole range of concentration of the acid. In the case of acetic acid, a maximum increase in hydrogen-ion concentration is observed which diminishes as the concentration of hydrogen-ion decreases, on the addition of sucrose. The addition of sucrose to sodium hydroxide appears to cause an increase in the thermodynamic concentration of

hydrogen-ion. The thermodynamic concentration of hydrogen-ion in the system remains appreciably constant during the course of the inversion process. The velocity of inversion of sucrose by hydrochloric acid is proportional to the thermodynamic concentration of hydrogen-ion only for the limited range of concentration of acid which lies between 0.01*N* and 0.001*N*. The bimolecular velocity constants, reduced to unit thermodynamic hydrogen-ion concentration, are constant with changing concentrations of sucrose only for each molecular concentration of hydrochloric acid between 0.01*N* and 0.3*N*. These constants vary considerably for different concentrations of acid. Evidence is adduced which shows that for acetic acid, the undissociated molecule is not a positive catalyst in the inversion process; or that there are other factors entering here which have never been considered. With strong acids, the inversion process does not appear to be strictly unimolecular, especially in the early periods of the reaction. Within the limits of the concentrations of the reactants used, no appreciable change in volume was noticed when the solutions of hydrochloric acid and sucrose were mixed.

J. F. S.

Generator Gas Equilibrium at High Pressures. KARL JELLINEK and ALOIS DIETHELM (*Z. anorg. Chem.*, 1922, **124**, 203—229).—The electric furnace employed was a modification of that used by Nernst (*Z. Elektrochem.*, 1907, **13**, 52); it allowed measurements to be carried out at 1300° and at 150 atmospheres. The reaction $C + CO_2 \rightleftharpoons 2CO$ was investigated between 800° and 1000° at pressures up to 50 atmospheres. Various forms of charcoal were employed, and the equilibrium, which was well defined, was practically the same in each case, and again the same in the case of graphite. The law of mass action was obeyed at all pressures. The integration constant of the reaction isochore of generator gas equilibrium was found to be 3.876; this agrees well with the value calculated by means of Nernst's heat theorem (3.80). The authors show that the maximum work of this reaction is equal to the heat effect if the reaction is carried out isothermally and reversibly and if the excess of oxygen has the same pressure as the carbon dioxide formed.

W. T.

Catalytic Activity of Copper. O. W. BROWN and C. O. HENKE (*J. Physical Chem.*, 1922, **26**, 715—727).—In continuation of previous work (this vol., i, 445), the authors have investigated the catalytic reduction of nitrobenzene to aniline by hydrogen in the presence of copper catalysts prepared by the reduction of the precipitated oxide. Sabatier's conclusion that a catalyst so prepared is more efficient than one prepared from an ignited nitrate was confirmed. By the use of the former catalyst, much lower rates of supply of hydrogen may be used without reduction in yield, and the reaction may be carried out at a much greater rate. The best temperature for carrying out the reduction was found to be about 260°. A small amount of iron in a copper catalyst prepared from an ignited oxide prevents the rapid decrease in activity of the

catalyst. Copper deposited on asbestos was found to be capable of effecting the reduction at a much greater rate per gram of copper than copper alone, but with high rates of supply of nitrobenzene, it quickly lost its activity. Copper on asbestos is a better catalyst than an equal volume of copper on pumice. J. S. G. T.

Selective Activation of Alumina for Decarboxylation or for Dehydration. HOMER ADKINS (*J. Amer. Chem. Soc.*, 1922, **44**, 2175—2186).—Alumina has been preferentially activated for decarboxylation or for dehydration by modifying the method of preparation. This has been accomplished by obtaining aluminium hydroxide and hydrated alumina by precipitation from its salts or esters in water or xylene solution, and by preparing it by the action of water vapour on aluminium alkyl oxides, both in the pure state and when the latter are impregnated in pumice. The extent to which selective activation has been accomplished is indicated by the following figures, which give the relative "ethylene efficiency" of the variously prepared catalysts with ethyl acetate vapour at 465°: 34, 38, 41, 50, 107, and 150. The catalysts indicated were prepared as follows: by melting aluminium isopropoxide on pumice and exposing to moist air for eighteen hours (34); as last, but aluminium isobutoxide was used (38); by the action of moist air on aluminium methoxide; this was used as compressed tablets and contained traces of mercury (41); alumina from aluminium butoxide supported on pumice as above (50); tablets made from the precipitate produced by the action of hydrochloric acid on solutions of sodium aluminate (107); and tablets made from alumina obtained by the action of water on aluminium amalgam (150). An hypothesis has been advanced in which it is considered that the catalytic activity of alumina is conditioned by its molecular porosity, or the distances between the aluminium atoms and this, in part, is determined by the size, shape, and position of the radicles attached to the aluminium when the aluminium compound passes into the solid state. All the experimental evidence obtained with alumina catalysts is in complete harmony with this hypothesis. In terms of this hypothesis, it is held that decarboxylation is favoured by large pores in the alumina and that ethylene formation is favoured by small pores, large and small referring to units of molecular dimensions. The work of Milligan and Mead (this vol., ii, 447) on the dehydration and X-ray pattern of aluminium hydroxide is discussed in its relation to catalytically active alumina. The results obtained by Palmer (A., 1921, ii, 542), in the use of electrolytic copper and copper by reduction for the hydrogenation of alcohol, are explained on the basis of the hypothesis noted above. Cf. Langmuir (this vol., ii, 629). J. F. S.

The Influencing of Catalysts and Specifically Active Catalysts. KARL W. ROSENMUND and F. ZETZSCHE (*Ber.*, 1922, **55**, [B], 2774).—A reply to Abel (cf. Rosenmund and Zetzsche, A., 1921, ii, 320, 392, 393; this vol., ii, 41; Abel, A., 1921, ii, 542; this vol., ii, 26). H. W.

Kinetics of Inductive Processes : Schönbein's Reaction.

A. V. PAMFILOV and N. N. PETIN (*Bull. Inst. Polyt. Ivanovo-Voznesensk*, 1922, 6, 221—231).—The authors discuss previous work published on the influence of ferrous oxide on the liberation of iodine from an iodide by the action of hydrogen peroxide, and give the results of their own experiments on this reaction. It is found that not only the velocity of the initial stage of the reaction, but also the nature of its dependence on the concentration of the iron salt and on the corresponding acidity are completely different according as the iron is in the ferric or the ferrous condition. The liberation of iodine by ferric oxide or hydrogen peroxide separately is considerably accelerated when the two reactions occur together, and the velocities of the separate, and that of the combined, reactions increase with increase of the concentrations of all the components; the acidity of the medium is of comparatively little influence, but in general accelerates the reaction.

On the other hand, in neutral and faintly acid media the reaction is accelerated more by ferrous oxide than by ferric oxide in low concentration, but for definite conditions of concentration the reaction is retarded by increasing the concentration of the ferrous oxide either absolutely or in relation to the potassium iodide; this retardation is observed also in an acid medium. Increase in the acidity also retards the reaction considerably. This phenomenon disappears when the concentration of the potassium iodide increases and the solution is rendered strongly acid, especially as liberation of iodine by the acid becomes pronounced under these conditions.

Hence the diminution in the sensitiveness of Schönbein's reaction in a neutral medium caused by increase in the concentration of the catalyst (cf. Meissner, "Untersuchungen über den Sauerstoff," 1868, 78—80; Struve, *Z. anal. Chem.*, 1869, 8, 319) is not fortuitous but holds generally, both in acid and in neutral solutions. The results of replacement of the acid by the corresponding concentration of a sulphate show, as was found by Brode (A., 1901, ii, 443) for ferric-ions, that the influence of increased acidity is not to be referred to diminished concentration of the ferrous ions and that the hydrogen-ions must here play a part.

The mechanism of the action of ferrous oxide, typical of inductors in general, is probably based on its spontaneous oxidation, and the retarding influence exerted on the reaction by acidity is related to the great stability of ferrous-ions in an acid solution. T. H. P.

Union of Hydrogen with Acetylene Derivatives. XV. Velocities of Catalytic Reactions.

J. S. ZALKIND (*J. Russ. Phys. Chem. Soc.*, 1920, 52, 199—211).—The author discusses the results obtained by various investigators on the course followed by reactions occurring under the influence of enzymes and other catalysts. The general conclusion drawn is that, even when catalysts so chemically simple as palladium and platinum are used, the course of the reaction is often quite complex, and that no essential difference exists between the actions of these simple catalysts and those of enzymes. In both cases, it is necessary to

assume the formation of intermediate compounds between the catalyst and the reacting compounds, although with regard to the means by which such intermediate compounds are formed—whether by chemical reaction or by simple adsorption—opinions differ. Adsorption phenomena may, indeed, exhibit complex character and a sharp distinction between adsorptive and chemical phenomena is scarcely possible.

T. H. P.

Speculations concerning the Positive Electron. [SIR] OLIVER LODGE (*Nature*, 1922, **110**, 696—697).—According to Larmor's theory, the positive and negative electrons can only differ in one being the mirror-image of the other. No positive electron in this sense has yet been discovered. Both positive and negative electrons are supposed to be extremely mobile, and the forces between them immense, so that they instantly bind themselves together into a compact and stable structure consisting of several thousands of each kind, the simplest and lightest of these composite structures being the hydrogen nucleus or proton. The proton for the first time allows a negative electron to revolve round it without being absorbed into its composition. On the mirror-image hypothesis, however, it becomes difficult to explain why only negative electrons should occur in the satellite systems; that is, why some atoms should not have nuclei with a surplus of negative charge, and be attended by positive electrons. The case of a number of primary electrons, both positive and negative, is considered. If, in the many possible ways of structural packing, something less than half the atomic nuclei formed were of the kind with positive satellites, whilst the other approximate half were of the negative satellite variety, the two classes would speedily combine with great violence and thereby form the tight-packed and stable nuclei of heavier atoms, until the complexity was too great to ensure stability. The combination of nuclei would cease only when they were protected by a screen of similar electrons, of which the sign might be positive or negative, but could not be both; that is, the resulting atoms could not be of opposite varieties. Thus the outlying satellites are all of one sign, either in every case or in so vast a preponderance of cases that no exceptions are as yet manifest. The free lifetime of the less plentiful variety would be too brief for ordinary detection, but it is suggested that by means of the shattering of nuclei and rapid methods of detection, the composite nature of the proton may possibly be demonstrated by the emission of something fractional of extreme instability. In this connexion, attention is directed to the fact that the atomic bombardment of aluminium yields particles of specially long range.

A. A. E.

Motions of Electrons in Argon and Hydrogen. J. S. TOWNSEND and V. A. BAILEY (*Phil. Mag.*, 1922, [vi], **44**, 1033—1052; cf. this vol., ii, 277, 494).—Further measurements have been made of the movement of electrons in argon and hydrogen, and in mixtures of the two gases, in a uniform electric field. The velocity of the electrons (W) in the direction of the electric force, their mean velocities of agitation in the gas (u), their mean free path (l), the

loss of energy on collision with a gas molecule (λ), and the factor (k) by which the energy of agitation of an electron exceeds the energy of a molecule of gas at 15° , are given for varying values of Z/p , where Z is the fall in potential in volts, and p is the gas pressure in millimetres. The loss in energy of an electron on collision with a molecule of argon is extremely small. When moving with a velocity of agitation of 12.6×10^7 cm. per sec., the fraction of energy lost by an electron on collision with a molecule is 1.6×10^{-5} in argon, 5×10^{-2} in nitrogen, and 4×10^{-2} in hydrogen, and the corresponding mean free paths are 0.147 cm. in argon, 0.029 cm. in nitrogen, and 0.035 cm. in hydrogen, the gases being at 1 mm. pressure.

In the case of argon, whereas W increases steadily with increase in Z/p , u increases to the constant value, 20.7×10^7 cm. per sec. Between the values of Z/p , 1.25—15, the velocity of agitation remains practically constant, whilst the loss of energy on collision steadily increases. This is due to a large loss in energy in collisions with velocities greater than the mean. The free path of an electron in argon at 1 mm. pressure has a maximum value of 1.6 cm. for the velocity 3.75×10^7 cm. per second, whereas the mean free paths of nitrogen and hydrogen show minima in the neighbourhood of 8×10^7 cm. sec. The large increases in the mean free paths of the electrons as the velocity diminishes are very striking.

The addition of argon to hydrogen, whilst reducing W , the velocity in the direction of the electric force, scarcely affects u , the mean velocity of agitation of the electrons. This is in agreement with the small loss in energy on collision with a molecule of argon. The mean free paths in argon, for velocities of agitation less than 11.5×10^7 cm. per second, were found by measurement of the mean free paths in mixtures of hydrogen and argon. W. E. G.

The Motion of Electrons in Carbon Dioxide. M. F. SKINKER (*Phil. Mag.*, 1922, [vi], 44, 994—999).—The apparatus used was similar to that of Townsend and Bailey (cf. this vol., ii, 277, 494). Curves are given comparing the speed of electrons in carbon dioxide, nitrogen, and hydrogen. Values for the mean free path of the electron, its speed in the direction of the electric force, its velocity of agitation, and the proportion of energy lost on collision with a molecule of gas, are tabulated against different values of Z/p (cf. Townsend and Bailey, preceding abstract). A sudden increase in the loss of energy which occurs on collision between an electron and a molecule of carbon dioxide is observed between the velocities of agitation 13×10^7 and 15×10^7 cm. per second. W. E. G.

The Constitution of the Chemical Elements. FRIEDRICH WÄCHTER (*Z. anorg. Chem.*, 1922, 123, 1—13).—A theoretical paper. The author assumes that the light ether is a ponderable gas, an atom of which has a mass $1/1800$ the mass of an atom of hydrogen. He regards the elements as different condensation forms of the light ether, the number of ether atoms in an atom of any element being 1800 times the atomic weight of the element. This is applied to the atomic heat of elements and to the spectral lines. W. T.

The Disintegration of Chemical Elements. FRIEDRICH WÄCHTER (*Z. anorg. Chem.*, 1922, **123**, 14—30).—A theoretical paper. The author assumes that hydrogen and helium atoms are made up of light ether atoms, and that other elements are built up of hydrogen and helium atoms. He then endeavours to explain the disintegration of the radio elements. W. T.

Electronic Structures of Atoms. MAURICE L. HUGGINS (*J. Physical Chem.*, 1922, **26**, 601—625).—A theoretical paper in which the Lewis hypothesis of valency and atomic structure is assumed to be correct for the lighter atoms. The evidence in favour of a tetrahedron of electron pairs, rather than a cube of single electrons, being the most stable arrangement for the valency shell of these atoms, is put forward. It is shown how the stability of such an arrangement may be the result of the deviation of the force law between two electrons from Coulomb's law at small distances. The chief requirement for this purpose is that as two electrons approach each other, the repulsion between them reaches a maximum at a distance of the order of magnitude of 1 Å., the force then decreasing, for a considerable proportion of the remaining distance at least. As a result of a law of this type, whenever two electrons, forming part of an atomic shell, are forced close enough together, they come still closer to each other that is, the pair off, and similarly from three pairs aided by the attraction of an atomic nucleus and the repulsion of other electrons, triplets are formed. Based on this assumption and on the idea that the electrons in an atomic shell tend to place themselves opposite the centres of the faces of the imaginary polyhedron formed by the electron groups in the next underlying kernel shell, an arrangement of electrons is obtained for each element in each valency stage, with a few exceptions which have not yet been deduced. These arrangements conform with the known properties of the elements, and account for the periodic relationships in a simple and logical manner. J. F. S.

Bohr's Model of the Hydrogen Molecules and their Magnetic Susceptibility. KÔTARÔ HONDA (*Nature*, 1922, **110**, 664—665).—Since, according to Langevin, hydrogen molecules should have a paramagnetic susceptibility, it has hitherto been assumed that Bohr's model does not explain the diamagnetic property of the gas. The actual diamagnetic susceptibility, as determined by Soné, is shown to lie between the two values calculated when the validity of Bohr's model is assumed in the case of $n+n'=1$ and $n+n'=2$, where n and n' are the azimuth and radial quantum numbers. A. A. E.

The Normal Helium Atom and the Quantum Theory. J. H. VAN VLECK (*Phil. Mag.*, 1922, [vi], **44**, 842—869).—A study is made of the Kemble model of the helium atom. In this model the two electrons are arranged with axial symmetry. The energy of this atom has been computed, and the calculation has given a value of 20.7 volts for the ionisation potential, instead of 25.4

demanding by experiment, the discrepancy being slightly greater than for the Bohr model. It does not seem possible to devise a satisfactory symmetrical model of helium based on the conventional quantum theory of atomic structure.

W. E. G.

The Neuburger Nuclear Model. MAXIMILLIAN CAMILLO NEUBURGER (*Physikal Z.*, 1922, **23**, 389).—A reply to Meitner (cf. this vol., ii, 702). The author's model of the structure of the atomic nucleus is not dependent on the existence of isohelium in the free state. The nuclear formula requires, however, that groups, composed of three hydrogen nuclei and an electron, shall be capable of existence in the nucleus itself.

W. E. G.

Negative Valency and Co-ordination Number. E. A. SCHILOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 281—290).—The most pronounced negative affinity is accompanied by non-metallic properties, so that, if it is assumed that negative affinity is the result of a tendency of the rings of valency electrons to attain saturation, it becomes necessary to make the supplementary assumption that only non-metallic rings of a special type exhibit such tendency. It is suggested that the origin of complex compounds may be represented on an analogous principle, co-ordinative affinity arising as a result of the tendency towards saturation of non-dissociating, non-metallic atomic skeletons.

T. H. P.

Quanta of the Ideal Monatomic Gas. K. SCHAPOSCHNIKOV (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 105—124).—A mathematical paper, in which the quantum theory is applied to gases at high and at low temperatures.

T. H. P.

Chemical Constants of some Diatomic Gases. J. R. PARTINGTON (*Phil. Mag.*, 1922, [vi], **44**, 988—993).—The investigations of Sackur (cf. A., 1913, ii, 128), and Tetrode (*Ann. Physik*, 1912, [iv], **38**, 434; **39**, 225) on the chemical constants of monatomic gases have been extended to the case of a hypothetical diatomic molecule. In the first case considered, the gas molecule is assumed to consist of two identical atoms rigidly attached to each other at a fixed distance apart. The method of calculation is based on generalised statistical mechanics, and it is shown that the following equation holds over a certain range of temperatures, $C = 2.5 \log M + 2 \log K + 12.730$, where K = radius of gyration and M the molecular weight. This gives values for the chemical constants $C_o = 1.001$, $C_N = 0.904$, and $C_E = -2.255$. On account of the very small mass and diameter of the hydrogen molecule, hydrogen should behave in a manner intermediate between that of a monatomic and a diatomic gas. In the second case, that of two different atoms rigidly bound together, it is necessary to add $\log 2$ to the above equation, and $C_o = 1.205$, and $C_{No} = 1.263$. These results are in all cases of the right order.

W. E. G.

A New Apparatus for Washing Gases. A. ERNST (*Chem. Listy*, 1922, **16**, 274—276).—The tube leading the gas to be purified

into the washing bottle is surrounded by a long spiral, along which the gas has to make its way and is thus well washed. The tube leading in the gas and the spiral are easily removed from the vessel.

W. T.

Protection of Brass Weights. J. J. MANLEY (*Phil. Mag.*, 1922, [vi], 44, 948—950).—The method introduced by Faraday for protecting iron from rust has been employed for protecting brass weights. A satisfactory method of procedure is to cover the weight with a thin film of linseed oil, and heat it, appropriately supported in a covered "vitreosil" crucible or closed muffle, until the weight assumes a golden tint. The protecting film which is formed is tough and may be polished. The weight of 1 sq. cm. of normal film is 0.00005 gram.

W. E. G.

Lecture Experiments with Hydronitric [Hydrazoic] Acid and the Trinitrides [Azides]. A. W. BROWNE and A. B. HOEL (*J. Amer. Chem. Soc.*, 1922, 44, 2116—2119).—A series of lecture experiments with azoimide is described which includes the following. *Nitridation of hydriodic acid*: 5 c.c. of hydriodic acid (*d* 1.5) are placed in a 15 cm. test-tube and 1 c.c. of 1% hydrazoic acid is added when both iodine and nitrogen are liberated according to the equation $N_3H + 2HI = NH_3 + N_2 + 2I$. This experiment illustrates the similarity between hydrazoic acid and hydrogen peroxide. *Nitridation of hydrochloric acid*: 5 c.c. of hydrochloric acid are treated with 1 c.c. of 1% hydrazoic acid and raised to the boiling point for one minute; the contents of the tube are then poured into 2½ litres of water containing starch and potassium iodide, when the free chlorine liberates iodine. The reaction is represented by the equation $N_3H + 2HCl = NH_3 + Cl_2 + N_2$. *Formation of potassium manganate by the action of potassium azide on manganese dioxide*: 0.5 gram of finely powdered potassium azide and 0.5 gram of manganese dioxide are mixed and gently heated in a 100 c.c. porcelain crucible covered by a 200 c.c. crucible. The reaction is violent and proceeds with a hissing noise and the emission of numerous sparks. When the reaction has moderated, the larger crucible is removed and the heating continued for a short time. After cooling the mass, it is thrown into 2½ litres of water, when the green solution produced speedily changes to that of a permanganate solution. In this experiment it is advisable that the operator should not come too close to the crucible at the commencement of the experiment. *Detonation of silver azide by means of a fuse consisting of paper impregnated with potassium azide*: Silver azide, prepared by adding a dilute solution of silver nitrate cautiously to 25 c.c. of a 1% solution of hydrazoic acid, filtering and washing with water, is made into a thin disk 18 mm. diameter and 1 mm. thick, while still moist. This is then stuck on a piece of filter-paper prepared as follows: a strip 0.5—1.0 cm. wide and 0.25—0.50 metre long is painted on a filter-paper by means of a small brush dipped in a 5% aqueous solution of potassium azide and dried. The disk of silver azide is attached to one end of the strip and the whole thoroughly dried. The dried paper is then suspended and a glowing

splint brought in contact with the end of the strip removed from the silver azide; the combustion gradually progresses toward the silver azide, which finally detonates with a sharp report. J. F. S.

Inorganic Chemistry.

Diffusion of Hydrogen and Helium through Silica Glass and other Glasses. G. A. WILLIAMS and J. B. FERGUSON (*J. Amer. Chem. Soc.*, 1922, **44**, 2160—2167).—The rate at which hydrogen and helium, respectively, leak into evacuated tubes of silica glass, pyrex glass, and Jena glass has been determined at a series of temperatures and pressures. It is shown that silica glass is permeable to hydrogen at high temperatures. The permeability is proportional to the gas pressure and is an exponential function of the temperature. It becomes appreciable at 300°. Silica glass is similarly permeable to helium, and this is easily measurable at 182°. At 500°, the permeability for helium is about twenty-two times that for hydrogen. Neither pyrex glass nor Jena combustion glass was found to be permeable to hydrogen, but apparently hydrogen reacts with pyrex glass causing it to blacken. At 610°, pyrex glass is permeable to helium. The permeabilities of a number of samples of glass have been determined and the results compared with those of Wüstner (*Ann. Phys.*, 1915, [iv], **46**, 1095) and others. J. F. S.

The Solubility of Oxygen in Various Organic Solvents. FRANZ FISCHER and GEORG PFLEIDERER (*Z. anorg. Chem.*, 1922, **124**, 61—69).—The solubility was determined by pumping the gas from the saturated solution by means of a mercury-air pump and measuring the amount obtained. The results embodying the solubility of oxygen in sixteen organic solvents are tabulated; the specific gravities and vapour pressures are also given. W. T.

A New Form of Ozoniser. H. NĚMEČEK (*Chem. Listy*, 1922, **16**, 276).—Two stout copper wires serve as electrodes in a horizontal glass cylinder, the arrangement being such that the distance between the electrodes can be varied. The energy can be obtained by means of a Rhumkorff's coil or an electric machine. W. T.

Hydrophobic and Hydrophilic Sols of Sulphur. H. FREUNDLICH and P. SCHOLZ (*Koll. Chem. Beihefte*, 1922, **16**, 234—266).—The behaviour of the hydrophobic and several hydrophilic sols of sulphur has been compared. As a markedly hydrophilic sol, that investigated by Odén, and prepared by the interaction of hydrogen sulphide and sulphur dioxide, and by the decomposition of thionic acids, has been considered, and as a hydrophobe sol, that prepared by Weimarn by pouring an alcoholic

solution of sulphur into water, is considered. The Weimarn sulphur sol has been shown to be completely hydrophobic; it is negatively charged and is coagulated by electrolytes according to the general laws concerning the coagulation of hydrophobic sols, namely, the strong influence of the absorbability and valency of the kations, the strong effect of the hydrogen-ion, and the slight effect of the hydroxyl-ion. The sols may only be prepared in relatively small concentrations, the coagulum is not peptised by washing with water, and the sols may be preserved for a day or two only. In keeping with Odén's results, the coagulation of Odén's sol is markedly different from that of Weimarn's sol, as is demanded by its greater hydrophilic behaviour. The difference is mainly shown in the following points: (i) alkali salts have a ten to twenty times weaker coagulating action than with Weimarn's sol; (ii) the lyotropic series of the kations is well defined; lithium-ions have a very weak coagulating action, whilst sodium-, potassium-, rubidium-, and cæsium-ions are markedly and increasingly stronger; (iii) acids have a still weaker coagulating action than the alkali salts; (iv) alkalis convert the Odén sol into one which has similar properties to the hydrophobic Weimarn sol. The assumption that the micellæ of Weimarn's sol consist of λ -sulphur and those of Odén's sol of μ -sulphur is insufficient to explain these differences; for neither the behaviour towards acids nor that towards bases is in the least explained by the above assumption, whilst a very possible explanation is that Odén's sol contains pentathionic acid, whereas Weimarn's sol does not. The presence of pentathionic acid in Odén's sol is proved by the following data: (i) the acid can be detected in the filtrate from coagulated sulphur by the fact that on the addition of alkali more sulphur is deposited; (ii) prolonged action of alkali on coagulated sulphur or sulphur micellæ brings about the formation of thiosulphate; this action is brought about by ammonia without the sulphur itself being markedly attacked. It is probable that the pentathionic acid is adsorbed in the sulphur particles, since this substance is very difficult to remove by washing. The quantity of pentathionic acid bound to the sulphur is found to be 0.1–0.7 millimol. per gram of sulphur. The influence of pentathionic acid on the stability of Odén's sol is explained as follows. This acid has a constitution which is closely related to that of water and sulphur and therefore it facilitates the formation of micellæ, which, in addition to sulphur and pentathionic acid, contain large quantities of water. The greater water content of Odén's sol is manifested by its greater transparency when compared with Weimarn's sol of equal sulphur content. The micellæ are to be represented in Odén's sol by the

formula $\begin{array}{c} S\mu \\ \boxed{S_5O_6H_2} \\ H_2O \end{array} S_5O_6''$, and in Weimarn's sols by $\begin{array}{c} S\lambda \\ \boxed{H_2O} \end{array}'$. The

structure of the micellæ of Odén's sol explains the behaviour on coagulation as regards the following points: (i) alkalis decompose the pentathionic acid, whereby the loose combination

between the sulphur and water is also disturbed and converted into one which is similar to that of the Weimarn sol; (ii) acids have such a feeble coagulating power because they increase the stability of the pentathionic acid and produce more pentathionic acid from the pentathionates which may be present. The structure also is in keeping with the fact that hydrogen sulphide has an action on the sol similar to that of the alkalis; that is, it converts it into an hydrophobic sol which is much less stable because the pentathionic acid is decomposed by hydrogen sulphide with separation of sulphur. Further, sols of the same nature as Odén's sol are obtained by reactions which produce both sulphur and pentathionic acid; for example, the decomposition of sulphur monochloride by water: $5\text{S}_2\text{Cl}_2 + 6\text{H}_2\text{O} = 5\text{S} + \text{H}_2\text{S}_5\text{O}_6 + 10\text{HCl}$. The stability of Odén's sol, which is due to pentathionic acid, does not depend on the charge of the micellæ. Whether or no Odén's sol contains S_μ cannot be definitely answered, although the yellow colour of the sol makes it extremely likely that this variety of sulphur is present. J. F. S.

The Existence of Sulphur Tetroxide. FRIEDRICH MEYER, GUSTAV BAILLEUL, and GERHARD HENKEL (*Ber.*, 1922, 55, [B], 2923—2929).—The experiments described owed their origin to a desire to examine Berthelot's sulphur heptoxide more fully, and as a considerable quantity of the product was desired, the original method was modified by submitting a current of sulphur dioxide and oxygen to the silent electric discharge instead of working with a fixed volume of the gases. Contrary to Berthelot's statements, the product which is formed does not appear to have an appreciable vapour tension even at 20° . The crystalline substance described by Berthelot is only formed when analysis shows that sulphur trioxide is present in excess. On the other hand, an amorphous product is obtained the analyses of which sometimes agree with the formula, S_2O_7 , but sometimes show more oxygen than is required by this expression. The latter substance has been prepared in a specially designed discharge tube (which is figured in the original), which is so constructed that it is sufficiently small and light to be weighed on an analytical balance, that it can be evacuated and kept vacuous, and has little dead space. The material, thus prepared in the tube from sulphur dioxide and oxygen, is weighed and analysed in situ. For the latter purpose, it is treated with an aqueous solution of potassium iodide with which, at a sufficiently low temperature, it reacts with unexpected slowness and with the liberation of a very small proportion of oxygen. The latter is measured together with the liberated iodine and sulphuric acid. The highest stage of oxidation yet reached corresponds with the formula, $\text{SO}_3 \cdot 2\text{SO}_4$. The authors, however, do not consider that this product represents the most highly oxidised form of sulphur which is possible, since in their work up to the present the imparted energy has not been sufficiently great in proportion to the volume of gas employed.

It appears possible that Berthelot's sulphur heptoxide is a

mixture of sulphur trioxide and sulphur tetroxide in equimolecular ratio. H. W.

The Isotopes of Selenium and some other Elements. F. W. ASTON (*Nature*, 1922, 110, 664).—Very satisfactory mass-spectra have been obtained in the case of selenium by vaporising the element in the discharge tubes. Selenium is shown to consist of six isotopes, giving lines at 80, 78, 76, 82, 77, and 74, respectively, in decreasing order of intensity. The results agree with the atomic weight as determined by chemical methods, and measurement of the lines shows no detectable deviation from the whole-number rule. The mass spectra of cadmium and tellurium could not be obtained by this method, but the experiments have incidentally shown that chlorine has no isotope of mass 39, and that aluminium is a simple element of mass 27. Two new isotopes of xenon, 124 and 126, making nine in all, are found to exist in minute amounts. The first of these is isobaric with tin, and the selenium lines 78, 80, and 82 are isobares of krypton; it is noted that all isobares so far discovered have even atomic weights. A. A. E.

Action of Compounds of Nitric Oxide and Hydroxylamine on Trisodium Arsenite. A. GUTMANN (*Ber.*, 1922, 55, [B], 3007—3012).—The oxidation of sodium arsenite to arsenate by sodium benzenediazoxide (which is not effected by the *iso*-diazoxide) has been attributed previously to the presence of a reactive, labile quadrivalent oxygen atom (A., 1912, i, 397; 1915, i, 127); an extension of the observations to a series of derivatives of nitric oxide and hydroxylamine indicates that sodium arsenite is a specific reagent for active oxygen.

Nitric oxide oxidises sodium arsenite in accordance with the equation: $2\text{NO} + \text{Na}_3\text{AsO}_3 = \text{N}_2\text{O} + \text{Na}_3\text{AsO}_4$; a similar change occurs when an excess of sodium arsenite is added to a solution of nitric oxide in freshly prepared, strongly alkaline potassium sulphite solution. Nitrosobenzene does not react with sodium arsenite at the atmospheric temperature but at the temperature of the boiling water-bath gives azoxybenzene and sodium arsenate.

The constitutions $\begin{smallmatrix} \text{N}\cdot\text{O} \\ | \quad | \\ \text{N} \quad \text{O} \end{smallmatrix}$ and $\begin{smallmatrix} \text{Ph}\cdot\text{N}\cdot\text{O} \\ | \quad | \\ \text{Ph}\cdot\text{N}\cdot\text{O} \end{smallmatrix}$, are suggested for nitric oxide

and nitrosobenzene, respectively. Sodium nitroprusside does not appear to react with sodium arsenite. With hydroxylamine, the reactions $\text{NH}_2\cdot\text{OH} + \text{Na}_3\text{AsO}_3 = \text{Na}_3\text{AsO}_4 + \text{NH}_3$ and $3\text{NH}_2\cdot\text{OH} = \text{NH}_3 + \text{N}_2 + 3\text{H}_2\text{O}$ occur concurrently. β -Phenylhydroxylamine gives sodium arsenate, aniline, and azoxybenzene, $4\text{NHPh}\cdot\text{OH} + \text{Na}_3\text{AsO}_3 = \text{Na}_3\text{AsO}_4 + 2\text{NH}_2\text{Ph} + \text{O} < \begin{smallmatrix} \text{NPh} \\ | \\ \text{NPh} \end{smallmatrix} + 2\text{H}_2\text{O}$, whereas the iso-

meric *p*-aminophenol is inactive. β -Ethylhydroxylamine, on the other hand, appears to give only arsenite and ethylamine. Dimethylaniline-*N*-oxide and sodium arsenite readily yield dimethylaniline and sodium arsenate. Quinine-*N*-oxide similarly gives quinine and sodium arsenate; the two oxides are therefore peroxidic in character. H. W.

Properties and Structure of Pernitric Acid. IV. TRIFONOV (*Z. anorg. Chem.*, 1922, **124**, 123—135).—Pernitric acid is formed by the action of hydrogen peroxide on an acidified nitrite solution; low temperature and low concentration are not essential for its formation. Above 70°, it decomposes rapidly. The per-acid can be estimated by the addition of potassium bromide in dilute solution, and the liberated bromine estimated by means of a potassium iodide solution. The author finds that the reaction of formation is represented by the equation $2\text{HNO}_2 + 3\text{H}_2\text{O}_2 + (n-1)\text{H}_2\text{O} = \text{N}_2\text{O}_6 \cdot n\text{H}_2\text{O} + 3\text{H}_2\text{O}$, and not as given by Raschig (*Ber.*, 1907, **40**, 4585) or Schmidlin and Massini (*A.*, 1910, ii, 498). It thus receives the formula $\text{NO}_2 \cdot \text{O} \cdot \text{O} \cdot \text{NO}_2 \cdot n\text{H}_2\text{O}$. The reactions of pernitric acid with some organic compounds are given. W. T.

Phosphorus. W. MARCKWALD and K. HELMHOLTZ (*Z. anorg. Chem.*, 1922, **124**, 81—104).—The authors find the melting point of scarlet phosphorus to be $592.5 \pm 0.5^\circ$, and the critical temperature of the yellow modification to be 720.6° . Rapid cooling of phosphorus vapour deposits a mixture of the yellow and scarlet forms; slow cooling deposits the pure yellow modification. To explain this the authors assume that phosphorus vapour at 900° and 120 mm. pressure consists of P_4 molecules and 10% P_2 molecules. On cooling, the P_2 and P_4 molecules combine to form the complex molecules of scarlet phosphorus and this is to a certain extent deposited. Slow cooling, however, allows the scarlet phosphorus vapour to change into the vapour of the yellow form. The phenomenon observed on cooling liquid scarlet phosphorus is explained as follows. The liquid contains molecules of 'yellow' (P_4) and scarlet (P_x) phosphorus in equilibrium: $n\text{P}_4 \rightleftharpoons m\text{P}_x$. Above 592.5° , most of the molecules are P_4 and on rapid cooling these solidify, giving the yellow variety. Slow cooling allows of a change of equilibrium to the right and therefore a deposit of the scarlet form on solidification. It is shown that the crystals isolated from a melt of the scarlet variety are identical with Hittorf's phosphorus. Black phosphorus changes into the scarlet form on being heated at 575° . W. T.

The Toxic Properties of Commercial Ferrosilicon. N. KURNAKOV and G. URASOV (*Z. anorg. Chem.*, 1922, **123**, 89—131).—Commercial ferrosilicon has been found to evolve poisonous and explosive gases. The alloys containing about 50% silicon, which is attacked by water, are very dangerous. The authors found that a solid phase of variable composition, *lebeauite*, makes its appearance in iron-silicon alloys with 33.4 to 100% by weight of silicon; *lebeauite* solidified at 1245° . *Lebeauite* can form ternary and quaternary solid solutions with phosphorus and aluminium. The ternary solid solutions (Fe, Si, P, and Fe, Si, Al) of *lebeauite* are stable towards water. The quaternary solution (Fe, Si, Al, P) is, however, attacked by water, phosphine being evolved. Ferrosilicon with less than 33.4% silicon in γ -iron can dissolve phosphorus and aluminium to the extent of 1.7% and 3%, respectively.

These ternary and quaternary solid solutions resist the action of water. Calcium phosphide will not dissolve in solid or liquid ferrosilicon. W. T.

The Mechanism of the Formation of Silane from Magnesium Silicide. I. ROBERT SCHWARZ and ERICH KONRAD (*Ber.*, 1922, 55, [B], 3242—3252).—The decomposition of magnesium silicide by aqueous hydrochloric acid leads ultimately to the production of a solid, white substance, $\text{H}_2\text{Si}_2\text{O}_3$, which shows all the properties of dioxodisiloxan. The substance, however, cannot be a primary product of the decomposition of the silicide, but is to be regarded as the final result of a series of intermediate reactions which cannot be followed in purely aqueous solution. Attempts are therefore made to arrest the reaction at intermediate stages by replacing the water to a greater or less extent by alcohol. Under these conditions, monosilane is not evolved during the first period of the action, and the solid product contains magnesium, which cannot be removed by washing, but is free from chlorine. It is a colourless substance (the usual brown tint is due to admixed elementary silicon) which explodes on contact with air, yielding silicon and silicon dioxide, is decomposed by water, decolorises potassium permanganate and alcoholic bromine, and reduces silver nitrate. Analysis of it gives the ratio $\text{Si} : \text{Mg} : \text{H} = 1 : 2 : 2$. The primary hydrolysis of magnesium silicide may therefore be expressed by the equation: $\text{Mg}_2\text{Si} + 2\text{H}\cdot\text{OH} = \text{H}_2\text{Si}(\text{Mg}\cdot\text{OH})_2$. In these circumstances, not more than 15% of the silicon actually present is found in the solid product, whilst also none escapes as monosilane. The remainder is found as a stable alcohol sol of silicic acid. A second reaction must therefore have occurred, possibly in accordance with the scheme: $\text{Mg}_2\text{Si} + 4\text{HCl} + 2\text{H}_2\text{O} = 4\text{H}_2 + 2\text{MgCl}_2 + \text{SiO}_2$, whereby account is rendered of the evolution of hydrogen. Approximately 10% of the magnesium silicide is decomposed in accordance with the first and about 90% in accordance with the second equation.

Many attempts have been made by varying the concentration of the alcohol and shortening the period of the action of the acid on the silicide to isolate other compounds intermediate between the primary product and the ultimate silicoformic anhydride. With increasing dilution of the alcohol, the production of silanes increases, but very little definite information is afforded by analysis of the solids. They can only be regarded as mixtures formed by further hydrolysis of the primary product, which they resemble in their ready inflammability on exposure to air. It appears probable that the initial product suffers further hydrolysis in two directions such as are suggested by the schemes: $\text{SiH}_2(\text{Mg}\cdot\text{OH})_2 + 2\text{H}\cdot\text{OH} = 2\text{Mg}(\text{OH})_2 + \text{SiH}_4$ and $\text{SiH}_2(\text{Mg}\cdot\text{OH})_2 + \text{H}_2\text{O} + 4\text{HCl} = 2\text{MgCl}_2 + 2\text{H}_2\text{O} + \text{SiH}_2\text{O} + 2\text{H}_2$.

Magnesium silicide is prepared by igniting an intimate mixture of finely-divided, ignited quartz and magnesium powder in an atmosphere of hydrogen and mechanical separation of the crystals of the silicide from the mixture. The crude product is freed from

admixed magnesium by the action of ethyl bromide and anhydrous ether. The purified material is a uniform, steel-blue, crystalline powder which contains traces of amorphous silicon and iron silicide. The apparatus used in studying the decomposition of the silicide is fully figured and described in the original. H. W.

Pressure of Saturated Carbonyl Chloride Vapour. N. I. NIKITIN (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 235—249).—The vapour pressure of carefully purified carbonyl chloride has been measured at a number of temperatures ranging from 12.6° to -99° . The pressure has the value 889.2 mm. at 12.6° , and diminishes rapidly with fall of temperature to 540.4 mm. at -0.41° , and then continually more slowly; at -19.43° , the value is 232.2 mm. and at -94.2° a few tenths of a millimetre. T. H. P.

Interaction of Carbon Tetrachloride and Fuming Sulphuric Acid. A. I. LEPIN (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 1—17).—The author has investigated the mechanism of the formation of carbonyl chloride and chlorosulphonic acid from carbon tetrachloride and fuming sulphuric acid (cf. Schützenberger, *Annalen*, 1870, **154**, 375; Armstrong, *J. pr. Chem.*, 1870, [ii], **1**, 246; Erdmann, A., 1893, i, 681). If the fuming acid contains 45% of dissolved sulphur trioxide, corresponding with the formula $\text{H}_2\text{S}_2\text{O}_7$, the reaction is expressed by the equation, $\text{CCl}_4 + \text{H}_2\text{SO}_4 \cdot \text{SO}_3 = \text{COCl}_2 + 2\text{SO}_3\text{HCl}$. If less than 45% of dissolved trioxide is present, so that the acid may be regarded as a solution of fuming in monohydrated acid, the fuming acid acts as above, the excess of monohydrate remaining together with the secondary product, chlorosulphonic acid. Finally, if the dissolved sulphur trioxide exceeds 45%, the acid may be considered as a mixture of pyrosulphuric acid with sulphur trioxide. In this case, part of the carbon tetrachloride reacts according to the equation $\text{CCl}_4 + \text{H}_2\text{SO}_4 \cdot \text{SO}_3 = \text{COCl}_2 + 2\text{SO}_3\text{HCl}$, and part according to $\text{CCl}_4 + 2\text{SO}_3 = \text{COCl}_2 + \text{S}_2\text{O}_5\text{Cl}_2$; both these reactions proceed quantitatively. T. H. P.

Reaction between Potassium Azide and Iodine in the Presence of Carbon Disulphide. A. W. BROWNE and A. B. HOEL (*J. Amer. Chem. Soc.*, 1922, **44**, 2106—2116).—Potassium azide reacts with iodine in the presence of carbon disulphide, with the formation of potassium iodide and the liberation of nitrogen. The first stage in this reaction consists in the formation of potassium azidodithiocarbonate, $\text{KS} \cdot \text{CS} \cdot \text{N}_3$, by interaction of potassium azide and carbon disulphide, as expressed by the equation $\text{KN}_3 + \text{CS}_2 = \text{KS} \cdot \text{CS} \cdot \text{N}_3$. This reaction is irreversible, consequently there is no regeneration of carbon disulphide after it has once reacted. The second stage consists in the reaction between potassium azidodithiocarbonate with iodine, which results in the precipitation of azidocarbon disulphide $\text{S}_2(\text{CS} \cdot \text{N}_3)_2$ according to the equation $2\text{KS} \cdot \text{CS} \cdot \text{N}_3 + 2\text{I} = \text{S}_2(\text{CS} \cdot \text{N}_3)_2 + 2\text{KI}$. The halogenoid substance azidocarbon disulphide liberates triatomic nitrogen from potassium azide, with resultant evolution of ordinary nitrogen, as shown by the equations $2\text{KN}_3 + \text{S}_2(\text{CS} \cdot \text{N}_3)_2 = 2\text{KS} \cdot \text{CS} \cdot \text{N}_3 + 2\text{N}_3$; $2\text{N}_3 = 3\text{N}_2$.

Combination of these equations with the preceding one leads to the simple expression of the final result obtained when carbon disulphide, potassium azidodithiocarbonate, or azidocarbon disulphide, in relatively small amount, is brought into contact with a solution containing potassium azide and iodine. These results have been confirmed by iodometric and nitrometric determinations: $2\text{KN}_3 + 2\text{I} = 2\text{KI} + 3\text{N}_2$. J. F. S.

Potassium Azidodithiocarbonate. A. W. BROWNE and A. B. HOEL (*J. Amer. Chem. Soc.*, 1922, **44**, 2315—2320; cf. preceding abstract; Sommer, A., 1916, ii, 29).—Potassium azidodithiocarbonate may be prepared by the action of carbon disulphide on an aqueous solution of potassium azide at 40° . It is obtained in colourless, deliquescent crystals, which decompose quantitatively when gently heated, yielding potassium thiocyanate, sulphur, and nitrogen. When rapidly heated, the substance explodes, with the formation of potassium sulphide, carbon dioxide, and sulphur dioxide and trioxide in addition to the above. Solutions of the salt when treated with various oxidising agents or when electrolysed yielded azidocarbon disulphide $(\text{SCSN}_3)_2$. The authors confirm the structure, $\text{K}\cdot\text{S}\cdot\text{CS}\cdot\text{N}:\text{N}:\text{N}$, as assigned to it by Sommer (*loc. cit.*). W. G.

Melting and Freezing Point of Sodium Chloride. JOHN BRIGHT FERGUSON (*J. Physical Chem.*, 1922, **26**, 626—630).—The melting point and freezing point of sodium chloride have been determined by means of a platinum-platinum-rhodium thermometer. As the mean of a number of experiments, the value 803.1° is found for the freezing point and 803.4° for the melting point. The author recommends the value $803^\circ \pm 1^\circ$ as the best value for the freezing point. J. F. S.

The Properties of Ammonium Nitrate. IV. The Reciprocal Salt-pair, Ammonium Nitrate and Sodium Chloride. EDGAR PHILIP PERMAN (*T.*, 1922, **121**, 2473—2483).

Colloidal Calcium Hydroxide. M. VON GLASENAPP (*Kolloid Z.*, 1922, **31**, 195—196).—Two varieties of colloidal calcium hydroxide have been obtained from a marly dolomite of the composition CaO 22.75%, MgO 15.50%, Al_2O_3 7.68%, Fe_2O_3 1.87%, SiO_2 15.27%, CO_2 34.83%, H_2O 1.81%. The dolomite was burnt at 720 — 780° until the magnesium carbonate was entirely decomposed and the calcium carbonate half decomposed. After the burnt product had been kept for twelve hours in water, the two colloidal varieties of calcium hydroxide were microscopically visible. The primary product separates first from solution as small droplets which grow speedily, and pass into the secondary product which forms agglomerates of drops having the appearance of a cell network. Both colloids are optically isotropic but strongly refracting. In reflected light, the primary colloid is light blue and the secondary bright orange in colour. The secondary colloid does not maintain the colloidal state very long, but passes into crystalline calcium hydroxide. J. F. S.

Valency. XVI. The Ammonia Compounds of Calcium Haloids. GUSTAV F. HÜTTIG (*Z. anorg. Chem.*, 1922, **123**, 31—42).—The methods of investigation were as previously communicated by the author (*A.*, 1920, ii, 293 and 318). The following ammonia compounds were found to exist in the stable state:— $\text{CaCl}_2 \cdot 8\text{NH}_3$; $\text{CaCl}_2 \cdot 4\text{NH}_3$; $\text{CaCl}_2 \cdot 2\text{NH}_3$; $\text{CaCl}_2 \cdot \text{NH}_3$; $\text{CaBr}_2 \cdot 8\text{NH}_3$; $\text{CaBr}_2 \cdot 6\text{NH}_3$; $\text{CaBr}_2 \cdot 2\text{NH}_3$; $\text{CaBr}_2 \cdot \text{NH}_3$; $\text{CaI}_2 \cdot 8\text{NH}_3$; $\text{CaI}_2 \cdot 6\text{NH}_3$; $\text{CaI}_2 \cdot 2\text{NH}_3$, and $\text{CaI}_2 \cdot \text{NH}_3$.

These determinations were carried out at various temperatures ranging from -80° to 230° . The isothermal curves pressure-composition are given.
W. T.

The Solubilities of Calcite and Aragonite. HANS L. J. BÄCKSTRÖM (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **4**, No. 11, 1—11).—An account of work published more fully elsewhere (*A.*, 1921, ii, 317).
E. H. R.

Setting and Velocity of Solution of Burnt Gypsum. P. P. BUDNIKOV and JA. K. SYRKIN (*Bull. Inst. Polyt. Ivanovo-Voznesensk.*, 1922, **6**, 235—247).—The authors have investigated the velocities of dissolution of gypsum after the latter had been heated at various temperatures, the concentrations being determined at different stages of the dissolution by means of conductivity measurements. For the samples which have been heated at 115° and 125° , the conductivity and hence the solubility increases rapidly to a point corresponding with a solution considerably supersaturated with respect to $\text{CaSO}_4 \cdot \text{H}_2\text{O}$, and afterwards diminishes, at first rapidly and then slowly, but still indicates a certain degree of supersaturation after twenty-four hours. Supersaturated solutions are obtained also with gypsum heated at 400° , but not when a temperature of 500° is reached. In so far as the setting of gypsum is conditioned by crystallisation from supersaturated solutions, the temperature at which "dead-burnt" gypsum is formed may therefore be assumed to be about 450° .

Burnt gypsum may be regarded as consisting of two components, one soluble, which dissolves readily, and the other relatively insoluble. The solubility of samples which have been burnt at temperatures between 500° and 800° is rapid at first, this being explained by the presence of appreciable proportions of the soluble modification in dead-burnt gypsum.

The time occupied by dissolution does not furnish an exhaustive explanation of the disappearance of the ability of gypsum to set, and the authors suggest that the presence of the insoluble component in the interstices of the crystals prevents the latter from growing.
T. H. P.

The Silicates of Strontium and Barium. PENTTI ESKOLA (*Amer. J. Sci.*, 1922, [v], **4**, 331—375).—The author has determined the equilibrium diagrams of the binary systems SrO-SiO_2 and BaO-SiO_2 , respectively, and also certain characteristics (crystal-line system and habit, refractive indices and dispersion, cleavage and density) of the compounds and eutectics formed in these

systems. The corresponding diagram and characteristics in the case of the system CaO-SiO_2 are given for purposes of comparison. In the system SrO-SiO_2 , compounds $2\text{SrO}, \text{SiO}_2$ and SrO, SiO_2 were found, and these, together with SrO , occurred in one form only, although the temperature of formation of the silicates was varied from the melting point down to about 900° . SrO, SiO_2 was found to be closely isomorphous and optically very similar to $\alpha\text{CaO}, \text{SiO}_2$. Its crystals are apparently hemimorphic and belong either to the dihexagonal pyramidal or monoclinic domatic class, probably the latter. In the system BaO-SiO_2 , compounds $2\text{BaO}, \text{SiO}_2$, BaO, SiO_2 , $2\text{BaO}, 3\text{SiO}_2$, and $\text{BaO}, 2\text{SiO}_2$ were found. Of these, $2\text{BaO}, 3\text{SiO}_2$ and $\text{BaO}, 2\text{SiO}_2$ were found to be isomorphous, of orthorhombic symmetry, forming a complete series of solid solutions. The melting-point diagram of this series is of Roozeboom's type I, without maximum or minimum, and the index of refraction varies continuously, but not linearly with the composition. Barium metasilicate, BaO, SiO_2 , is not isomorphous with the calcium and strontium meta-silicates. It is optically biaxial, probably of orthorhombic symmetry, and forms no solid solutions with $\alpha\text{CaO}, \text{SiO}_2$, but a double compound, $2\text{CaO}, \text{BaO}, 3\text{SiO}_2$, is formed, which decomposes on heating into $\alpha\text{CaO}, \text{SiO}_2$ and liquid. Crystals of the double compound are uniaxial and negative, are probably hexagonal, and show good cleavages in their prismatic zone. Neither strontium nor barium metasilicate forms with magnesium metasilicate a double compound analogous to diopside. Felspars analogous to anorthite are formed by both strontium and barium. Strontium felspar and anorthite resemble one another very closely in optical properties, and the two appear to be completely miscible. Barium felspar is monoclinic and readily forms Carlsbad twins of the contact type.

J. S. G. T.

The System Ammonium Sulphate-Glucinum Sulphate-Water at 25° . HUBERT THOMAS STANLEY BRITTON (T., 1922, 121, 2612—2616).

Preparation and Properties of Magnesium Perchlorate and its Use as a Drying Agent. H. H. WILLARD and G. FREDERICK SMITH (*J. Amer. Chem. Soc.*, 1922, 44, 2255—2259).—The hexahydrate of magnesium perchlorate may be prepared by dissolving magnesia in perchloric acid, evaporating the solution until fumes of perchloric acid are evolved and crystallisation commences at the surface. The mass is then cooled to the ordinary temperature with the addition of sufficient water to keep the mass semi-fluid. The crystals are separated by centrifuging, redissolved in water, and crystallised. The hexahydrate, m. p. $145\text{--}147^\circ$, d_4^{25} 1.970, is now deliquescent. The trihydrate is prepared by keeping the hexahydrate over phosphoric oxide at $20\text{--}25^\circ$ for a month. The product has m. p. $145\text{--}147^\circ$, d_4^{25} 2.044. The anhydrous compound is obtained by heating either hydrate at 170° in a current of dry air for some time and then at 250° for a short time. Magnesium perchlorate decomposes at 400° without melting, forming a mixture of the oxide and chloride. When moist gas is

passed over anhydrous magnesium perchlorate at a rate not greater than 5 litres per hour, it is found to be as efficient a desiccating agent as phosphoric oxide. The trihydrate is as efficient as the anhydrous salt at 0°, but much less so at higher temperatures. J. F. S.

Crystal Structure of Cadmium Iodide. RICHARD M. BOZORTH (*J. Amer. Chem. Soc.*, 1922, **44**, 2232—2236).—The crystal structure of cadmium iodide has been investigated by means of X-ray spectra and Laue photographs. It is shown that cadmium iodide is not hexagonal, as has generally been supposed, but trigonal. The unit parallelepiped contains one molecule, and the shortest distance between the centres of the cadmium and iodine atoms is 3.00 Å.U., which is exactly the sum of the radii of these atoms as found by Bragg (A., 1920, ii, 537). Because of the nature of the structure, the iodine atoms are also "in contact" on the Bragg hypothesis. The shortest distance between their centres is 4.21 Å.U., whilst Bragg's value of the diameter of this atom is 2.80 Å.U. This separation indicates that the atoms which are presumably similarly charged may be expected to be farther apart than Bragg's hypothesis requires. The structure may be divided into electrically neutral layers by passing planes parallel to the base midway between the cadmium atoms, and this may well account for the excellent basal cleavage of the crystal. J. F. S.

The Ammoniates of Lead Haloids. Mixed Compounds and the Parent Salts. WILHELM BILTZ and WILHELM FISCHER (*Z. anorg. Chem.*, 1922, **124**, 230—247).—The following ammoniates of the haloids of lead are described in literature: $\text{PbCl}_2, 1.5\text{NH}_3$; $\text{PbCl}_2, 2\text{NH}_3$; $\text{PbBr}_2, 2\text{NH}_3$; $\text{PbI}_2, \text{NH}_3$; $\text{PbI}_2, 2\text{NH}_3$; and $\text{PbI}_2, 4\text{NH}_3$. The authors were able to show also the existence of the following: $\text{PbCl}_2, \text{NH}_3$; $\text{PbCl}_2, 3.25\text{NH}_3$; $\text{PbBr}_2, \text{NH}_3$; $\text{PbBr}_2, 3\text{NH}_3$; $\text{PbBr}_2, 5.5\text{NH}_3$; $\text{PbI}_2, 0.5\text{NH}_3$; and $\text{PbI}_2, 5\text{NH}_3$. The method of investigation was the same as that employed in previous work (cf. Hüttig, A., 1920, ii, 293, 318; this vol., ii, 849). The authors regard the compound $\text{PbCl}_2, 3.25\text{NH}_3$ or $4\text{PbCl}_2, 13\text{NH}_3$ as a mixed compound of the salts $\text{PbCl}_2, 8\text{NH}_3$, $\text{PbCl}_2, 2\text{NH}_3$, and $2\text{PbCl}_2, 3\text{NH}_3$. Similarly, $2\text{PbBr}_2, 11\text{NH}_3$ is a compound of $\text{PbBr}_2, 8\text{NH}_3$ and $\text{PbBr}_2, 3\text{NH}_3$, and $2\text{PbI}_2, 10\text{NH}_3$ a compound of $\text{PbI}_2, 8\text{NH}_3$ and $\text{PbI}_2, 2\text{NH}_3$. These mixed compounds are not characterised by great stability or by instability; methods of detecting their formation are desirable. W. T.

Action of Ammonium Nitrate and of Aqueous Ammonia on Copper. Properties of Cupric Tetrammine Nitrite and Nitrate. HENRY BASSETT and REGINALD GRAHAM DURRANT (T., 1922, **121**, 2630—2640).

The Solubility of Copper Hydroxide in Sodium Hydroxide Solutions. G. SVENSEN MELBYE (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1922, **4**, No. 8, 1—11).—The solubility of copper hydroxide in sodium hydroxide solutions between 2.65 and 6.6N increases at a linear rate with the concentration of sodium hydroxide according to the equation $[\text{Cu}(\text{OH})_2] = 0.045[\text{NaOH}] - 0.095$.

The solutions were prepared by running a solution of copper sulphate very gently into the sodium hydroxide solution until turbidity appeared, they were then filtered and analysed. Assuming that a true solution of a cuprate is formed of the composition $\text{Na}_2\text{Cu}_2\text{O}_3$ and that its degree of dissociation is equal to that of sodium silicate, the ion product of the labile cupric acid, $\text{H}_2\text{Cu}_2\text{O}_3$, is found to be $K_1 = 0.9 \times 10^{-17}$. For the hydrate H_2CuO_2 the ion product is $K_2 = 1.3 \times 10^{-18}$. The solutions of sodium cuprate gradually deposit cupric oxide on keeping.

E. H. R.

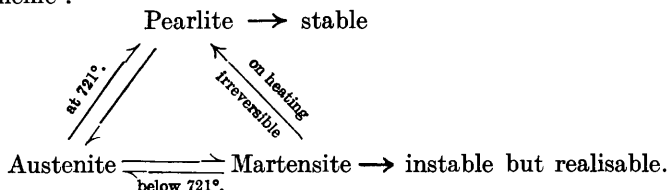
The Composition of Scheele's Green. G. BORNEMANN (*Z. anorg. Chem.*, 1922, **124**, 36—38).—The author finds that Scheele's green is not acid copper ortho-arsenite, CuHAsO_3 , but a normal arsenite, $3\text{CuO} \cdot \text{As}_2\text{O}_3 \cdot x\text{H}_2\text{O}$. The composition was found to vary with the method of preparation; the greater the excess of alkali employed the richer is the product in copper oxide.

W. T.

The Rate of Formation of some Nitrides. G. TAMMANN (*Z. anorg. Chem.*, 1922, **124**, 25—35).—The rate of increase in thickness of the nitride was measured by the change in colour of the films. In the case of cerium, lanthanum, and a mixture of the two, the rate of increase of the film plotted against the logarithm of the time gave two straight lines cutting in each case at a definite temperature. The same applies to the metals in oxygen. The presence of moisture in the gases greatly accelerates their action. The film of nitride on iron protects the metal. Cobalt, nickel, molybdenum, tungsten, tantalum, and silicon do not change in an atmosphere of nitrogen at 700° ; magnesium and calcium are converted into their grey nitrides.

W. T.

Honda's Conception of the A^1 Transformation and the Quenching of Steels. MASUMI CHIKASHIGE (*Z. anorg. Chem.*, 1922, **124**, 59—60).—A theoretical paper, in which the author criticises the views of Honda (*Sci. Rep. Tohoku Imp. Univ.*, 1919, **8**, 181), and claims that a better interpretation is given by the following scheme :



W. T.

The Ternary System Iron-Boron-Carbon. R. VOGEL and G. TAMMANN (*Z. anorg. Chem.*, 1922, **123**, 225—275).—The authors discuss the results of Hannesen (A., 1915, ii, 464) and Tschischevsky and Herdt (A., 1917, ii, 372), who investigated the system iron-boron. The disagreement of their results is found to be due to differences in the rate of cooling. Rapid cooling (as carried out by the former) results in the separation of supersaturated mixed crystals. The

present authors carried out a systematic study of the ternary system iron-boron-carbon and their results are given in detail. Equilibrium sets in so slowly that the structure and properties of the iron-boron-carbon alloys depend to a large extent on the preliminary heating. The limit of the influence of boron on the structure was found to be 0.02%.

W. T.

The Constitution of Erdmann's Salt and its Derivatives.

E. H. RIESENFELD and R. KLEMENT (*Z. anorg. Chem.*, 1922, **124**, 1—21).—The authors claim that Erdmann's salt, $[(\text{NO}_2)_4\text{Co}(\text{NH}_3)_2]\text{R}$, has the two ammonia molecules in the *cis*-position. They base their conclusions on the fact that (1) by the action of ethylenediamine the trinitro-ethylenediamine-monammine derivative is obtained, $[(\text{NO}_2)_3\text{Co en NH}_3]\text{R}$; (2) the dioxalato-diammine derivative, $[(\text{C}_2\text{O}_4)_2\text{Co}(\text{NH}_3)_2]\text{R}$, prepared from Erdmann's salt, could not be resolved into optical antipodes; (3) the non-resolvability again of the monoxalato-derivative, $[\text{C}_2\text{O}_4(\text{NO}_2)_2\text{Co}(\text{NH}_3)_2]$; (4) the ease with which the dichloro-derivative was prepared, $[(\text{NO}_2)_2\text{Cl}_2\text{Co}(\text{NH}_3)_2]$.

The oxalate group could not be replaced by the malonate radicle on account of the solubility and reducibility of the malonate. Methods of preparing the above derivatives are given.

W. T.

Preparation of Colloidal Solutions of Nickel and Cobalt Hydroxides and some other Compounds of these Metals.

O. F. TOWER and MARTHA C. COOKE (*J. Physical Chem.*, 1922, **26**, 728—735).—Two methods are described for preparing colloidal suspensions of nickel hydroxide, one by dialysing a solution of nickel tartrate in the presence of an alkaline solution of potassium tartrate, and the other by treating a *N*/10-solution of nickel chloride with a little more than the equivalent quantity of a solution of potassium hydroxide, allowing the precipitated nickel hydroxide to settle, siphoning off the supernatant liquid, adding water, and repeating the process several times. Only very weak suspensions of cobaltous hydroxide could be obtained by these methods. Any solids obtained from the solutions referred to in a previous work on this subject (*A.*, 1900, i, 587) are composed of nickel tartrate with potassium tartrate adsorbed in it. Glycerol does not prevent the precipitation of nickel hydroxide from aqueous solutions of nickel salts. In alcoholic solution, interesting transformations occur in the gel on keeping, and finally a solution is obtained from which nickel hydroxide cannot be precipitated by dilution with water. Colloidal solutions of nickel sulphide, which are readily formed in the presence of an alkaline solution of a tartrate, immediately decompose with precipitation of the sulphide on dialysing out the tartrate.

J. S. G. T.

Hydrated Oxides. IV. HARRY B. WEISER (*J. Physical Chem.*, 1922, **26**, 654—686; cf. this vol., ii, 575).—A continuation of previous work in connexion with the oxides of tin. It is shown that the so-called stannic and metastannic acids are not acids, but are hydrated stannic oxides the composition and properties of which are

determined by the conditions of formation. Stannic oxide, freshly prepared by precipitation from a solution of a stannic salt at the ordinary temperature, is a loose, highly hydrated mass which is readily peptised by dilute acids and alkalis, forming a colloidal solution, and is dissolved by concentrated acids and alkalis, forming salts. The oxide is more compact, less hydrated, less soluble, and less easily peptised the higher the temperature of formation. Freshly-prepared stannic oxide undergoes these changes on keeping at the ordinary temperature. Experiments on the peptisation by nitric acid of oxides prepared under different conditions show that the different products are not mixtures of varying amounts of a definite α -oxide peptisable by nitric acid with a definite β -isomeride which is not peptisable by nitric acid. Hydrated stannic oxides prepared at different temperatures or aged for varying lengths of time are chemical individuals which differ from each other in the size of the particles and the structure of the mass, and hence in their adsorbability and mordanting action, their ease of peptisation, and their solubility. There are no definite hydrates of stannic oxide. Salts of the general formulæ SnR_4 and M_2SnO_3 are formed by the action of concentrated acids and alkalis on newly-formed hydrated stannic oxide. Numerous oxy-salts and complex stannates and metastannates have been prepared by the action of acids and alkalis on different hydrated stannic oxides. These are not definite compounds, but are adsorption products, the composition of which is determined by the age of the hydrated oxide and the concentration of acid or base with which they were treated. Colloidal solutions of hydrated stannic oxide can be prepared by peptisation of the freshly-formed oxide with dilute acids or alkalis. The colloid ages slowly on keeping and rapidly on heating. Any number of colloidal solutions are possible, each differing from the others in the size of the hydrated particles and hence in their reactivity, adsorbability, and stability under given conditions. Hydrated stannic oxide adsorbs colloidal gold, silver, and platinum, forming purple masses, the most common of which is the gold compound, purple of Cassius. All these purple substances are colloidal in character, the composition varying with the conditions of formation. When freshly prepared, they are readily peptised by dilute acids and alkalis, but when aged by drying they are peptised but slightly even by concentrated reagents. A mixture of the hydrated oxides of iron and tin in certain proportions is soluble in dilute ammonia. The reason for this is that hydrated stannic oxide is peptised by the hydroxyl-ion, whilst ferric oxide is not, but colloidal stannic oxide adsorbs ferric oxide and carries it into colloidal solution as long as tin is present in excess. At the same time, hydrated ferric oxide adsorbs stannic oxide and tends to take it out of colloidal solution, so that when the former is present in large excess none of the latter remains peptised. Stannic oxide does not precipitate in the usual way from a solution of tin in nitric acid containing a suitable amount of iron. The reason for this is that hydrated stannic oxide peptised by nitric acid coagulates spontaneously, since the aged oxide is neither peptised nor dis-

solved by this acid. Ferric nitrate peptises the oxide both when newly formed and when aged. Hence if freshly-prepared stannic oxide is peptised either by ferric nitrate or by a suitable mixture of ferric nitrate and nitric acid, coagulation does not take place on keeping or boiling on account of the stabilising action of the strongly adsorbed ferric ion; but if the concentration of ferric ion in the nitric acid solution is too low, complete or partial coagulation takes place on keeping or boiling. Stannic oxide jellies are prepared by coagulation of colloidal solutions of the oxide with suitable concentrations of electrolytes. The results of the present investigation support the author's general hypothesis of the formation of jellies.

J. F. S.

The Occurrence of Germanium in Cassiterite. ASSAR HADDING (*Z. anorg. Chem.*, 1922 **123**, 171—172).—The author examined cassiterite from Finbo by means of the X-ray spectrograph and found it to contain the following elements: tin, tantalum, iron, manganese, germanium, and zinc. The intensity of the lines shows that the amount of germanium was less than that of manganese and more than that of zinc. A similar analysis of cassiterite from Mamacka gave like results. No germanium was indicated in cassiterite from Finland and Bohemia. W. T.

Germanium Hydride. RUDOLF SCHENCK [with ALBERT IMKER] (*Rec. trav. chim.*, 1922, **41**, 569—575).—The preparation of an alloy of germanium and magnesium could not be effected by the action of magnesium on germanium oxide, as the reaction is too violent. The germanium was obtained as oxide from argyrodite; this was purified by conversion into germanium silicofluoride, thence into sulphide, and finally into oxide. Reduction to the metal was then effected by heating in a stream of hydrogen, and an alloy was prepared by heating one part of the powdered germanium so obtained with two parts of magnesium powder in an atmosphere of hydrogen. The hydride, prepared by the action of hydrochloric acid on the alloy in a stream of hydrogen, was obtained pure by cooling to the temperature of liquid air. Small quantities of germanium chloroform were produced simultaneously with the hydride and condensed in a freezing mixture in the preliminary stages of cooling. The uncondensed gases were passed through silver nitrate solution and again through a tube cooled in liquid air, but were not completely freed from the hydride, which could still be detected by its nauseating odour and by the deposition of metallic germanium on porcelain when the gas was burnt. The hydride condensed to a white solid which was purified by sublimation, m. p. -165° , b. p. $-126^{\circ}/757$ mm. Values for the vapour pressure from -164° to -125° are given. Three determinations of molecular weight by Regnault's method gave a mean value of 76.93, the theoretical value being 76.50. The gas readily decomposes into its elements on heating (cf. Paneth and Schmidt-Hebbel, this vol., ii, 776), and an analysis was carried out by passing it through a heated tube, the hydrogen formed being estimated in a eudiometer and the germanium weighed

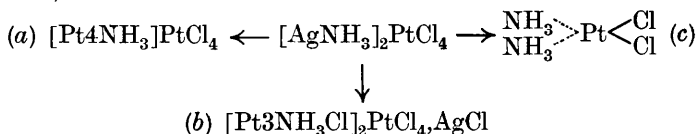
as such. Three determinations gave 94.70% Ge and 5.29% H as mean values, the calculated percentages for GeH_4 being 94.73 and 5.27. The volume ratio of germanium hydride to the hydrogen obtained by its decomposition was found to be 1:2.05. The general reactions of the gas show that it is endothermic and analogous in properties to the hydrides of arsenic, antimony, tin, and bismuth (cf. Voegelen, A., 1902, ii, 401). H. J. E.

Sulphide Sols. III. Sol Preparation by Hydrolysis. F. V. VON HAHN (*Kolloid Z.*, 1922, **31**, 200—203; cf. A., 1921, ii, 577).—Fairly stable antimony pentasulphide sols may be prepared by the hydrolysis of the alkali salts of stibiothiosulphuric acid. The hydrolysis takes place extremely readily according to the equation $2\text{Na}_3\text{Sb}(\text{S}_2\text{O}_3)_3 = \text{Sb}_2\text{S}_5 + 3\text{Na}_2\text{SO}_4 + 3\text{SO}_2 + \text{S}$ (Szilágyi, A., 1920, ii, 207). The preparation is carried out as follows: a 0.5% solution of sodium antimony thiosulphate is kept until it commences to turn yellow and to show a definite Tyndall cone; it is then placed in a dialyser and washed with warm distilled water. After several hours' dialysis, the solution has taken on a deep red colour. The main point to be observed in the preparation is the rapid removal of the alkali sulphate. In the presence of sodium chloride the sol cannot be prepared, nor can a sol having a greater molecular concentration than 0.4 be obtained. Sols of one-tenth this concentration are stable for a few hours only. The sols prepared from the sodium salt are more stable than those prepared from either lithium or potassium antimony thiosulphate. Attempts to prepare arsenic pentasulphide sols by the hydrolysis of alkali arsenic thiosulphates failed entirely owing to the greater instability of these compounds. J. F. S.

Complex Platinum Compounds. III. Molecular Rearrangements observed with Complex Platinum Compounds. L. A. TSCHUGAEV and N. K. PSCHENICYN (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 47—62).—The depolymerisation of bicomplex salts of the type $[\text{Pt}4A]\text{PtX}_4$ (where A =a molecule of ammonia, amine, organic sulphide, etc.), resulting in the formation of the monomeric type $[\text{Pt}2A, \text{X}_2]$ and in the accompanying transference of one-half of the total A molecules from one platinum atom to another is frequently encountered among complex platinum compounds, but has not previously been observed with the simplest purely inorganic, in particular with the ammino-, complexes of platinum. This gap has now been filled by the authors, who show that tetraamminoplatinous platinochloride (Magnus's green salt) is capable of undergoing depolymerisation in accordance with the scheme $[\text{Pt}4\text{NH}_3]\text{PtCl}_4 = [\text{Pt}2\text{NH}_3, \text{Cl}_2]$, the chloride of Reiset's Base II being thus formed. The reaction is effected by cautious heating over a naked flame to 270° , and never proceeds to completion, part of the green salt decomposing with separation of metallic platinum.

Experiments have been made also with certain heterometallic bicomplex compounds in which the platinum occurs only in the anion, $[\text{PtX}]_4$, whilst the kation is formed of another metal in com-

ination with a known number of A molecules giving the so-called neutral part of the complex : for example, $[M, nA]PtX_4$. If as the component M is taken an element such as silver, zinc, copper, mercury, etc., which, according to all the available data, holds molecules of ammonia, etc., less stably than does platinum, the transference of these molecules from the metal M to the platinum should take place with great readiness. With the aminiosilver platinichlorides, the transference of ammonia from the silver to the platinum atom occurs at comparatively low temperatures : At 60—70°, monoamminiosilver platinichloride yields, together with silver chloride, also (a) tetra-amminoplatinous platinichloride (Magnus's green salt), (b) chlorotriamminoplatinous platinichloride (Cleve's salt), and (c) *cis*dichlorodiamminoplatinum (Peyrone's chloride)



whilst at a higher temperature (100°) the last two compounds disappear and are replaced by *trans*-dichlorodiamminoplatinum (chloride of Reiset's Base II); in either case, the loss of ammonia is negligible. At all temperatures between 100° and 200°, diamminiosilver platinichloride yields a new product, namely, tetra-amminoplatinous chloride (chloride of Reiset's Base I), the loss of free ammonia being considerable. At 100°, the only compound, besides silver chloride, accompanying the chloride of Reiset's Base I is Magnus's salt; at 150°, the chloride of Reiset's Base II also appears, whilst at 200° Magnus's salt disappears and the chlorides of Reiset's Bases I and II form the sole products. The Base II chloride, which appears in all cases at the highest temperatures, is evidently a secondary product formed from Magnus's salt.

When heated at 50—60°, diethylamminiosilver platinichloride readily undergoes transformation into the analogues of the chloride of Reiset's Base I and Magnus's green salt, part of the ethylamine being liberated : $[Ag2NH_2Et]_2PtCl_4 = 2AgCl + [Pt4NH_2Et]Cl_2$ and $2[Ag2NH_2Et]_2PtCl_4 = 4AgCl + [Pt4NH_2Et]PtCl_4 + 4NH_2Et$. Under the same conditions, monoethylamminiosilver platinichloride gives the analogues of Magnus's green salt and Peyrone's chloride, part of the original compound also decomposing with complete loss of the amine and formation of silver platinichloride.

Tetramminozinc platinichloride, $[Zn4NH_3]PtCl_4$, gives, at 111°, Peyrone's chloride, Magnus's green salt, and the chloride of Reiset's Base I.

T. H. P.

The Alkali-Ruthenium Double Sulphites. HEINRICH REMY (*Z. anorg. Chem.*, 1922, **124**, 248—274).—The following definite double sulphites of ruthenium and the alkali metals were prepared,

$$\begin{array}{l} K_2SO_3, Ru(OH)SO_3, 3H_2O; \quad K_2SO_3, 3RuSO_3, 6H_2O(?); \\ 7Na_2SO_3, 2RuSO_3, 7H_2O; \quad 7Na_2SO_3, 2RuSO_3, 9H_2O; \\ 3K_2SO_3, 4RuSO_3, 6H_2O. \end{array}$$

There were also obtained substances which on analysis did not correspond with any simple formula, probably being mixtures of the above. The properties of the above double sulphites are given. The author discusses the difficulties of analysis. W. T.

Mineralogical Chemistry.

The Examination of Naturally Occurring Gases. II. F. HENRICH [with G. PRELL] (*Ber.*, 1922, **55**, [*B*], 3021—3025).—The method for the collection and examination of naturally occurring gases has been simplified and extended (cf. A., 1920, ii, 767). The gases from a number of springs have been analysed, since such data appear to the author to form the most trustworthy basis for a judgment as to the atmospheric or terrestrial origin of the water. Re-examination of the gas from a cold spring near Leupoldsdorf, Bavaria, confirms the previous analysis (Henrich, *loc. cit.*), showing it to contain oxygen 13%; nitrogen and the rare gases being the only other constituents. The gas from a second spring situated about a hundred metres above the foregoing was also composed of the constituents of air, but with only 18.8% of oxygen. The gas from a third spring was found to contain oxygen (18.2%), nitrogen (81.8%), argon, and neon (1.1%). Since the ratio of nitrogen to rare gas in these gases is approximately the same as in air, it appears that the latter in some unexplained manner has got below the water in the spring. The low oxygen content of the gases in comparison with that of air is explained by the greater solubility of oxygen than of nitrogen in water, so that a gas richer in nitrogen is evolved. The extent to which the air is depleted of its oxygen appears to depend on the pressure of the water in the spring. H. W.

The Examination of Naturally Occurring Gases. III. F. HENRICH [with G. PRELL] (*Ber.*, 1922, **55**, [*B*], 3026—3030).—Analyses are given of the gases from a number of pools on the Luisenburg near Wunsiedel and Alexandersbad (Fichtelgebirge) of which one may be quoted
 H_2S (traces), CO_2 3.1%, O_2 1.7%, CH_4 , 53.9%, N_2 + rare gases 41.3%. Methane, carbon dioxide, and the small amounts of hydrogen sulphide appear to owe their origin to a bacterium which is not completely identical with *Bacillus methanigenes*. Nitrogen and the rare gases must be derived originally from the air. H. W.

Dopplerite. Studies in the Composition of Coal. FREDERICK VINCENT TIDESWELL and RICHARD VERNON WHEELER (*T.*, 1922, **121**, 2345—2362).

Massive Troilite from Del Norte Co., California. ARTHUR S. EAKLE (*Amer. Min.*, 1922, **7**, 77—80).—The bronze-tarnished

mineral (light greyish-brown when untarnished) resembles pyrrhotite, but differs from this in being non-magnetic and in being readily soluble in dilute sulphuric acid. Analysis of the soluble portion gave Fe 62.70, S 35.40% agreeing with the formula FeS ; d 4.67. The mineral is thus identical with the meteoric troilite. It occurs with chalcopyrite and magnetite in serpentine, and has probably resulted by the action of hydrogen sulphide solutions on the magnetite. Troilite and pyrrhotite are regarded as distinct species, and the suggestion that pyrrhotite is $\text{FeS} + \text{S}$ in solid solution (A., 1912, ii, 354) is not accepted. The magnetic character of pyrrhotite suggests the formula Fe_3S_4 for the end-member of the series $\text{Fe}_n\text{S}_{n+1}$.
L. J. S.

Keeleyite, a new Lead Sulphantimonite from Bolivia, SAMUEL G. GORDON (*Proc. Acad. Nat. Sci. Philadelphia*, 1922, 74, 101—103).—This occurs as radiating aggregates of acicular (perhaps orthorhombic) crystals with pyrites and quartz in the San José mine at Oruro. It is dark grey with bright metallic lustre and gives a greyish-black streak; d 5.21, H 2. Analysis by J. E. WHITFIELD gave:

Pb.	Sb.	Cu.	Fe.	S.	Quartz.	Total.
25.80	43.46	2.25	2.77	24.54	(1.18)	100.00

Deducting 8.15% of admixed sulphides, this gives the formula $2\text{PbS}, 3\text{Sb}_2\text{S}_3$, corresponding with rezbanyite ($2\text{PbS}, 3\text{Bi}_2\text{S}_3$). The compositions of the known lead sulphantimonites are represented on a triangular diagram.
L. J. S.

An Andorite-bearing Silver Ore from Nevada. EARL V. SHANNON (*Proc. U.S. Nat. Museum*, 1922, 60, art. 16, 1—5).—An ore specimen from Keyser mine, Nye Co., Nevada, shows rough prisms of andorite with pyrite and sphalerite in a gangue of rhodochrosite and quartz. Analysis I of the andorite gives, after deducting zinc and iron as sphalerite, the formula $\text{PbAgSb}_3\text{S}_6$. The crystals are usually altered and filled in a central cavity with a matted mass of fine fibres. Analysis II of this alteration product suggests the formula $\text{Pb}_3\text{AgSb}_3\text{S}_8$, and shows that there has been a removal of silver and antimony sulphides.

	Pb.	Ag.	Fe.	Zn.	Sb.	S.	Total.
I	23.35	12.09	1.55	3.56	37.64	22.63	100.82
II	45.14	7.78	2.72	1.56	23.22	[19.58]	100.00

The pale pinkish-buff rhodochrosite gave:

MnO.	FeO.	CaO.	MgO.	CO ₂ .	Total.	MnCO ₃ .
49.49	7.68	3.13	0.93	[38.87]	100.10	80.15

L. J. S.

Sodium Carbonate Minerals from Lake Magadi, Kenya Colony. P. WALTHER (*Amer. Min.*, 1922, 7, 86—88).—The extensive trona deposit of Lake Magadi consists of an aggregate

of pale-yellow, bladed crystals up to 9 cm. in length. Analysis of an average sample with $d\ 2.14$ gave :

Na_2CO_3 .	NaHCO_3 .	H_2O .	NaCl .	Fe_2O_3 , Al_2O_3 .	SiO_2 .	$\text{CaO}, \text{MgO}, \text{SO}_3$.	Total.
43.55	40.41	15.55	0.36	0.04	0.07	traces	99.98

agreeing with the formula $\text{Na}_2\text{CO}_3, \text{NaHCO}_3, 2\text{H}_2\text{O}$. The mineral has evidently been formed by the action of carbon dioxide and water on sodium silicates, since the rocks in the neighbourhood show extensive bands of flinty silica and carbon dioxide issues from numerous cracks at the surface. The salt crusts of Little Magadi, a dry salt pan 25 miles to the south, consist of harder, bladed (monoclinic ?) crystals which on analysis proved to be pure sodium hydrogen carbonate. This, owing to ready loss of carbon dioxide and conversion into trona, has not hitherto been recognised as a mineral. It here owes its existence to the presence of a large excess of carbon dioxide, which issues from cracks in the soil and rocks with a hissing sound. Optical examination by E. T. Wherry detected only trona, but the material had evidently been altered in the meantime. A new mineral name for sodium hydrogen carbonate is therefore avoided for the present. L. J. S.

Constitution of Thaumassite. EDW. F. HOLDEN (*Amer. Min.*, 1922, 7, 12—14).—Calculations by the Lorentz-Lorenz formula of the molecular refractivity of thaumassite, directly and from its components, point to the presence of 2OH (rather than 4OH) in the formula $\text{CaCO}_3, \text{CaSO}_4, \text{CaSiO}_3, 15\text{H}_2\text{O}$. L. J. S.

Minerals from Ljubija, Bosnia. RUDOLF KOEHLIN (*Tsch. Min. Mitt.*, 1921, 35, 1—12).—The iron-ore at Ljubija, near Prijedor, consists of crystalline-granular chalybite with impregnations of galena, pyrites, and chalcopyrite. Near the surface, the chalybite is altered to limonite, with which are various other secondary minerals. These, including the rarer species leadhillite, pyrochroite, and beudantite, are described. L. J. S.

A New Mineral which Contains the Rare Earths as its Main Component. F. HENRICH [with G. HILLER] (*Ber.*, 1922, 55, [B], 3013—3021).—*Weinschenkite* occurs in very small quantity in the Bavarian Oberpfalz in white, matted, globular deposits and in radiating needles on brown hæmatite from which it is readily detached. It appears to be mainly a hydrated phosphate of yttrium and erbium, $\text{PO}_4(\text{Er}, \text{Y}), 2\text{H}_2\text{O}$; but indications of the presence of other rare earths have been obtained. The small amount available was insufficient for a complete analysis.

Pseudowavellite, also occurring in minute amount in the same locality, resembles wavellite in that it contains aluminium as its main component, with calcium oxide (13%), barium oxide, and strontium oxide (about 1%) and rare earths (2—3%). Erbium and yttrium appear to be present in addition, possibly, to the cerium earths. H. W.

Supplementary Note on Ishikawaite, a New Mineral from Ishikawa, Iwaki Province. YŪJI SHIBATA and KENJIRO KIMURA (*J. Chem. Soc. Japan*, 1922, **43**, 648—649).—The unnamed mineral from Ishikawa, of which an analysis was given (this vol., ii, 517), is now termed *ishikawaite*; the crystals are rhombic [$a : b : c = 0.9451 : 1 : 1.147$]. K. K.

Glaucanite from Lewes, Sussex : Constitution of Glaucanite. A. F. HALLIMOND [with analysis by E. G. RADLEY] (*Min. Mag.*, 1922, **19**, 330—333).—A boring through the Gault at Iford Manor, near Lewes, struck the Greensand at a depth of 325 feet. The upper bed of this consists almost entirely of small grains of dark-green glaucanite. The grains consist of a felted mass of minute, birefringent flakes with mean n 1.62; d 2.70. Analysis gave :

SiO ₂ .	Al ₂ O ₃ .	Fe ₂ O ₃ .	FeO.	CaO.	MgO.
48.12	9.16	19.10	3.47	0.76	2.36
K ₂ O.	Na ₂ O.	H ₂ O at 105°.	H ₂ O >105°.	Total.	
7.08	0.22	4.78	5.28	100.33	

From this and a selection of earlier analyses, the formula is deduced as $R_2O, 4(R_2O_3, RO), 10SiO_2, nH_2O$, in which $Al_2O_3 + Fe_2O_3$ and $FeO + MgO$ are regarded as mutually replaceable. In some cases, there is a considerable replacement of potassium by sodium, and the variety soda-glaucanite is suggested. L. J. S.

Structure and Composition of the Strathmore (Perthshire) Meteorite. W. F. P. McLINTOCK and F. R. ENNOS (*Min. Mag.*, 1922, **19**, 323—329).—Four stones were observed to fall along a track six miles in length on December 3, 1917; the largest weighed 9932 grams and the total weight was 13,255 grams. The structure is that of the intermediate chondrite group; d 3.53. The bulk-analysis, deduced from analyses of the attracted and unattracted portions, is :

Fe.	Ni.	Co.	Fe.	S.	SiO ₂ .	TiO ₂ .	Al ₂ O ₃ .	Cr ₂ O ₃ .	Fe ₂ O ₃ .
7.31	1.26	0.05	4.00	2.29	40.32	0.14	2.57	0.44	0.35
FeO.	MnO.	CaO.	MgO.	K ₂ O.	Na ₂ O.	H ₂ O.	P ₂ O ₅ .	Cl.	Total.
12.99	0.29	1.84	24.96	0.11	0.90	0.17	0.23	0.03	100.25

From this is calculated the following mineral composition : feldspar 10.93, ilmenite 0.27, chromite 0.65, magnetite 0.51, chlorapatite 0.56, olivine 41.13, bronzite 30.91, troilite 6.29, nickel-iron 8.62, water 0.17%. L. J. S.

Analytical Chemistry.

A Microcolorimeter and Nephelometer. A. BAUDOUIN and H. BÉNARD (*Compt. rend. Soc. biol.*, 1920, **83**, 602—603).—A description of a miniature Duboseq colorimeter, of which the cups have a capacity of 2 c.c., and the tube an adjustment of 20 mm. The apparatus can also be used as a nephelometer or ultraphotometer, and, by replacing the ocular with a small, direct-vision spectroscope, can be converted into a spectroscope comparator.

CHEMICAL ABSTRACTS.

Colorimeter. ED. MOREAU and A. BONIS (*Ann. Falsif.*, 1922, **15**, 357—360).—The apparatus consists essentially of two graduated cylinders placed side by side in a suitable frame; one of these contains the test solution and the other the standard or comparison solution. The latter is admitted through a side tube at the bottom of the cylinder, this tube being connected with a tapped funnel or reservoir containing the solution.

W. P. S.

The Application of Coloured Glasses instead of Liquids in Colorimetric Researches. KLAS SONLÉN (*Arkiv Kem. Min. Geol.*, 1922, **8** No. 7, 1—10).—Combinations of coloured glasses are used as standards in colorimetry. Coloured glasses suitable for this purpose may be prepared by dyeing the gelatin films on photographic plates from which the silver has been removed by treatment with thiosulphate.

W. O. K.

A New Apparatus for Exact Gas Analysis. K. A. SCHALLER and W. BERNDT (*Chem. Ztg.*, 1922, **46**, 972—973).—The apparatus consists of a manometer, a measuring tube immersed in a water-jacket with air agitation, and a detachable absorption vessel with an adjustable mercury reservoir. The passage of the mercury from the manometer into the measuring tube is prevented by placing between them a U-tube containing at its lowest point either a constriction or a throttle cock. All the operations of gas analysis can be carried out in this apparatus except explosions, for which the absorption vessel is replaced by a eudiometer. The procedure for estimating carbon dioxide, heavy hydrocarbons, oxygen, carbon monoxide, and the combustion of hydrogen, methane, and ethane is described.

H. C. R.

A Modified Methyl-orange Indicator. KENNETH CLAUDE DEVEREUX HICKMAN and REGINALD PATRICK LINSTEAD (*T.*, 1922, **121**, 2502—2506).

Apparatus for Electrometric Titration. W. E. GARNER and C. A. WATERS (*J. Soc. Chem. Ind.*, 1922, **41**, 337—338T).—The electrode vessel, which carries a small bulb, is attached to a rotating stirrer; two side tubes on the vessel are turned downwards and constricted at the ends. The bulb is convenient in the preparation of a calomel electrode. The side tubes are packed with asbestos, the

vessel is filled completely with electrolyte, and it is supported from the glass tube of the stirrer by means of a waxed cork. The metal used as an electrode is fused or waxed into a thin glass tube and attached by means of a small binding screw to the rotating spindle, electrical connexion being made through a small steel mercury cup to another binding screw. The outer electrode is of any convenient form; the turned-down side tubes on the electrode vessel make it possible to commence a titration with 5 c.c. of solution in the beaker.

W. P. S.

Quantitative Analysis by Measurement of the Degree of Supersaturation. ERNST FRITZ HÖPPLER (*Chem. Ztg.*, 1922, 46, 957—958).—The time elapsing between the addition of a reagent and the formation of a precipitate or coloration can be utilised as an approximate quantitative measure of traces of substances in solution. The method is particularly applicable to water analysis. Sulphuric acid and calcium can be estimated in this way between the dilutions of 2.3 and 100 mg. per litre. Nitrous acid can also be estimated by this means when not in greater concentration than 0.5 mg. per litre.

H. C. R.

The Rapid Estimation of Chlorine in Organic Compounds. E. VOTOČEK (*Chem. Listy*, 1922, 16, 248—249).—The author combines the method of Marcusson and Dröschner (A., 1910, ii, 543) with his titration of chlorides against a mercuric salt in the presence of sodium nitroprusside as an indicator. The present author carries out the combustion in a funnel-shaped vessel of several litres capacity fitted with a stopcock. Since sufficient hydrogen is present in the molecule to convert all the chlorine into hydrogen chloride, the products of combustion are absorbed by water and titrated directly against mercuric nitrate. The estimation takes about an hour and a half.

W. T.

Potassium Dichromate as a Standard in Iodimetry and the Estimation of Chromates by the Iodide Method. WARREN C. VOSBURGH (*J. Amer. Chem. Soc.*, 1922, 44, 2120—2130).—It is shown that titration of iodine with thiosulphate in dilute acid solutions gives results which are 0.1—0.3% higher, and more concordant than the results of titration in a neutral solution. The presence of air affects the titration of iodine with thiosulphate when the acidity of the solution is equivalent to 0.3*N*-hydrochloric acid or greater, causing too much thiosulphate to be required. An apparent excess of oxidising action of dichromate is caused by the titration of the iodine in a solution of too high an acid concentration. This can be corrected by the exclusion of air, but more easily by dilution to such an hydrogen-ion concentration that the presence of air will not interfere. Chromates may be estimated to within 0.1% by the iodide method under the proper conditions. Potassium dichromate as a standard for thiosulphate solutions agrees with pure iodine to within 0.1%, but gives a slightly lower value. Errors in the iodine standardisation leading to such a difference appear to be about as probable as errors in the dichromate standardisation.

A standard solution of potassium permanganate is not trustworthy as a standard for thiosulphate solutions. J. F. S.

The Estimation of Sulphuric Acid as Barium Sulphate. Evidence of the Existence of a Complex Barium Sulphuric Acid. D. BALAREFF (*Z. anorg. Chem.*, 1922, **123**, 69—82).—The sources of error in the estimation of sulphuric acid as barium sulphate are: (1) occlusion of salts by the precipitate, for example, barium chloride; (2) occlusion of the mother-liquor; (3) the formation of the complex ion $[\text{Ba}_5(\text{SO}_4)_6]$, and this leads to the chief error. The author isolated the potassium salt of this complex ion $[\text{Ba}_5(\text{SO}_4)_6]\text{K}_2$. The most accurate results are obtained when barium sulphate is precipitated slowly from a dilute, boiling solution acidified with hydrochloric acid. Crystals in the precipitate have various forms; the prismatic form corresponds with the simple salt BaSO_4 . The chlorine content of barium sulphate is not caused by the salt $\text{SO}_4(\text{BaCl})_2$. W. T.

Application of Conductometric Titrations to Precipitation Analysis. V. Conductometric Titrations with Barium Salts. I. M. KOLTHOFF (*Z. anal. Chem.*, 1922, **61**, 433—448).—Sulphates may be accurately titrated conductometrically by means of barium chloride in solutions as dilute as 0.001*N*. The titration may be carried out more rapidly and exactly if alcohol is added to the solution than if an excess of barium sulphate is stirred in. The presence of mineral acids, aluminium, and calcium leads to low results, whereas the presence of iron salts generally causes the results to be too high. Nitrates in moderate amount do not interfere. The method is not applicable to the determination of sulphates in water owing to the presence of calcium.

Carbonates and chromates, as well as oxalates, tartrates, citrates, and malates in the presence of sufficient alcohol may all be titrated with barium chloride in a similar manner to sulphates, but phosphates, pyrophosphates, succinates, benzoates, and salicylates cannot be titrated by conductometric methods with barium chloride. A. R. P.

Some new Volumetric Methods. (Estimation of Sulphate, Lead, Acids, and Ammonia.) KARL JELLINEK and H. ENS (*Z. anorg. Chem.*, 1922, **124**, 185—202).—The volumetric methods of estimating sulphate are unsuitable on account of the filtrations involved. The authors have worked out the following method. Excess of barium nitrate is added to a sulphate solution, to this is added excess of potassium chromate and this excess estimated by running in a barium solution until the yellow colour disappears. Error by this method 0.3%. The use of silver salt as an indicator is not possible because the solubilities of silver and barium chromates are very near to one another. The following is given as a volumetric method of estimating lead; excess of chromate is added to a lead salt, a little silver nitrate is then added, and the excess of chromate is determined by titrating against a lead salt until the disappearance of the reddish-brown silver chromate. The latter method can also

be employed for the indirect estimation of sulphate. Titration of metals against arsenates and arsenites does not give positive results. The authors suggest the use of a copper solution as an indicator in acidimetry, the alkali being added until the precipitated hydroxide makes its appearance.

W. T.

Estimation of Selenium. LUIGI LOSANA (*Giorn. Chim. Ind. Appl.*, 1922, **4**, 464—466).—The method used for estimating sulphur (this vol., ii, 582, 656) may be employed also for the estimation of selenium if a larger excess of iron is taken and the exclusion of air during the reduction is rendered as complete as possible. By suitable modification of the procedure, sulphur and selenium may be estimated simultaneously (cf. *J. Soc. Chem. Ind.*, 1922, Dec.).

T. H. P.

Rapid Method for Estimating Ammonia in Ammonium Salts. HERMANN BURKARDT (*Chem. Ztg.*, 1922, **46**, 949).—Attention is directed to a rapid method for estimating ammonia in its salts, in which formaldehyde solution (containing no free acid) is added to the solution containing an ammonium salt, and the acid formed according to the equation $6\text{CH}_2\text{O} + 4\text{NH}_4\text{Cl} = 6\text{H}_2\text{O} + 4\text{HCl} + (\text{CH}_2)_6\text{N}_4$ is then directly titrated with a standard solution of sodium hydroxide, using phenolphthalein as an indicator.

A. J. H.

Titration of Nitrous Acid, and the Estimation of Nitrous and Arsenious Acids in the Presence of Each Other. ALFONS KLEMENC (*Z. anal. Chem.*, 1922, **61**, 448—454).—The titration of acidified solutions of nitrites with permanganate in the air is attended with possible errors due to loss of nitrogen oxides and the slowness with which the reaction proceeds towards the end. These disadvantages may be overcome by adding the nitrite solution without acidifying to a solution containing an excess of potassium permanganate and sulphuric acid and enclosed in a glass-stoppered flask containing carbon dioxide under slightly reduced pressure. The solution is warmed at 40° to complete the reaction and the excess of permanganate is then titrated with standard oxalic acid.

[With F. POLLAK.]—The method is extended to the estimation of nitrous and arsenious acids in the same solution, one portion of which is titrated in the presence of sodium hydrogen carbonate with iodine for arsenious acid and another portion with permanganate as described above to obtain the sum of the two acids. Nitrous acid is then found by difference.

A. R. P.

The Use of Benzidine in the Detection of Phosphoric Acid. F. FEIGL (*Z. anal. Chem.*, 1922, **61**, 454—457).—The yellow precipitate produced by ammonium molybdate in the usual test for phosphoric acid is often contaminated with arseno-molybdate and with molybdic acid, especially if an old solution of the reagent is used. To test this precipitate for the presence of phosphoric acid, it is collected on a close, ashless filter and washed somewhat, then moistened with a solution of benzidine hydrochloride containing acetic acid. The moist paper is held over an ammonia bottle, the vapour from which turns the precipitate blue in those parts con-

taining phosphoric acid. Even when no visible precipitate is produced in the test solution it should be poured through the paper and the paper tested as described. The blue colour is apparent when the original solution contains only 1 part of phosphorus as phosphoric acid in 460,000 parts of water. A. R. P.

The Volumetric Estimation of Phosphoric Acid and of Sodium Phosphate and Pyrophosphates. FRANK X. MOERK (*Amer. J. Pharm.*, 1922, **94**, 641—650).—Phosphoric acid and disodium hydrogen phosphate can be estimated volumetrically by titration with sodium hydroxide and hydrochloric acid, respectively, using a mixture of methyl-orange and indigo-carmin as indicator. To obtain results in consistent agreement with the silver phosphate precipitation method followed by titration of the liberated acid with alkali hydroxide until a permanent brown coloration of silver oxide is obtained, the dilution of the reacting solutions must be specified, and a definite quantity of sodium chloride must be added, the silver phosphate method being apparently unaffected by these factors. For the neutralisation method, using the indicator, the procedure is as follows. To 100 c.c. of water 0.2 c.c. each of 0.1% methyl-orange solution and 0.3% indigo-carmin solution are added, followed by dilute hydrochloric acid until the green colour changes without producing a violet colour. The solution thus prepared is divided into two equal parts, one being set aside and the other being added to the phosphoric acid or phosphate solution to be estimated, and the mixture titrated to match the tint of the reserved portion of the indicator solution with sodium hydroxide, or hydrochloric acid, as the case may be. The end-point corresponds in each case with the formation of NaH_2PO_4 . Under these conditions and using $N/2$ solutions, results in agreement with the silver phosphate method were obtained by titrating in presence of 7.5% of sodium chloride for the phosphoric acid, and 2.5% for the phosphate. Under similar conditions, sodium pyrophosphate can be titrated with acid as a diacid base. G. F. M.

Methyl-red in the Assay of Phosphoric Acid and Sodium Phosphate. FRANK X. MOERK and EDWARD J. HUGHES (*Amer. J. Pharm.*, 1922, **94**, 650—655).—Of the two methods described in the preceding abstract and the U.S.P. IX method for the volumetric estimation of phosphoric acid and phosphates, the latter process always gives low results. The mixed indicator method is the most rapid, but is influenced by the weight taken, by the amount of sodium chloride present, and by the strength of the volumetric solutions. The best results when working with unknown quantities, are obtained by the silver phosphate method, titrating back the liberated acid with alkali hydroxide and using methyl-red as indicator. The procedure is as follows. To 50 c.c. of standard silver nitrate solution one drop of methyl-red and a trace of alkali to produce a yellow colour are added, followed by 10 c.c. of the solution to be assayed. The liberated nitric acid (3 mols. per mol. of H_3PO_4 , or 1 mol. per mol. of Na_2HPO_4) is titrated with alkali hydroxide until the supernatant liquid is again yellow. During the neutralisation,

the pink colour may fade, in which case one or two drops more of methyl-red must be added.

G. F. M.

The Iodometric Micro-estimation of Phosphoric Acid, and of Phosphorus in Organic Compounds. O. SVANBERG, K. SJÖBERG, and G. ZIMMERLUND (*Arkiv Kem. Min. Geol.*, 1922, No. 10, 1—17).—An improvement on Neumann's method (A., 1903, ii, 243; 1905, ii, 68) for the micro-estimation of phosphorus is described, in which the phosphorus is precipitated as ammonium phosphomolybdate, and the nitrogen in the precipitate estimated by Bang's micro-Kjeldahl method, in which the ammonia is absorbed in acid, the excess of the latter being estimated by adding excess of potassium iodide and potassium iodate and titrating the liberated iodine with thiosulphate. If a correction is made for a systematic error, 0.05—1.00 mg. of phosphorus may be estimated to within 2—3%.

W. O. K.

Titration of Boric Acid in Presence of Phosphoric Acid. I. M. KOLTHOFF (*Chem. Weekblad*, 1922, 19, 449—450).—Addition of sodium citrate to solutions containing phosphoric and boric acids prevents interference by the latter in the titration of the phosphoric acid with sodium hydroxide. After the neutralisation, addition of mannitol allows of the titration of the boric acid by further addition of sodium hydroxide, addition of the alkali being continued until the pink colour of the phenolphthalein remains for at least three minutes, and is not destroyed by further addition of mannitol. Neither calcium nor magnesium interfere.

In boiling solutions containing boric acid, a reflux condenser is scarcely necessary, since after half an hour's boiling the loss is less than 1%.

S. I. L.

The Estimation of Boric Acid. W. W. DEERNS (*Chem. Weekblad*, 1922, 19, 480—481).—The author's method of estimating boric acid in presence of phosphoric acid by means of potassium iodide-iodate is simpler than the method proposed by Kolthoff (preceding abstract) of adding sodium citrate and titrating with alkali, and the interference of calcium compounds is not apparent. The citrate method is not new, having been proposed by Littmann (*Chem. Ztg.*, 1898, 22, 691) and Pfyl (A., 1914, ii, 290).

S. I. L.

Quantitative Estimation of Carbon and Hydrogen by means of the Sulpho-chromic Mixture. L. J. SIMON and A. J. A. GUILLAUMIN (*Compt. rend.*, 1922, 175, 525—527; cf. Guyot and Simon, A., 1920, i, 285, and ii, 332).—The method indicated is limited in scope, but is applicable to dibasic straight-chain acids, their methyl esters, and to all sugar derivatives which do not contain a methyl group directly linked to carbon, to aromatic acids, and to phenols which contain no alkyl substituents in the ring. The substance is completely oxidised by a known excess of reagent, the volume of carbon dioxide obtained is noted, and hydrogen estimated by determining volumetrically the excess of chromic acid. An alternative method depends on estimating the residual chromic

acid by addition of a known excess of a suitable organic substance and a second reading of the volume of carbon dioxide. A table is given of results obtained by the method as compared with standard figures for the same substances. The authors suggest that the method would be more generally applicable if silver chromate were used as the oxidising agent. H. J. E.

The Function of Chromic Oxide in Oxidation by means of Sulpho-chromic Mixture. L. J. SIMON (*Compt. rend.*, 1922, 175, 768—770; cf. preceding abstract).—Chromic oxide formed in the reaction may play an important part in the oxidation. Control experiments in which chrome alum was added to the reagent showed that, in absence of oxidisable organic matter, the addition enables the liberation of oxygen to take place more readily and that the quantity of alum added influences the amount of oxygen evolved. If sufficient chromic oxide is added, sulphuric acid will completely decompose chromic anhydride on heating at 100°. Thus the addition of chromic oxide or its derivatives, when dealing with organic substances which are only partly oxidised by sulpho-chromic mixture, transforms what would otherwise be partial into complete oxidation, and in extreme cases gives rise to the evolution of free oxygen.

H. J. E.

The Tannic Acid Method for the Estimation of Carbon Monoxide in Blood. R. R. SAYERS and W. P. YANT (*U.S. Bur. Mines, Rep. Investigations*, 1922, No. 2356).—Standards are prepared containing 10—100% of carbon monoxide-haemoglobin in 90—0% of oxyhaemoglobin as follows: 5 c.c. or more of blood are collected, 0.05 gram of potassium citrate or 0.02 gram of sodium fluoride being used for each 10 c.c. Half of the blood is saturated with carbon monoxide, and both parts are diluted to 10 vols. with water, and mixed in varying proportions. Then 0.1 c.c. of the blood to be tested is drawn from the finger into 1 c.c. of 0.05% potassium citrate or 0.03% sodium fluoride solution. To each of the blood samples contained in tubes of $\frac{5}{16}$ inch inside diameter is added 1 c.c. of 1% tannic acid in 1% pyrogallol solution. The tubes are inverted and comparison is made in eight to ten minutes. The standards, when properly sealed, may be kept for several weeks, but the reagent should be freshly prepared. CHEMICAL ABSTRACTS.

Physical Method for the Estimation of Carbon Dioxide in the Respiratory Air. A. K. NOYONS (*Arch. Néerland. physiol.*, 1922, 7, 488—495).—A method is described for the estimation of carbon dioxide by the measurement of the heat conductivity of the mixture of gases. W. O. K.

Estimation of Silica in Filtered Sea-water. ROGER C. WELLS (*J. Amer. Chem. Soc.*, 1922, 44, 2187—2193).—The author has investigated the estimation of silica in sea-water and finds that the most effective method is to add an aluminium salt if such is not already present and precipitate with a quantity of ammonia sufficient to produce a pink colour with rosolic acid; the silica carried down with the alumina is then recovered and estimated in

the usual way. It is shown that silica cannot be estimated by the loss on evaporation with hydrofluoric acid in the presence of calcium sulphate. An excess of at least two parts of alumina to one of silica is essential for the complete inclusion of silica in the alumina precipitate. An excess of ammonia favours the inclusion of silica in the ammonia precipitate, but this has a slightly solvent action on the aluminium hydroxide. A Sørensen value of 7—8, as shown by the pink colour with rosolic acid, is advisable in making the ammonia precipitation. A very small quantity of silica, roughly 0.3 mg., escapes precipitation and an equal quantity is generally found in the wash waters from the ammonia precipitate. In rock analysis, a single evaporation with hydrochloric acid is sufficient, provided silica is also determined in the ammonia precipitate. Eleven samples of water collected one mile south of Eastern Point Light, Gloucester, Mass., during eleven months gave contents of dissolved silica varying between 0.0029 and 0.0003 gram per litre. J. F. S.

The Estimation of Alkali Carbonates in Presence of Phenolphthalein. BONNIER (*Compt. rend.*, 1922, 175, 765—767).—Warder's method (A., 1881, 848) of estimating carbon in steel involves a titration of alkali hydroxide with sulphuric acid in presence of alkali carbonate. That of Winkler (Treadwell, "Analytische Chemie," 9th ed., 2, 485) necessitates titration of the hydroxide in presence of barium chloride. Neither gives a sharp end-point. In the former case, the instability of the alkali hydrogen carbonate, on the formation of which the end-point depends, leads to errors and a study of the various factors which influence the result shows that the excess of sodium sulphate formed, the temperature, and the method of stirring have no effect. The initial colour of the indicator, the method of adding the acid, and the dilution (cf. Mestrezat, A., 1918, ii, 274) all affect the estimation to some extent. Winkler's method is satisfactory if carried out with normal solutions; with less concentrated solutions, however, the end-point tends to lose sharpness. H. J. E.

The Cobalt Nitrite Reaction for Potassium in Animal and Vegetable Cells. A. B. MACALLUM (*Arch. Néerland. physiol.*, 1922, 7, 304—308).—Sodium cobaltinitrite is a very sensitive reagent for the microchemical detection of potassium in animal and vegetable cells. The possibility of ammonia being precipitated by the cobaltinitrite may be avoided by the addition of formalin to the reagent, which converts the ammonia into hexamethylenetetra-amine. The only difficulty in the use of the reagent is that in animal tissue creatine may give a precipitate likely to be mistaken for potassium. W. O. K.

The Volumetric Estimation of Calcium. A. VÜRTHEIM and G. H. C. VAN BERS (*Chem. Weekblad*, 1922, 19, 450—452).—Excess of ammonium oxalate is added to the solution, and after heating to boiling, calcium oxalate is precipitated by addition of ammonia; after filtration, the excess of ammonium oxalate is titrated with permanganate in the usual way. It is necessary to

use at least double the amount of oxalate theoretically required for the precipitation; on account of the rapid alteration of ammonium oxalate solutions, blank titrations must be carried out with each series of estimations.

The results agree very well with those obtained by the gravimetric estimation, and within very wide limits are independent of the temperature and degree of acidity of the solution to be titrated and of the strength of the permanganate solution employed.

S. I. L.

The Volumetric Estimation of Magnesium in Potassium Salts. A. VÜRTHEIM (*Chem. Weekblad*, 1922, **19**, 461—462).—The method proposed by Precht (A., 1879, 1053), namely precipitation of magnesia by addition of carbonate-free alkali, and back titration of the excess after filtration, has been examined, and found to give satisfactory results for mixtures containing very large quantities of sodium, potassium, and calcium salts. Where calcium is present, oxalate is added to the alkali to ensure complete precipitation.

S. I. L.

Estimation of Lead in Lead Amalgam. M. G. MELLON (*J. Amer. Chem. Soc.*, 1922, **44**, 2167—2174).—A résumé is given of the principles of the methods which have been used previously for the estimation of lead in lead amalgams. Data are presented which show the possibility of estimating quantities of lead of about 0.5 gram of lead in 30—50 grams of mercury with an accuracy of 0.05%. The method consists in the displacement of the lead by copper from an aqueous solution of copper nitrate, followed by the precipitation of the lead as chromate from the solution. It is shown that 0.4 gram of lead may be displaced from the amalgam in thirty minutes at the ordinary temperature if the mixture is stirred, but if allowed to remain stationary many hours are required for complete precipitation. The following procedure is recommended: the sample of amalgam is covered with water containing one drop of 10% acetic acid, 10 c.c. of a 2*N*-solution of copper nitrate are added and the mixture is stirred for thirty minutes and filtered to remove any metallic copper which has not dissolved in the mercury. One drop of 10% acetic acid is added to the filtrate, and the lead is precipitated as chromate by the method usually adopted.

J. F. S.

A Peculiar Catalytic Reaction for the Detection, and a Method for the Estimation, of the Smallest Traces of Copper [also a Lecture Experiment]. FRIEDRICH L. HAHN and G. LEIMBACH (*Ber.*, 1922, **55**, [B], 3070—3074).—When a solution of a ferric salt is added to a solution of sodium thiosulphate a dark violet coloration is developed which gradually disappears as the ferric becomes reduced to ferrous salt and the sodium thiosulphate is converted into tetrathionate. The reaction is greatly accelerated by the presence of copper salts and its completion can be made more obvious by the addition of ammonium thiocyanate to the mixture; the latter substance has also the advantage of retarding the reaction.

The following solutions are required. Copper sulphate solution (3.9 grams of the hydrated salt per litre, of which 1 c.c. is diluted to 1 litre before use); ferric solution (5 grams of iron alum and 25 c.c. of 2*N*-hydrochloric acid per litre); 5*M*-ammonium thiocyanate solution; 1/15*M*-sodium thiosulphate solution. For the recognition of the minutest traces of copper, two litres of the iron solution should be mixed with 10–20 c.c. of thiocyanate; for the estimation of larger amounts more thiocyanate (up to 200 c.c.) may be used.

A neutral solution of the substance under investigation is placed in a beaker (500 c.c. capacity) and in a similar series of beakers known quantities of copper solution are placed. The solutions are made up to a fixed volume with distilled water, and to each are added 100 c.c. of the iron thiocyanate solution. Simultaneously (by means of a row of test-tubes fastened to a rod which can be rotated horizontally) 25 c.c. of thiosulphate solution are added to each beaker and the contents well mixed. The times required for decolorisation (which are conveniently 10–20 minutes) are then compared.

The velocity of the reaction is rather greatly dependent on small variations in the ratio of the concentrations, iron : thiocyanate : thiosulphate, on the degree of acidity and the temperature, so that it is scarcely possible at present to indicate definite intervals of time for definite quantities of copper. It is necessary to observe the progressive decolorisation in the solution under investigation and in solutions of known copper content simultaneously and to use a sufficient volume of solution (about 100 c.c.) to avoid the effect of local variations of temperature. The smallest amount of copper which can be identified with certainty under these conditions is 0.002 m.g.; further refinement is probable if a thermostat is used.

A similar effect on the course of the reaction has not been observed with any other substance yet investigated. Acceleration is caused by relatively large amounts of platinum, but the effect is so little marked that a confusion with copper is impossible. Aluminium, zinc, nickel, and arsenic in particular retard the action, especially in strongly acid solution. If such metals are to be investigated with regard to their copper content, it is essential that an equal weight of "foreign" metal should be added to the control solutions; in this manner, 0.001% of copper in nickel can be rapidly and certainly detected.

H. W.

Potentiometric Titration of Copper. E. ZINTL and H. WATTENBERG (*Ber.*, 1922, 55, [B], 3366–3370).—The method consists in the reduction of the cupric to cuprous salt in hydrochloric acid solution by means of titanium trichloride and subsequent re-oxidation with standard potassium bromate or dichromate solution in an atmosphere of carbon dioxide.

The apparatus consists of a beaker placed on an electrically heated hot plate and covered with a clock glass provided with four holes for the introduction of the nozzle of the burette, a stirrer, a T-tube which holds the indicator electrode (a stout smooth platinum

wire) and serves also for the introduction of carbon dioxide and the limb of the normal electrode (a calomel cell charged with solid potassium chloride and saturated potassium chloride solution). The *E.M.F.* of the titration cell is measured by compensation in the usual manner with the aid of a capillary electrometer. The copper solution is treated with a sufficient quantity of hydrochloric acid and reduced by a slight excess of titanium trichloride, whereby a colourless solution results if sufficient hydrochloric acid is present to prevent precipitation of cuprous chloride. The addition of standard bromate or dichromate solution causes the oxidation of the excess of tervalent titanium and subsequently that of the copper, the end-points of the two actions being marked by abrupt changes in the potential. Titration is effected at about 80°, at which temperature the potentials adjust themselves almost instantaneously; in cold solution, the bromate in particular reacts somewhat slowly with titanium trichloride. The concentration of the hydrochloric acid has not a very marked influence, and is suitably maintained at 4–8%. Considerable quantities of ammonium salts have no disturbing effect, but iron is titrated with the copper. Small quantities of nitric acid are reduced by the excess of titanium trichloride, after which they do not influence the change further. The use of stannous chloride in place of titanium chloride is not recommended, since the potentials, even in hot solution, only become constant slowly as long as an excess of stannous salt is present.

H. W.

Volumetric Estimation of Copper by means of Sodium Nitroprusside. GEORGES JORET (*Ann. Falsif.*, 1922, 15, 354–356).—A solution of the copper salt, containing about 0.1 gram of copper, is neutralised with ammonia, then acidified slightly with nitric acid, treated with 40 c.c. of *N*/10-sodium nitroprusside solution (14.895 grams per litre), diluted to 200 c.c., and filtered; 100 c.c. of the filtrate are treated with 20 c.c. of *N*/10-silver nitrate solution, the mixture is filtered, and the excess of silver nitrate titrated with *N*/10-thiocyanate solution in an aliquot portion of the filtrate. The copper solution must not contain silver, nickel, cobalt, or halogens.

W. P. S.

Separation of Copper by means of Thiophenylhydantoic Acid. H. H. WILLARD and DOROTHY HALL (*J. Amer. Chem. Soc.*, 1922, 44, 2253–2254).—In solutions slightly acidified with acetic acid, thiophenylhydantoic acid precipitates quantitatively copper, lead, mercury, cadmium, bismuth, and antimony, whilst arsenic, tin, and metals not precipitated by hydrogen sulphide are not precipitated under these conditions. When the copper precipitate is ignited to oxide, the product contains sulphate sufficient to cause an error of 0.1–0.6 mg. in the total weight. The copper compound is very unstable and quite unsuitable for direct weighing. To estimate copper by means of the precipitate with thiophenylhydantoic acid, it is best to fuse it with potassium pyrosulphate, dissolve in water, and estimate the copper by any of the well-known methods. The bismuth and antimony compounds

with thiophenylhydantoic acid are soluble in alcohol. To separate copper from the metals of the iron and zinc groups, the solution is neutralised with ammonia and 5 grams of glacial acetic acid are added. If metals precipitated by ammonia are present, 7 grams of citric acid are added before neutralising for every gram of such metal present. The solution is made up to 300—400 c.c., raised to the boiling point, and treated with 0.5 gram of thiophenylhydantoic acid in a little hot water, then dilute ammonia is added until a yellow precipitate begins to form. The solution is boiled, and if all the copper is precipitated the precipitate separates at the top, leaving a clear solution below. If this does not happen, a little more ammonia is added, but this may cause the precipitate to turn brown, due to the formation of sulphide. The precipitate is filtered hot, washed with hot water, and treated as stated above. The method is very good for small quantities of copper.

J. F. S.

Contradictions and Errors in Analytical Chemistry. I. The Precipitation of Aluminium by Thiosulphate and its Separation from Iron. II. The Ageing of Volumetric Thiosulphate Solutions. FRIEDRICH L. HAHN [with G. LEIMBACH (I) and H. WINDISCH (II)] (*Ber.*, 1922, **55**, [B], 3161—3165).—I. The precipitation of aluminium by means of thiosulphate under the usual conditions (boiling the solution until sulphur dioxide is completely expelled and then adding ammonia) is only very incomplete; the apparent accuracy of the results is due to a balance of errors, the unprecipitated aluminium hydroxide being compensated by the alkali carried down by the precipitate. Precipitation is almost quantitative when the solution is boiled for only a short time and the remainder of the metal is precipitated by addition of a base. An almost complete separation from iron can be achieved if a very weak base, preferably phenylhydrazine, is used.

II. The addition of a very small amount of alkali enables thiosulphate solutions to be preserved without alteration in strength from the first day. The change which they otherwise suffer appears to be caused by the faintly acid reaction of distilled water; it certainly does not depend on the formation of sulphite or sulphide.

H. W.

The Separation of Ferric Oxide and Aluminium Oxide from Magnesium Oxide by the Nitrate Method. ANDRÉ CHARRIOU (*Compt. rend.*, 1922, **175**, 693—695; cf. this vol., ii, 319).—In separating the oxides of iron and aluminium from that of magnesium by heating with ammonium nitrate, the retention of magnesium oxide by the other oxides increases with the magnesium content; aluminium oxide retains a relatively smaller amount than ferric oxide. By increasing the concentration of the ammonium nitrate solution from 4% to 10%, the magnesium oxide is almost completely removed, and if the mixture is treated three times in this way, no trace of magnesium remains.

H. J. E.

Separation and Estimation of Cobalt. I. Separation of Cobalt by means of Thiophenylhydantoic Acid. I. Separation of Cobalt from other Metals. H. H. WILLARD and DOROTHY HALL (*J. Amer. Chem. Soc.*, 1922, **44**, 2219—2226).—Cobalt may be quantitatively separated from arsenic, uranium, vanadium, titanium, tungsten, molybdenum, zinc, manganese, chromium, aluminium, magnesium, and calcium by precipitation with thiophenylhydantoic acid in slightly ammoniacal solution. In the presence of iron, the precipitate is rarely free from this impurity, and usually contains from one to five mg. regardless of the amount originally present. This does not, however, interfere with the volumetric estimation of cobalt. Nickel is always partly precipitated. The cobalt precipitate has not a definite composition, and is probably mixed with some cobalt sulphide, thus making it necessary to convert the cobalt into some other more definite form. The various separations of cobalt from other metals are effected as follows. *Separation from iron.* A solution containing 1 gram of iron and 25 mg. of cobalt in 300 c.c. is placed in an Erlenmeyer flask, treated with 8 grams of citric acid, and neutralised with ammonia (*d* 0.90) and 5 c.c. of excess ammonia are added. The solution is warmed at 35°, 0.7—1.0 gram of thiophenylhydantoic acid dissolved in 30 c.c. of water or alcohol added, and the mixture shaken vigorously for several minutes. The cobalt is precipitated and after boiling the precipitate may be easily filtered. *Separation from manganese.* This separation is effected as in the case of iron. *Separation from zinc.* The procedure is the same as for iron, except that an excess of 10 c.c. of ammonia is necessary and the solution must be boiled for several minutes to ensure complete precipitation of the cobalt. The other metals named are separated in the same way as zinc, except that 7 grams of citric acid are used. J. F. S.

Separation and Estimation of Cobalt. II. Gravimetric Estimation of Cobalt. H. H. WILLARD and DOROTHY HALL (*J. Amer. Chem. Soc.*, 1922, **44**, 2226—2231; cf. preceding abstract).—Various methods for the gravimetric estimation of cobalt have been examined, and it is shown that, although pure cobalt nitrate may be accurately ignited to the oxide Co_2O_3 and the latter reduced by hydrogen to the metal, the oxide obtained by the ignition of the thiophenylhydantoic acid precipitate (*vide supra*) contains a little sulphate. If the oxide obtained in this ignition is assumed, empirically, to be Co_2O_3 , the results for cobalt are fairly good. The ignition of cobalt sulphate at 550° is the most accurate method for the estimation of cobalt, but when this method is applied to the thiophenylhydantoic acid precipitate the results are usually slightly high and the sulphate is not completely soluble in water. The electrolytic estimation of cobalt is very satisfactory when the proper conditions and precautions are observed. Precipitation as cobalt ammonium phosphate followed by ignition to cobalt pyrophosphate is less accurate than the preceding methods. J. F. S.

Separation and Estimation of Cobalt. III. Volumetric Estimation of Cobalt. H. H. WILLARD and DOROTHY HALL (*J. Amer. Chem. Soc.*, 1922, **44**, 2237—2253; cf. preceding abstracts).—A number of methods have been examined for the volumetric estimation of cobalt. It is shown that in general volumetric methods are the most accurate and satisfactory for the estimation of cobalt. The most accurate method involves the oxidation of cobalt to cobaltic hydroxide in strongly alkaline solution by means of a perborate or hydrogen peroxide, followed by its volumetric reduction to a cobaltous salt. This reduction may be accomplished by the following methods: (a) By the addition of potassium iodide in acid solution, the iodine liberated being titrated with sodium thiosulphate; in this method iron must be absent. (b) By adding the cobaltic hydroxide to an acid ferrous sulphate solution, the excess of which is titrated with potassium permanganate; an empirical factor must be used in the calculation. (c) By the addition of a strongly acid solution of stannous chloride, the excess of which is titrated with iodine, iodate, bromate, or dichromate solution. The last, titrated electrometrically, is especially recommended. If iron is present, iodine will oxidise it quantitatively only in a neutral solution. (d) By adding titanous sulphate, the excess of which is titrated with permanganate. Since titanous hydroxide decomposes water with the liberation of hydrogen, the alkaline solution must be first almost completely neutralised by one of the several methods suggested. The presence of nickel does not interfere with this titration, but the oxidation is incomplete when more than 7 mg. of iron are present. In the presence of a large excess of potassium hydrogen carbonate, cobalt is oxidised by hydrogen peroxide to a green tervalent compound, which is reduced in the presence of pyrophosphate by ferrous sulphate, the excess of which is titrated with permanganate after acidifying with sulphuric acid. Iron and manganese in small amounts do not interfere in this method, but the principal source of error is in the removal of the excess of peroxide without decomposing the cobalt compound.
J. F. S.

Gravimetric Estimation of Nickel as Nickel Dioxide. WILHELM VAUBEL (*Chem. Ztg.*, 1922, **46**, 978).—Nickelous hydroxide is precipitated from the solution with sodium hydroxide, collected, washed, and ignited. The ignited precipitate is again washed until free from alkali metals, dried, and dissolved in nitric acid. The excess of nitric acid is evaporated and the residue heated for thirty minutes in an air-bath at 280—330°. Pure black nickel dioxide results. The oxides of nickel at present known are NiO, Ni₃O₄, and NiO₂. The oxide Ni₂O₃ has not yet been obtained.

H. C. R.

Electrometric Estimation of Nickel with Silver Nitrate. ERICH MÜLLER and HANS LAUTERBACH (*Z. anal. Chem.*, 1922, **61**, 457—464).—The nickel solution is treated with a slight excess of potassium cyanide solution, sufficient to decolorise the mixture, and connected with a normal calomel electrode, a galvanometer,

and a sliding resistance, the ends of which are connected with an accumulator, and one end and the sliding contact with a voltmeter. A silver wire in the solution acts as indicator electrode, and the solution is agitated by means of a motor-driven stirrer. The sliding resistance is adjusted until the voltmeter indicates 0.075 volt and silver nitrate solution is added slowly until the galvanometer indicates zero. The results are calculated as in the older chemical process.

A. R. P.

Electrometric Titration of Dichromate with Ferrous Sulphate. MARION EPPLEY and WARREN C. VOSBURGH (*J. Amer. Chem. Soc.*, 1922, **44**, 2148—2156).—The conditions under which dichromate may be estimated by electrometric titration with ferrous sulphate have been investigated. The practical limits of acidity for hydrochloric and sulphuric acids have been determined. It is shown that the amount of ferrous sulphate required to titrate a given amount of chromic acid varies with the concentration of the latter. Dissolved air has a negligible effect on the titration. Hydrofluoric acid in sufficient concentration reduces the amount of ferrous sulphate required by about 0.1%. When ferrous sulphate, standardised by means of a standard solution of potassium permanganate, is used to standardise a known amount of dichromate in 0.01*N*-solution, the value found for the latter is about four parts per thousand higher than the calculated value. When the dichromate concentration is 0.003*N*, the amount of ferrous sulphate required is about 1% higher than the calculated quantity. The titration of the ferrous ion with a potassium dichromate solution gives results which agree with those obtained by the reverse titration.

J. F. S.

The Analysis of High-percentage Tungsten Alloys. K. SEEL (*Z. angew. Chem.*, 1922, **35**, 643—644).—The serious loss of platinum involved in the customary fusions of tungsten alloys with sodium and potassium carbonates and nitrates may be avoided by fusing the finely divided alloy with sodium hydroxide and nitrate in silver crucibles. The fusion takes about 1 hour, and the crucibles are not seriously attacked. 0.5 Gram of the finely divided alloy is fused with 6 grams of sodium hydroxide and 3 grams of sodium nitrate. The fused mass is dissolved in water and filtered, the iron oxide remaining on the filter being dissolved in hydrochloric acid containing a little potassium chlorate, filtered, and the two filtrates united. The iron is estimated as ferric oxide as usual. The aluminium and the greater part of the silica are removed from the filtrate with ammonia, filtered off, and the tungsten in the filtrate precipitated with mercurous nitrate after acidifying, boiling off the carbon dioxide and concentrating to about 150 c.c. The tungstic acid obtained by ignition of the precipitate is strongly contaminated with alkali, which is removed by repeated extractions with 7% hydrochloric acid, and traces of silica are finally removed by treatment with hydrofluoric acid. In the case of alloys rich in iron, a residue containing iron and tungsten remains after the original fusion. This is fused with pyrosulphate and the tungsten

precipitated with nitric acid, estimated as tungstic acid and added to the figure obtained above. The iron in the filtrate is estimated in the usual way and added to the figure obtained above.

H. C. R.

Separation of Antimony from Arsenic and Tin. FRIEDRICH L. HAHN (*Z. anorg. Chem.*, 1922, **123**, 276).—Antimony can be separated quantitatively from arsenic and tin by oxidation to pyroantimonate (cf. A., 1916, ii, 266). This method is due to Hampe.

W. T.

The Estimation of Bismuth as Metal. ALBIN KURTENACKER and FELICITAS WERNER (*Z. anorg. Chem.*, 1922, **123**, 166—170).—The authors find that metallic bismuth can be accurately estimated by dissolving it in a ferric salt and titrating the ferrous salt produced by means of potassium permanganate, the reaction being $\text{Bi} + 3\text{Fe}^{+++} = \text{Bi}^{+++} + 3\text{Fe}^{++}$. Ferric chloride was found more suitable than the sulphate. The reduction of bismuth nitrate by formaldehyde, hypophosphorous acid, and alkali stannite gave results about 5% too low, this being due to the metal being mixed with some bismuthous oxide. Conditions for complete reduction to the metal could not be found.

W. T.

New Method for Estimating Volatile Substances in Air. E. FRITZMAN and K. MACJULEVITSCH (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 212—226).—To estimate the content of light petroleum vapour in air, the latter is first freed from dust, moisture, and carbon dioxide by passing it through tubes containing, in order, soda-lime, calcium chloride, phosphoric oxide, and cotton wool, the light petroleum being retained in two U-tubes packed with magnesium turnings and cooled in liquid air.

T. H. P.

Estimation of Toluene, Xylene, and Benzene. G. ZABOROWSKI (*Mat. grasses*, 1922, **14**, 6160—6161).—Commercial samples of the above hydrocarbons or their respective mixtures with "gasoline" may be examined, either volumetrically by sulphonation with a known quantity of sulphuric acid and titration of the excess of acid, or densimetrically. (a) About 3.5 grams of the sample and three times its weight (for xylene, four times) of (preferably 100%) sulphuric acid are warmed to 45° in a 50 c.c. glass-stoppered flask, shaken thoroughly for five minutes, allowed to cool, poured into 100 c.c. of water, boiled to remove light oils, and titrated with standard sodium hydroxide solution, using phenolphthalein. For toluene, the quantity of acid used is multiplied by 1.876; for xylene, by 2.163. In the case of benzene, sulphonation must be effected in a reflux apparatus. (b) The densimetric estimation consists in the use of the expression $T = -[100D(d_1 - d_2)] / (D - d_2)d_1$, where d_1 represents the d_{15} of the sample, d_2 the d_{15} of the un-sulphonated residue after sulphonation, and D the d_{15} of pure toluene (0.8706), xylene, or benzene.

CHEMICAL ABSTRACTS.

The Detection of Nitro-compounds. H. J. PRINS (*Perf. Essent. Oil Rec.*, 1922, **13**, 355).—The accelerating effect of nitro-

benzene on the reaction velocity of metals with weak acids is applied to the detection of this substance in benzaldehyde. The reaction is carried out by heating 2 c.c. of the oil and 6 c.c. of 80% acetic acid for one minute with a small piece of tin foil. In presence of 5% of nitrobenzene, the tin disappears immediately on boiling, with 1% the tin turns dark and disappears about ten minutes after the mixture has been heated, with 0.1% the tin turns black after about ten minutes, with 0.01% the tin becomes greyish-black after remaining over-night, whilst with pure benzaldehyde the metal retains its bright surface. In a similar way, the presence of 0.1% of artificial musk can be detected in perfumes. The reaction is not exclusively specific for nitro-compounds, as organic peroxides have the same property, but only oils rich in terpenes which contained peroxides owing to exposure to air show the reaction and then only feebly. Likewise worm-seed oil containing the peroxide caridol can scarcely give rise to confusion, as 5% of nitrobenzene in benzaldehyde reacts more rapidly than pure worm-seed oil. Peroxidised benzaldehyde does not show the nitrobenzene reaction at all.

G. F. M.

Estimation of Phenol in Mixtures of Tar Acids. W. H. HOFFERT (*J. Soc. Chem. Ind.*, 1922, **41**, 334—337r).—The method proposed depends on the fact that the freezing point of phenol hydrate (16°) is lowered to the same extent by equal weights of each of the three cresols. In the case of a mixture of phenol and cresols, the freezing point may be determined directly, after the addition of water amounting to 10% of the weight of the mixture, if the quantity of phenol present exceeds 55%; if the proportion of phenol is less, a known quantity of pure phenol (m. p. 40.5°) must be added to bring the proportion above 55%. With a mixture of tar acids, it is first necessary to remove neutral hydrocarbons and pyridine bases by distilling with steam from a sodium hydroxide solution of the sample, or by extracting the same solution with ether or benzene; the recovered tar acids are then distilled. If the mixture distils completely below 203° , the estimation is made directly on the distillate, but otherwise, higher homologues must be separated by fractional distillation. A known weight of pure phenol is added to the distillate and the mixture is treated with 10% of its weight of water. Directions are given in detail regarding the procedure adopted for determining the freezing point and the amount of phenol corresponding with the freezing point obtained is found by reference to a graph. The method may be applied to the estimation of phenol in crude carboic acid.

W. P. S.

Iodometric Estimation of Sugars. FR. AUERBACH and E. BODLÄNDER (*Z. angew. Chem.*, 1922, **35**, 631—632).—In the iodometric titration of the excess of Fehling's solution used in the estimation of a reducing sugar, the volume of $N/10$ -thiosulphate solution required is not strictly proportional to the amount of sugar present. A table is given showing the quantities of invert-sugar corresponding with different quantities of thiosulphate

solution. Replacement of a part of the potassium iodide used by potassium thiocyanate, as proposed by Bruhns, is not recommended.
W. P. S.

The Modified Lehmann Method for the Estimation of Dextrose. Adaptation to Small Quantities of Reducing Sugars. PAUL FLEURY and LOUIS BOUTOT (*Bull. Soc. Chim. Biol.*, 1922, 4, 361—374).—In the estimation of dextrose by Bruhns's method (A., 1920, ii, 773) the reagents should be added to the copper solution in the following order: iodide, acid, thiocyanate. The method has been used for the estimation of small quantities of reducing sugars in biological fluids.
E. S.

Trustworthiness of the Benedict and Folin-Wu Blood-sugar Estimations. F. A. CSONKA and GRACE C. TAGGART (*J. Biol. Chem.*, 1922, 54, 1—3).—The different results obtained by the Folin-Wu (A., 1920, ii, 337) and the Benedict (A., 1918, ii, 247) methods are due to the presence in blood of a substance which reacts with picric acid but does not reduce copper solutions. The former method is thus the more trustworthy.
E. S.

Estimation of Starch. I. Estimation of Starch in Barley and in Wheat. ARTHUR R. LING [with E. H. CALLOW and W. J. PRICE] (*J. Inst. Brewing*, 1922, 28, 838—853).—The method proposed depends on the hydrolysis of the starch by malt diastase as suggested by Brown and Morris (T., 1885, 47, 527). Since the amount of maltose yielded by a pure starch varies with the diastatic power of the malt, the authors have determined the relation between the percentage of maltose obtained from pure barley and wheat starches when these are hydrolysed under definite conditions, and the diastatic power of the malt employed. The results of these experiments are given in graphic form. To estimate starch in barley or wheat, 5 grams of the finely-powdered grain are extracted in a Soxhlet apparatus for 3—3½ hours with alcohol (*d* 0.920), the powder is then rinsed into a beaker with about 100 c.c. of water, and the mixture is boiled for ten minutes. The starch paste thus obtained is cooled to 57°, 10 c.c. of malt extract (prepared from a malt of known diastatic power) are added, the mixture is kept at 57° for one hour, then boiled, filtered, and the insoluble portion washed. The filtrate is diluted to 200 c.c. and 30 c.c. of this solution are diluted to 100 c.c. and titrated against 10 c.c. of Fehling's solution. The cupric reducing power of the malt extract is determined at the same time and under the same conditions, and the value obtained is used to correct the reducing power of the conversion product.
W. P. S.

Identification of Inulin by a Mycological Method. ALDO CASTELLANI and FRANK E. TAYLOR (*Biochem. J.*, 1922, 16, 655—658).—*Monilia macedoniensis*, Castellani, ferments inulin with the production of gas. It also ferments dextrose, lævulose, galactose, and sucrose. The method consists of the utilisation of the above mould in conjunction with other fungi.
S. S. Z.

Estimation of Volatile Acids in Wine. PHILIPPE MALVEZIN (*Ann. Falsif.*, 1922, **15**, 360—362).—In reply to criticism, the author states that he sees no reason for altering the procedure described in his ether-extraction method for the estimation of volatile acids in wine. Tartaric and lactic acids are not extracted by the ether under the conditions given. W. P. S.

The Separation of Solid and Liquid Fatty Acids. W. MEIGEN and A. NEUBERGER (*Chem. Umschau*, 1922, **29**, 337—342).—The methods of Varrentrapp, Bull and Fjellanger, Farnsteiner, David, Niegemann, and Facchini and Dorta were tested on known mixtures of solid and liquid fatty acids and by none was a true quantitative separation obtained. By the methods of Bull and Fjellanger, Facchini and Dorta, and David about one-half of the liquid acids was recovered in a nearly pure state. By recrystallising the solid fraction, part of this was also obtained nearly pure. By precipitating the aqueous solution of the potassium salts with excess of thallous sulphate, however, an almost quantitative separation of stearic, palmitic, and elaidic acids from oleic acid was attained, and no recrystallisation was necessary. A mixture of 0.502 gram of oleic acid with 0.505 gram of stearic acid gave 0.509 gram of solid acids of iodine value 0.3 and m. p. 68°, whilst a mixture of 0.200 gram of oleic acid and 0.502 gram of stearic acid gave 0.529 gram of solid acids of iodine value 0.9 and m. p. 67.5°. H. C. R.

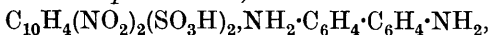
The Neutralisation of Tartaric Acid by Potassium Hydroxide in Presence of Chlorides of Alkaline Earths. L. J. SIMON and L. ZIVY (*Compt. rend.*, 1922, **175**, 620—622).—The fact that titration of alkali hydroxide against tartaric acid gives two end-points; that with helianthin indicating formation of the acid salt and that with phenolphthalein the normal salt, may be used in estimating mixtures of tartaric acid with other acids which give an end-point in presence of helianthin indicating the formation of normal salt. The presence of alkaline-earth chlorides in the solution introduces an error, as each molecule behaves towards potassium hydroxide as an equivalent quantity of hydrochloric acid. This effect is produced by any quantity and is quantitative in each case, the limiting value of the effect being the amount of tartaric acid present. Chlorides of other metals do not interfere with the titration in this manner. H. J. E.

Estimation of Salicylic Acid in Blood-serum and other Fluids of the Body. H. HERISSEY (*Compt. rend. Soc. biol.*, 1922, **87**, 333—336).—A mixture of 10 c.c. of serum, 5 c.c. of water, 0.5 c.c. of a solution of 1 gram of sulphuric acid in 5 c.c. of water, and 40 c.c. of ether is shaken together for one minute in a stoppered glass bottle of 125 c.c. capacity. After an interval of a few minutes, 4.5 c.c. of sulphuric acid solution are again added and the contents well mixed by rotation of the flask, the supernatant ethereal layer

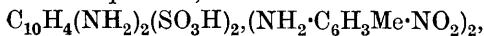
being decanted after five minutes. Of this solution, 30 c.c. are shaken in a funnel with 2—3 grams of anhydrous sodium sulphate; 3 c.c. of water containing one drop of dilute ferric chloride solution are then added, and the whole is vigorously shaken. In the presence of salicylic acid, a violet colour appears in the water layer on keeping. Should a positive reaction be given, the contents are thoroughly mixed and transferred to a small crystallising dish, the ether being allowed to evaporate spontaneously at room temperature. It is necessary to use a stirring-rod to prevent the formation of deposits on the sides of the dish. The solution is then filtered into a test-tube, together with a few drops of rinsing water, and its coloration compared with standards prepared from 10 c.c. of normal serum, 5 c.c. of water, and varying quantities of salicylic acid. A definite coloration is obtained with only 10 mg. of sodium salicylate per litre.

CHEMICAL ABSTRACTS.

Substituted Naphthalenesulphonic Acids. I. A Method for Identifying H-Acid and its Intermediates Obtained from Naphthalene-2 : 7-disulphonic Acid. D. F. J. LYNCH (*J. Ind. Eng. Chem.*, 1922, **14**, 964—965).—A method for the detection of 1 : 8-dinitronaphthalene-3 : 6-disulphonic, 1 : 8-diaminonaphthalene-3 : 6-disulphonic, 1-amino-8-naphthol-3 : 6-disulphonic (H-acid), and 1 : 8-dihydroxynaphthalene-3 : 6-disulphonic (chromotropic) acids in their mixtures by means of their reactions with solutions containing 2-cymidine sulphate, cobalt chloride, zinc sulphate, or the hydrochlorides of benzidine, α -naphthylamine, ψ -cumidine, toluidine, and *p*-nitrotoluidine, is developed. The tests are carried out with 3—5 c.c. of less than one-tenth gram-molecular solutions of the naphthalenesulphonic acids. The following substances were prepared. *Benzidine* salt of 1 : 8-dinitronaphthalene-3 : 6-disulphonic acid,



light yellow prisms, m. p. 275° (decomp.). Solubility 0.036 part at 20°. *Cymidine* 1 : 8-dinitronaphthalene-3 : 6-disulphonate, $\text{C}_{10}\text{H}_4(\text{NO}_2)_2(\text{SO}_3\text{H})_2 \cdot (\text{C}_6\text{H}_3\text{MePr}^s \cdot \text{NH}_2)_2$, straw-coloured prisms, m. p. 265° (decomp.), solubility 0.059. *Benzidine* salt of chromotropic acid, $\text{C}_{10}\text{H}_4(\text{OH})_2(\text{SO}_3\text{H})_2 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$, brown prisms, m. p. 278° (decomp.), solubility 0.085. *p*-Nitrotoluidine 1 : 8-diaminonaphthalene-3 : 6-disulphonate,



greyish-tan needles, m. p. 270° (decomp.), solubility 0.186. Mono- α -naphthylamine salt of H-acid, $\text{NH}_2 \cdot \text{C}_{10}\text{H}_4(\text{OH})(\text{SO}_3\text{H})_2 \cdot \text{NH}_2 \cdot \text{C}_{10}\text{H}_7$, light violet-grey prisms, m. p. 278° (decomp.), solubility 0.1006. Mono- ψ -cumidine salt of H-acid, $\text{C}_{10}\text{H}_9\text{O}_7\text{NS}_2 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_2\text{Me}_3$, grey prisms, m. p. 272° (decomp.), solubility 0.097. Mono-*p*-nitrotoluidine salt of H-acid, $\text{C}_{10}\text{H}_9\text{O}_7\text{NS}_2 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NO}_2 \cdot \text{H}_2\text{O}$, grey prisms, m. p. 265° (decomp.), solubility 0.106. Toluidine salt of H-acid, $\text{C}_{10}\text{H}_9\text{O}_7\text{NS}_2 \cdot \text{NH}_2 \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{C}_6\text{H}_3\text{Me} \cdot \text{NH}_2 \cdot 3\text{H}_2\text{O}$, greyish-violet prisms, m. p. 260° (decomp.), solubility 0.102. *Zinc* 1 : 8-diamino-3 : 6-disulphonate, $\text{C}_{10}\text{H}_4(\text{NH}_2)_2\text{S}_2\text{O}_6\text{Zn} \cdot 3\text{H}_2\text{O}$, grey needles,

solubility 6.4; *cobalt* salt, $C_{10}H_4 \cdot (NH_2)_2 S_2O_6 Co, 2H_2O$, brown needles, solubility 6 at 20°. The solubilities are parts per 100 parts of water, at room temperature unless otherwise specified.

A. J. H.

Estimation of Anthraquinone. O. A. NELSON and C. E. SENSEMAN (*J. Ind. Eng. Chem.*, 1922, **14**, 956—957).—The following volumetric method has been devised for the estimation of anthraquinone in order to avoid the difficulties of filtration experienced in the method of Lewis (A., 1918, ii, 338). To about 0.5 gram of the sample of anthraquinone, intimately mixed with 3—4 grams of zinc dust, is added 100 c.c. of boiling 5% sodium hydroxide. After five minutes, the mixture is filtered through asbestos contained in a glass tube, about 24 cm. long and 3.5 cm. in diameter, and tapered at one end. This funnel is electrically heated at 90—95° and contains a mechanical stirrer. The red filtrate containing oxanthranol is received in a suction flask and is there directly titrated with a standard solution of potassium permanganate (3.8 grams per litre). Usually three to eight washings of the residue with hot sodium hydroxide solution are necessary in order completely to free it from unreduced anthraquinone, and the apparatus is arranged so that aerial oxidation of the filtrate is prevented. In the titration, the end-point is reached when the filtrate becomes colourless, except when phenanthraquinone is present when a bluish-green colour is obtained which changes to brownish-green on addition of excess of potassium permanganate. Accurate results are obtained by this method even when the anthraquinone contains phenanthraquinone, anthracene, phenanthrene, phthalic acid, phthalic anhydride, or other oxidation products of anthracene and phenanthrene.

A. J. H.

A Chemical Method of Assaying the Active Principles of Digitalis. ARTHUR KNUDSON and MELVIN DRESBACH (*J. Pharm. Expt. Ther.*, 1922, **20**, 205—220).—The pharmacological activity of extracts of digitalis is found to be parallel with the colour developed on treating the digitalis preparation, decolorised with lead acetate, with an alkaline picrate solution. In order to evaluate the activity of the extract, comparison is made in the colorimeter with a standard ouabain solution treated in the same way.

W. O. K.

The Use of Sodium α -Naphthol-2-sulphonate for the Spectrophotometric Estimation of Aromatic Amino-compounds. W. E. MATHEWSON (*J. Assoc. Off. Agric. Chem.*, 1922, **6**, 16—28).—The method consists essentially of coupling the naphtholsulphonate with the diazo-compound of the amine, and determining the concentration of the dye photometrically, in comparison with a standard solution of the pure dye. Sodium α -naphtholsulphonate is suited to the purpose because of the ease with which it is to be obtained pure, and to the rapidity and completeness of its reaction with diazo-compounds in dilute solution.

"Extinction coefficients" or "transmissive indices" (Priest, *J. Opt. Soc. Amer.*, 1920, 186) are determined by the König-Martens spectrophotometer, using the light from a mercury vapour lamp. Standard figures for aniline, *o*- and *p*-toluidines, α - and β -naphthylamines, benzidine, anthranilic acid, methyl anthranilate, and *p*-sulphanilic acid are given. The dye from methyl anthranilate is saponified in alkaline solution and direct determinations of its concentration are impossible. In this case the velocity coefficient of saponification is determined; and for purposes of estimation photometric readings are taken at intervals, and the original concentration is determined by calculation. The presence of small quantities of the nitroso-compound of α -naphtholsulphonate has a negligible effect on the transmissive index. Hydrazine may be used in certain cases (for example, β -naphthylamine) to remove excess of nitrous acid, but in others (for instance naphthionic acid) the results obtained are uncertain. Details of the method for estimating amino-impurities in dyes are given. The process may also be used for the estimation of nitrites. A. G. P.

Pernitric Acid as an Analytical Reagent. IV. TRIFONOV (*Z. anorg. Chem.*, 1922, **124**, 136—139).—Pernitric acid reacts with aniline, yielding an intensely yellow product. The per-acid is formed by the action of hydrogen peroxide on an acidified solution of a nitrite. The above reaction with aniline can therefore be employed for the detection of hydrogen peroxide or a nitrite. Benzene is coloured by pernitric acid yellow, which changes into dark red on the addition of alkali. Toluene and xylene are also coloured yellow but fainter, which, however, does not change on the addition of alkali. Thus benzene in the presence of toluene, xylene, and the aliphatic hydrocarbons can be detected; the aliphatic members are not coloured. Similarly, benzene can be detected in methylated spirits. W. T.

The Analysis of β -Naphthylamine. H. R. LEE and D. O. JONES (*J. Ind. Eng. Chem.*, 1922, **14**, 961—963).—Methods for the determination of β -naphthylamine, m. p. 110.1—110.2° (corr.), in the presence of its common impurities, β -naphthol, m. p. 121.2—121.3° (corr.), $\beta\beta$ -dinaphthylamine, m. p. 172.2° (corr.), and α -naphthylamine, m. p. 49.2—49.3° (corr.), are suggested, using specially purified samples of these substances. The direct nitrite titration method usually gives results which are too high, due partly to oxidation of the diazo- β -naphthylamine and partly, when β -naphthol is present, to formation of nitroso- β -naphthol. A more accurate method, based on the fact that β -naphthol-1-sulphonic acid does not absorb nitrous acid, consists of sulphonating 0.65 gram of the sample of β -naphthylamine with 20 c.c. of 25% of fuming sulphuric acid at 0—5° and finally at 15°, diluting the mixture with ice, boiling it to remove sulphur dioxide and afterwards adding 15 c.c. of concentrated hydrochloric acid and estimating the β -naphthylamine by titration with 0.1N-sodium nitrite

at 0—5°. For estimation of the β -naphthol present, the sample dissolved in dry benzene is saturated with hydrogen chloride, and after removal of β -naphthylamine hydrochloride by filtration, the β -naphthol in the filtrate is determined by titration with 0.05*N*-diazotised-*p*-nitroaniline solution. Impurities insoluble in acids are estimated by boiling 0.5 gram of the sample in 150 c.c. of 1.5% hydrochloric acid, filtering the solution through a Gooch crucible, washing the residue with hot water, and afterwards drying it to constant weight at 100°. Under these conditions, at least 10% of the β -naphthol passes into the filtrate, but only 0.10—0.20% of the $\beta\beta$ -dinaphthylamine is soluble, so that this may be extracted from the residue by means of solvents and weighed or analysed for nitrogen. Moisture is determined by drying 5 gram of the finely powdered sample over concentrated sulphuric acid in a vacuum. A modified Kjeldahl-Gunning method for the estimation of total nitrogen is described and the melting-point curves of the binary systems, β -naphthylamine- β -naphthol, β -naphthylamine- $\beta\beta$ -dinaphthylamine, and β -naphthylamine- α -naphthylamine are also given.

A. J. H.

Identification of Alanine by Crystallo-chemical Analysis.

IV. S. JAITSCHNIKOV (*J. Russ. Phys. Chem. Soc.*, 1920, **52**, 145—147).—Polarimetric identification of active alanine is sometimes impossible owing to the marked opalescence of the solution. In such case, use may be made of crystallographic measurements. The results of the author's measurements are compared with those of Groth and of Fischer (A., 1906, i, 145).

T. H. P.

Detection of Urea. Estimation of Proteolytic Ferments.

LUDWIG PINCUSSEN (*Biochem. Z.*, 1922, **132**, 242—244).—Urea is best detected in a liquid free from ammonia by addition of urease at P_H 7.0—7.2, keeping at 55° for fifteen minutes, then addition of two drops of saturated sodium carbonate solution and detection of the production of volatile ammonia by litmus paper. If the liquor contains ammonia originally, it is removed by shaking with powdered permutite, 0.2 gram per c.c.

A quantitative method for estimating proteolytic ferments is described which depends on the micro-Kjeldahl estimation of the non-protein nitrogen formed by the digestion. Unchanged protein is removed by colloidal iron.

H. K.

Detection of the Veronal Group. Diagnosis of Veronal Intoxication. HEINRICH HANDORF (*Z. ges. expt. Med.*, 1922, **28**, 56—80; from *Chem. Zentr.*, 1922, iv, 576).—A modification of the murexide test is described for the detection of barbituric acid derivatives in urine. The different members of the veronal group are distinguished by their behaviour when the reaction is carried out in the presence of ammonium chloride, sodium chloride, and barium chloride, respectively.

G. W. R.

Inconstancy of the Precipitation of Uric Acid from Urine in the Form of Cuprous Urate. J. KHOURI (*Bull. Soc. Chim. Biol.*, 1922, **4**, 375—378).—Denigès's method for the estimation of uric acid in urine gives low and irregular results owing to the incomplete precipitation of the copper salt. This may be remedied to some extent by first treating the urine (100 c.c.) with five drops of sulphuric acid and heating for one hour at 100°. E. S.

Use of the Newer Indicators in Titrations of Alkaloids. WILLIAM J. MCGILL (*J. Amer. Chem. Soc.*, 1922, **44**, 2156—2160).—The Sørensen values of aqueous solutions of the hydrochlorides of quinine, cinchonine, morphine, atropine, and strychnine have been determined from *E.M.F.* determinations at various dilutions; measurements were also made in the presence of such quantities of alkali salts as would normally be present in the titration of an alkaloid hydrochloride by alkali. From the results, the most suitable indicators for the titration of such alkaloids are deduced and tested experimentally. It is shown that the indicators generally used in the titration of morphine, atropine, and quinine give results which are not nearly so accurate as should be obtained. Thus in the case of morphine the average error using methyl-red is 1.4%, whereas bromophenol-blue gives an average error of 0.5%, and in some cases it is as low as 0.1%. The most trustworthy indicator for quinine is bromocresol-purple, whilst this indicator is not superior to methyl-red in the titration of cinchona residues. Cocchineal and methyl-red give low results with morphine, whilst bromophenol-blue gives a satisfactory value and end-point; the same is also true for atropine and mydriatic residues. Methyl-red can best be used in the titration of strychnine. J. F. S.

The Estimation of Carnosine in Muscle Extract. GEORGE HUNTER (*Biochem. J.*, 1922, **16**, 640—654).—Further details are given for the estimation of carnosine in muscle by the application of Koessler and Hanke's diazo-method (this vol., ii, 328). Histidine can be estimated in muscle in the presence of carnosine by utilising Knoop's reaction, since the reaction is not characteristic of carnosine. This fact affords, further, the opportunity of estimating carnosine by a new method, namely, by hydrolysing it and determining the resulting histidine by Knoop's reaction. In ox-muscle, purines are responsible for about 3% of the diazo-colour value reckoned as carnosine, and 2% of the colour may be due to substances other than carnosine. The carnosine content of muscle varies both with the species of the animal and with the individual of the same species. S. S. Z.

Knoop's Test for Histidine. GEORGE HUNTER (*Biochem. J.*, 1922, **16**, 637—639).—Different intensities of colour are produced in solutions of the same concentration of histidine by Knoop's test. This is due to the variation in the excess of bromine. The proportion of three atoms of bromine per molecule of histidine is found to give the maximum colour on heating. S. S. Z.

Precipitation of Proteins by Metaphosphoric Acid. Application to the Analysis of Blood, Pathological Liquids, and Cerebrospinal Fluid. A. GRIGAUT and P. ZIZINE (*Bull. Soc. Chim. Biol.*, 1922, 4, 388—406).—In the precipitation of proteins from serum, etc., by means of sodium metaphosphate and hydrochloric acid, the amount of acid employed, provided it is within the limits necessary for the complete precipitation of protein, has little influence on the amount of non-protein nitrogen which passes into the filtrate. Preliminary dilution of the serum, on the other hand, exerts considerable influence; the greater the dilution the smaller the amount of non-protein nitrogen which passes into the filtrate. For serum and pathological liquids the following method is recommended: The serum (10 c.c.) is diluted with water (6 c.c.). A 20% solution of sodium metaphosphate (2 c.c.) is then added, followed by 2*N*-hydrochloric acid (2 c.c.). In the case of certain liquids (for instance, whole blood, cerebrospinal fluid) modifications depending on the viscosity and content in protein must be made both in the dilution and the amount of reagents employed. Contrary to the statement of Cristol (this vol., ii, 583), metaphosphoric acid does not produce a partial hydrolysis of the proteins; the higher values obtained with this reagent are probably due to the presence of polypeptides in the filtrate. When trichloroacetic acid is employed these are retained by the proteins in the form of complexes owing to the high acidity of the solution. Metaphosphoric acid has been used for the removal of proteins in the estimation of urea, uric acid, non-protein nitrogen, and dextrose in blood and other fluids. E. S.

The Gradual Darkening of Hæmatin Solutions in Colorimetric Estimations, and its Prevention. H. C. GRAM (*Acta med. Scand.*, 56, 52—70; from *Chem. Zentr.*, 1922, iv, 576).—The darkening of hæmoglobin solutions is not attributed to change of oxyhæmoglobin to hæmatin. It is affected by strength of acid and to a less degree by temperature. It may be prevented, in the Autenrieth method, by addition of 2 c.c. of 3% hydrogen peroxide to 98 c.c. of the hydrochloric acid used. The wedge used for comparison must be specially graduated. The modification is not applicable to the Sahli method. G. W. R.

Estimation of Pepsin. MAKI TAKATA (*Tohoku J. Exptl. Med.*, 1921, 2, 127—130).—One gram of magenta-fibrin is added to gastric juice and the mixture incubated for thirty to forty-five minutes at 38°, then chilled, centrifuged, and the clear liquid compared colorimetrically with a magenta standard solution:

CHEMICAL ABSTRACTS.

Estimation of Total Protein, of Protein and Non-protein Nitrogen in Blood Plasma. H. BERRY and L. MOQUET (*Compt. rend. Soc. biol.*, 1922, 87, 329—331).—The authors found that in estimating the total proteins in blood by precipitation by heat and weighing the dry precipitate, attention must be directed to the hydrogen-ion concentration of the solution. The amount of precipitate and the quantity of nitrogen contained in it varies, the

maximum being obtained at $p_H=5.6$. Their own procedure is to neutralise 2 c.c. of plasma, diluted to 20 c.c. with water, either with 0.01*N*-hydrochloric acid or 0.1*N*-acetic acid, one drop of alizarin being used. This is then boiled for fifteen minutes, and the precipitate collected and dried. The nitrogen is estimated by the regular Kjeldahl method in a portion of the precipitate. The alternative procedure is to measure into a tall cylinder 1 c.c. of plasma, add to it 3 c.c. of acetone free from hydrogen sulphite and leave the precipitate to settle for twelve hours. This is then filtered, washed with acetone, boiling water, boiling alcohol, and finally with ethyl ether. The quantitative results are the same by both methods.

CHEMICAL ABSTRACTS.

Estimation of the Total Non-protein-nitrogen of Serum.
Choice of a Suitable Albumin Precipitant. P. CRISTOL and M. SIMONNET (*J. Pharm. Chim.*, 1922, [vii], 26, 298—309).—Whilst trichloroacetic acid and tungstic acid are excellent precipitants for albumin in the estimation of the total non-protein-nitrogen of serum, and allow neither lipid- nor protein-nitrogen to pass into the filtrate, metaphosphoric acid, on the contrary, is unsuitable as complete precipitation is not obtained and the results are always correspondingly high when estimation of total non-protein-nitrogen is in question, although the defecation with this precipitant is sufficiently good for carbohydrate or lactic acid estimations. Of all the precipitants tried, trichloroacetic acid is the best and most convenient, as the estimation of the non-protein-nitrogen can be carried out with as little as 2 c.c. of filtrate, whereas with tungstic acid 5 c.c. of filtrate are required. The evaporation and hydrolysis are more rapid and the estimation more exact. Further, any losses due to too violent ebullition are not to be feared.

G. F. M.

Examination of the Duodenal Fluid obtained through a Tube. R. DAMADE (*Compt. rend. Soc. biol.*, 1922, 86, 947—948).—With a 2% solution of methyl-orange the alkalinity of the duodenal fluid was found to vary from 1.4 to 12.5 c.c. of *N*-hydrochloric acid for 10 c.c. Amylase is estimated by determining the amount, in milligrams, of dextrose found in 5 c.c. of 2% starch solution incubated at 37° for one hour with 1 c.c. of the duodenal fluid. This value generally varies from 15 to 35. For the estimation of lipase, 10 c.c. of a 10% solution of ethyl butyrate is treated with 1 c.c. of the duodenal fluid and neutralised to phenolphthalein with 0.1*N*-sodium carbonate. After incubating the mixture at 37° for one hour, the free acid formed is titrated. Usually 1.2—3.2 c.c. are required. For the estimation of trypsin, 1 c.c. of the fluid is added to 50 c.c. of 5% gelatin solution; this is then neutralised to phenolphthalein and kept at 37° for one hour, 20 c.c. of the digested mixture being titrated with 0.1*N*-sodium hydroxide solution, whilst another portion of 20 c.c. is titrated after the addition to it of 5 c.c. of formaldehyde solution and 5 c.c. of 90% ethyl alcohol. The tryptic activity is expressed by the sum of the volumes of sodium

hydroxide solution required; the value varies between 4.9 and 7.5, with an average of 5.35 c.c. CHEMICAL ABSTRACTS.

Detection of Urobilin in Urine. GEORGES RODILLON (*J. Pharm. Chim.*, 1922, 26, 379—381).—An alcoholic solution of zinc acetate is prepared by mixing 15 grams of zinc oxide with 250 c.c. of 95% alcohol and 15 c.c. of glacial acetic acid, and, after frequently shaking during forty-eight hours, filtering the clear liquid. Equal volumes of this reagent and the urine are mixed in a test tube, 1 drop of a 1 in 10 dilution of tincture of iodine is added and a tenth of the total volume of chloroform. After shaking, the chloroform layer is allowed to separate, and if necessary is clarified by gentle warming. In presence of urobilin, an emerald-green fluorescence will be observed when a beam of light is directed on to the chloroform layer. When considerable quantities of urobilin are present, the chloroform solution will also show a rose-coloured tint. G. F. M.

Mechanical Analysis of Humus Soils. GILBERT WOODING ROBINSON (*J. Agric. Sci.*, 1922, 12, 287—291).—The mechanical analysis of peaty soils by the usual methods is frequently of little value, owing to the cementing together of the finer soil particles by the organic colloids.

The removal of the latter by means of hydrogen peroxide causes a considerable increase in the clay fraction, which by microscopical examination is shown to consist almost entirely of mineral particles.

Ten grams of soil are heated for thirty minutes on a steam-bath with 50 c.c. of hydrogen peroxide (20 vols.). A further treatment with 25 c.c. of peroxide is usually sufficient to bring about a thorough dispersion of the soil particles. A. G. P.

A New Method for the Mechanical Analysis of Soils and Other Suspensions. GILBERT WOODING ROBINSON (*J. Agric. Sci.*, 1922, 12, 306—321).—The existing method of soil analysis is considerably shortened by the means suggested. A suspension of soil (2%) in dilute sodium carbonate solution (about 0.025%) is placed in a cylinder and samples are withdrawn by means of a pipette at measured depths and after known periods of settling. The results are most conveniently represented by a graphical indication of summation percentages as a function of the logarithm of the settling velocity. By suitable choice of times and depths of sampling, figures corresponding with any of the systems of fractional sedimentation can be obtained. The diameter of the cylinder should not be less than 4 cm. Small errors in the depth of sampling have negligible effects on the final results.

The effect of a gel coating on the settling velocity of a particle is a reduction which is a simple function of the thickness of the gel. It is shown that below the first few centimetres of a settling column the change in concentration with depth is very small. A. G. P.

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1417875, A., i, 943

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1419091, A., i, 938

1419092, A., i, 938

1424236, A., i, 1128

ERRATA.

VOL. 104 (ABSTR., 1913).

Page Line

- i. 681 11 for "4- β -iminoethylglyoxaline" read "4- β -aminoethylglyoxaline."

VOL. 106 (ABSTR., 1914).

- ii. 135 10* for "Thorium" read "Thallium."
ii. 874 8* col. ii. for "thorium" read "thallium."

VOL. 108 (ABSTR., 1915).

- i. 719 8* delete "VERNIER."
ii. 891 17 col. ii. ,, "Vernier."
ii. 965 29 col. ii. ,, "Vernier see Léon Givaudin."
ii. 1103 { 18 col. i. } ,, "VERNIER."
26 }

VOL. 120 (ABSTR., 1921).

- i. 165 25 for "ZEIGLER" read "ZIEGLER."
i. 796 16* ,, "ethyl r-pinate" read "ethyl r-pinonate."

VOL. 122 (ABSTR., 1922).

- i. 224 24 for "Digitoxone" read "Digitoxose."
i. 319 1* ,, "furfuran" read "furan."
i. 371 18 ,, "Bis-1:3'-indyl" read "Bis-1:3'-indil."
22 ,, "3:3'-indyl" read "3:3'-indil."
27 ,, "1:1'-indyl" read "1:1'-indil."
31 ,, "3:3'-Methylketyl (3:3'-dimethylketoyl)" read "2:2'-Dimethyl-3:3'-indil (2:2'-dimethyl-3:3'-diindyl)."
i. 554 17 ,, "SCHLICHTUNG" read "SCHLICHTING."
i. 563 16 ,, "TELECKY" read "TELECZKY."
i. 758 25 ,, "bis-3-carbethoxy-2:4-dimethylpyrrolmethene" read "ethyl methenylbis-2:4-dimethylpyrrole-3-carboxylate."
"CO₂Et·C:Me" $\begin{matrix} \diagup \\ \text{C} \\ \diagdown \end{matrix}$ etc." read "CO₂Et·C:Me" $\begin{matrix} \diagup \\ \text{C} \\ \diagdown \end{matrix}$ etc."
i. 758 17* ,, $\begin{matrix} \text{MeC}=\text{N} \\ \diagup \\ \text{C} \\ \diagdown \end{matrix}$ etc." read $\begin{matrix} \text{MeC}=\text{N} \\ \diagup \\ \text{C} \\ \diagdown \end{matrix}$ etc."
i. 848 13* insert "[cf. Stevens, A., 1921, i, 735]."
i. 945 13 for "Cynpopogan" read "Cynbopogan."
ii. 77 8 ,, "PbO₅UO₃·4H₂O" read "2PbO₅UO₃·4H₂O."
ii. 415 20 ,, "122" read "121."
ii. 519 18* ,, "KANAKER" read "KARRAKER."
ii. 582 bottom ,, "30% of hydrogen peroxide" read "30% hydrogen peroxide."
ii. 685 3 ,, "christobalite" read "cristobalite."
ii. 710 16* ,, "lead tetraethyl" read "magnesium ethyl iodide."
ii. 714 5 ,, "navrite" read "navruite."
ii. 714 12 ,, "variszite" read "variscite."
ii. 768 2* ,, "HALLE" read "HALLA."
ii. 830 13* ,, "HAMMERSTEN" read "HAMMARSTEN."

* From bottom.